



Cite this: *Dalton Trans.*, 2025, **54**, 16328Received 30th September 2025,
Accepted 22nd October 2025

DOI: 10.1039/d5dt02337h

rsc.li/dalton

Dinitrogen-bridged diruthenium complexes bearing 2,6-pyridinedicarboxylate in the mixed-valence state

Kazunari Uehara, Nayoung Kim, Aya Benzaki, Midori Otsuka,
Tomoyo Misawa-Suzuki  and Hirotaka Nagao *

A dinitrogen-bridged diruthenium complex bearing 2,6-pyridinedicarboxylate (pydc^{2-}), which coordinates in a κ^2 -ON bidentate mode, with ammine and hydroxido ligands has been synthesized by reactions of ruthenium(III) and/or ruthenium(II) complexes with hydrazine or dinitrogen as a dinitrogen source. A reaction of the diruthenium complex with pyridine affords a pyridine-substituted diruthenium complex. The electronic structures of the diruthenium complexes in a mixed-valence state have been investigated using UV-vis-NIR and IR spectroscopy and electrochemical methods.

Nitrogen-containing compounds exist in a variety of chemical forms with oxidation numbers of the nitrogen atom ranging from $-III$ to $+V$. Conversion reactions of nitrogen-containing compounds are very important processes in nature and most of the reactions occur *via* oxidation or reduction reactions on metal centres.^{1–4} One of the important reactions from dinitrogen to ammonia is called nitrogen fixation, in which the oxidation state of the nitrogen atom changes from 0 to $-III$. In natural reactions, nitrogenase acts as a catalyst to produce ammonia from atmospheric dinitrogen by generating diazene and hydrazine as intermediates under ambient conditions,^{5,6} while the industrial nitrogen fixation, the Haber-Bosch process, requires high temperature and pressure conditions. Therefore, the development of an artificial nitrogen fixation reaction under mild conditions has been attracting attention.^{7–12} Dinitrogen transition metal complexes have been synthesized from gaseous dinitrogen, and cleavage reactions of the N–N bond have been studied under various conditions.^{13–17} In connection with the natural nitrogen fixation, disproportionation and reduction reactions of hydrazine to ammonia on metal complexes have also been investigated.^{18–21} Coordination modes of dinitrogen include terminal and bridging modes,^{15,22,23} and many transition metal complexes with bridging dinitrogen have been reported to have symmetric structures. Dinitrogen-bridged diruthenium

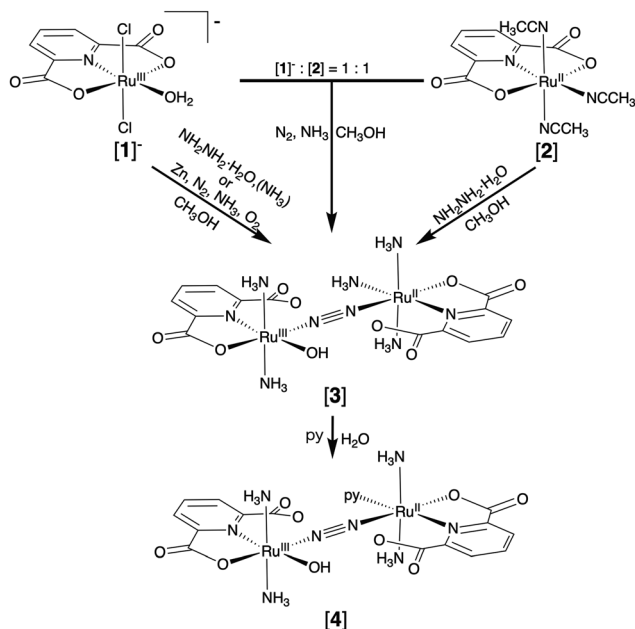
complexes have been synthesized and characterized, and all these complexes are isolated as iso-valent species.^{24–49}

In this study, the formation reaction of a dinitrogen-bridged diruthenium complex has been investigated using gaseous dinitrogen and hydrazine which is one of the intermediates in the conversion reaction from dinitrogen to ammonia.^{5,6} Since hydrazine is classified as a hard base according to the HSAB rule, 2,6-pyridinedicarboxylic acid (pydcH_2) is used as a source of a supporting ligand to stabilize ruthenium complexes in the Ru(III) state and coordinates in a tridentate, bidentate or bridging mode. Ruthenium complexes bearing 2,6-pyridinedicarboxylate (pydc^{2-}) have been reported.^{50–63} In these investigations, the ruthenium complexes bearing pydc^{2-} exhibit catalytic activity for oxidation reactions.

Formation reactions of dinuclear ruthenium complexes are summarized in Scheme 1 (see SI 2.3). Two ruthenium centres are bridged by dinitrogen with ammine and hydroxido as coexisting ligands, and the pydc^{2-} ligands coordinate to each ruthenium centre in a bidentate mode through the pyridyl nitrogen and carboxylic oxygen atoms, [$\{\text{Ru}(\text{NH}_3)_3(\kappa^2\text{-pydc})\}(\mu\text{-N}_2)\{\text{Ru}(\text{NH}_3)_2(\text{OH})(\kappa^2\text{-pydc})\}$] ([3]). The diruthenium complex [3] was obtained by a reaction of tetraethylammonium aqua-dichlorido(2,6-pyridinedicarboxylato- κ^3 -ONO)ruthenate(III), $(\text{C}_2\text{H}_5)_4\text{N}[\text{Ru}^{\text{III}}\text{Cl}_2(\text{OH}_2)(\kappa^3\text{-pydc})]$ ($(\text{C}_2\text{H}_5)_4\text{N}[1]$), with excess amounts of hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; 30 molar equivalents based on the amount of the starting complex) in methanol under atmospheric conditions and was characterized. A ^{15}N -labeled diruthenium complex was synthesized from $(\text{C}_2\text{H}_5)_4\text{N}[1]$ using ^{15}N -hydrazinium sulfate ($^{15}\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$) instead of hydrazine monohydrate. For the formation reaction of [3], hydrazine will act as a source of ammonia and dinitrogen. In reactions in which the amounts of hydrazine were varied from 5 to 30 molar equivalents, the yield and purity of the obtained complex [3] decreased as the amounts of hydrazine decreased. A reaction with 10 molar equivalents of hydrazine in addition to aqueous ammonia in the reaction mixture also afforded [3], which was characterized by UV-vis-NIR spectroscopy and cyclic voltammetry (CV), in a similar yield. Under

Department of Materials and Life Sciences, Faculty of Science and Technology,
Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan.
E-mail: h-nagao@sophia.ac.jp





Scheme 1 Formation of the dinitrogen-bridged mixed-valence diruthenium complexes.

conditions where air oxidation occurs, [3] was obtained using a Ru(II) complex, triacetonitrile(2,6-pyridinedicarboxylato- κ^3 -ONO) ruthenium(II) $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\kappa^3\text{-pydc})]$ ([2]), while the yield and purity of the obtained products were lower than those of the reactions of $(\text{C}_2\text{H}_5)_4\text{N}[1]$. As the nitrogen source, dinitrogen gas with aqueous ammonia was used in methanol. [3] was also formed from the following reactions at 60 °C in similar yields: (i) a mixture with a 1 : 1 molar ratio of $(\text{C}_2\text{H}_5)_4\text{N}[1]$ and [2] and (ii) $(\text{C}_2\text{H}_5)_4\text{N}[1]$ in the presence of zinc powder as a reducing agent, followed by exposure to air after removing the remaining zinc. The diruthenium complex [3] is only soluble in water. To improve the solubility toward organic solvents, a similar mixed-valence diruthenium complex, in which one ammine ligand was substituted by pyridine, $[\{\text{Ru}^{\text{II}}(\text{NH}_3)_2(\text{py})(\kappa^2\text{-pydc})\}(\mu\text{-N}_2)\{\text{Ru}^{\text{III}}(\text{NH}_3)_2(\text{OH})(\kappa^2\text{-pydc})\}]$ ([4]), was synthesized through a reaction of [3] with pyridine in water. [4] is soluble in both water and methanol.

Single crystals of $[\text{3}] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ were obtained by vapor diffusion of acetone into a solution of [3] in methanol–water. Structures of $(\text{C}_2\text{H}_5)_4\text{N}[1]$, $[\text{2}] \cdot \text{H}_2\text{O}$, and $[\text{3}] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ were characterized by single-crystal X-ray crystallography. The crystallographic data and selected structural parameters are summarized in Tables S2–S6. The details of the analysis for [3] are given in SI 6. The geometry of each ruthenium center in all complexes is characterized as a distorted octahedron. For [1][−] and [2], the pydc^{2-} ligand coordinates in a tridentate mode with one nitrogen atom and two oxygen atoms and three co-existing ligands (Fig. S5, S6 and Tables S3, S4). The ruthenium centres of [3] are coordinated with four nitrogen atoms of bridging dinitrogen, two ammine and pyridine groups and one oxygen atom of the carboxy group in pydc^{2-} , whose coordi-

nation mode was changed from the $\kappa^3\text{-ONO}$ type of the starting complex to the $\kappa^2\text{-ON}$ one, and each sixth coordination site is occupied by an ammine or a hydroxido ligand (Fig. 1 and S7). In the unit cell of [3], water and methanol molecules exist as crystal solvents (see the SI). The uncoordinated carboxy oxygen atoms of pydc^{2-} show weak interactions with the water molecule of crystallization and the coordinating ammine ligands. No significant differences were observed in two ruthenium units and the bridging dinitrogen structure, regardless of the hydrogen bonds between ammine, carboxylate and hydroxido ligands and the crystallization solvent. The N–N bond distance of the bridging dinitrogen (N1–N5; 1.162(5) Å) is slightly longer than those of the previously reported dinitrogen-bridged complexes of Ru(II)–Ru(II) (1.104–1.138 Å)¹¹ and the free nitrogen molecule (1.098 Å).⁶⁴ The bond distances between the ruthenium centre and the oxygen atom of the carboxy group, Ru–O (Ru1–O2; 2.081(2) and Ru2–O6; 2.094(2) Å), are found to be intermediate between those of the mono-nuclear complexes of [1][−] (2.0503(17) and 2.0572(18) Å) and [2] (2.1246(13) and 2.1217(14) Å). The C–O bond distances of the uncoordinated carboxy groups of [3] are similar to those of [1][−] and [2] ($\kappa^3\text{-pydc}^{2-}$), suggesting coordination as a doubly deprotonated pydc^{2-} in [3] as well. The Ru–N bond distances between the ruthenium centre and the ammine ligands (2.106–2.119 Å) are slightly shorter than those in the previously reported complexes of Ru(III) bearing pydc^{2-} (2.120–2.151 Å).^{50–53} The metric parameters of [3] are consistent with the oxidation state of the ruthenium centers being a mixed-valence state of Ru(II)–Ru(III) (Ru(2.5)–Ru(2.5)).

The IR absorption spectra of [3] and [4] showed a unique characteristic intense absorption band of the bridged dinitrogen ($\nu(\text{N}_2)$) at 1994 and 1984 cm^{-1} , respectively, with bands assigned to the carboxy group of the pydc^{2-} ligand ($\nu_s(\text{COO})$; 1320 and $\nu_{\text{as}}(\text{COO})$; 1583 for [3] and $\nu_s(\text{COO})$; 1314 and $\nu_{\text{as}}(\text{COO})$; 1584 cm^{-1} for [4]), as shown in Fig. S3. On the other hand, the weak $\nu(\text{N}_2)$ Raman shift of [3] was observed at 1986 cm^{-1} (Fig. S4). The $\nu(\text{N}_2)$ bands in the IR spectra were shifted to 1963 and 1953 cm^{-1} for [3] and [4] by ¹⁵N-labelling, although the isotope shift values were smaller than those predicted by the N–N model. The isotopic shift to the lower wavenumber region revealed that the source of the bridging dinitrogen in these diruthenium complexes is confirmed to originate from hydrazine. In the case of previously reported dinitrogen-

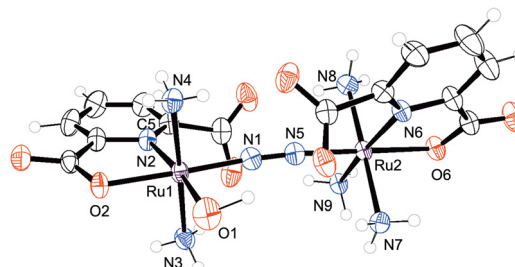


Fig. 1 Structure of [3] with thermal ellipsoids at 50% probability.



bridged diruthenium complexes having a symmetric axis at the bridging unit, the absorption of dinitrogen is hardly observed in the IR absorption spectrum but is observed in the Raman spectrum.^{24–36} The present dinitrogen-bridged diruthenium complexes [3] and [4] show an intense characteristic IR absorption band at the lowest wavenumber among the reported dinitrogen-bridged diruthenium complexes, indicating that the N–N bond becomes polarized and is activated, since the two ruthenium centres in these diruthenium complexes are asymmetric due to the difference in the electrostatic properties of the coexisting ligands, ammine and hydroxido ligands, the mixed-valence state, and interactions between the bridging dinitrogen and the uncoordinated carboxy groups and the crystal solvents.

The effective magnetic moments of [3] and [4] at 298 K are 2.11 and 1.92 μ_B , respectively, assigned to one unpaired electron in the diruthenium complexes. The electronic structure is shown to be a mixed-valence state of Ru(II)–Ru(III), taking into account the results of electrochemical measurements in aqueous solutions. The electrochemical properties of [3] and [4] in water, whose pH was adjusted to 5.0 using 0.2 M perchloric acid and 0.2 M sodium hydroxide, were measured by CV and normal pulse voltammetry (NPV). Reversible oxidation and reduction waves were observed at 0.51 and –0.26 V and at 0.53 and –0.16 V for [3] and [4], respectively, vs. Ag|AgCl (3 M NaCl aq.) within the potential window between –1.3 and 1.3 V, as shown in Fig. 2 and S14. A difference of redox potentials between [3] and [4] was observed due to the electronic effects of ammine and pyridine, consistent with that of their electronic properties. Analyses of redox processes using normal pulse voltammograms revealed that both were one-electron

transfer processes (Fig. S13 and S15–S18). The oxidation and reduction processes could be assigned to the electrode reactions of Ru(III)–Ru(III)/Ru(II)–Ru(III) and Ru(II)–Ru(III)/Ru(II)–Ru(II), respectively. From the potential separation between these redox couples (0.77 V for [3] and 0.69 V for [4]), the comproportionation constants K_C were estimated to be 1.1×10^{13} and 4.7×10^{11} , respectively (Table S7). These values revealed a stable mixed-valence state of Ru(2.5)–Ru(2.5) and these diruthenium complexes would be categorized into Class III according to the Robin–Day classification.⁶⁵

In the absorption spectra of [3] and [4] in water, absorption bands were observed at 931, 410, 355 and 271 nm for [3] and 1007, 413, 331 and 272 nm for [4] (Fig. S2 and Table S1). The spectrum of [4] in methanol was the same as that in water, indicating that the absorption maxima were solvent independent. In spectroelectrochemical measurements in an aqueous solution (pH 5) of [3] using an Optically Transparent Thin Layer Electrode (OTTLE) cell (see SI 8), UV-vis-NIR absorption spectral changes were observed during reduction from the Ru(II)–Ru(III) state to the Ru(II)–Ru(II) one and oxidation to the Ru(III)–Ru(III) one at –0.40 and 0.75 V, respectively, as shown in Fig. S20. The absorption band at around 930 nm decreased with oxidation and reduction, indicating that this absorption band is characteristic of the mixed-valence Ru centres. From the results of the spectral changes accompanying the electrochemical oxidation and reduction of [3], the absorption band observed in the lower energy region (931 nm) can be attributed to an absorption band corresponding to intervalence electron transfer between the two Ru centres. The absorption band observed at around 400 nm is attributed to the charge transfer between the ligand and the metal, and the band observed in the highest energy region is attributed to the π – π^* transition of the pydc²⁻ ligand.

In this study, we have succeeded in synthesizing the rare mixed-valence dinitrogen-bridged diruthenium complex of Ru(2.5)–Ru(2.5), [3], by reactions using hydrazine and dinitrogen as nitrogen sources. The diruthenium complex has been generated under atmospheric dinitrogen from a 1 : 1 mixture of mononuclear Ru(II) and Ru(III) complexes in a methanol solution containing ammonia. To improve solubility toward organic solvents, the methanol-soluble diruthenium complex, [4], has been synthesized by a reaction of [3] with pyridine. For the formation of the dinitrogen-bridged complex, electron-donating ligands such as ammonia, hydroxido, and carboxylato play important roles as co-ligands. These complexes show the characteristic N–N vibration band in a lower infrared region than that of the free dinitrogen molecule (2331 cm^{-1}),⁶⁶ indicating that the N–N bond is activated and polarized due to infrared activity. In addition to the redox waves observed in regions where oxidation and reduction are easily achieved, it is expected that cleavage of the N–N bond will occur accompanying reduction and protonation, and new knowledge on the conversion reactions of dinitrogen to afford ammonia can be obtained by investigating the electronic structure and reactivity of dinitrogen-bridged complexes. The properties and reactions of [3] and [4] are under investigation.

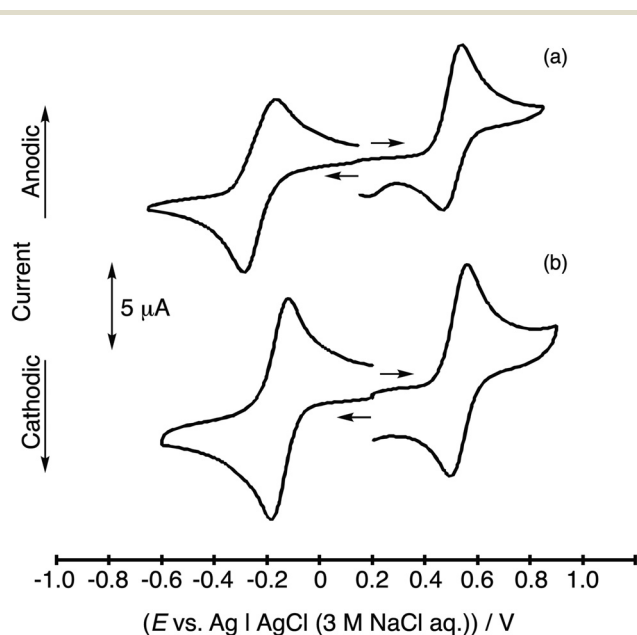


Fig. 2 Cyclic voltammograms of diruthenium complexes in an aqueous solution at pH 5 at 25 °C; (a) [3] and (b) [4] (scan rate; 100 mV s^{-1}).



Author contributions

Kazunari Uehara: investigation and formal analysis. Kim Nayoung: investigation and formal analysis. Aya Benzaki: investigation and formal analysis. Midori Otsuka: investigation and formal analysis. Tomoyo Misawa-Suzuki: investigation, formal analysis, methodology and writing – review & editing. Hirotaka Nagao: conceptualization, investigation, methodology, writing – original draft, writing – review & editing, resources and supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): NMR spectra, IR spectra, UV-vis spectra, electrochemical measurements, and X-ray structural analysis. See DOI: <https://doi.org/10.1039/d5dt02337h>.

CCDC 2465787, 2465926 and 2465788 contain the supplementary crystallographic data for this paper.^{67a-c}

Acknowledgements

The authors thank Prof. Shigeki Kuwata (Ritsumeikan Univ.) for the synthesis of ¹⁵N-labeled complexes, Prof. Tohru Wada (Rikkyo Univ.) for the measurements of Raman spectra and Prof. Takakazu Nakabayashi (Tohoku Univ.) for advice on infrared and Raman spectroscopy. This research was supported by JSPS KAKENHI grant No. 22K05302.

References

- X. Yang, S. Mukherjee, T. O'Carroll, Y. Hou, M. R. Singh, J. A. Gauthier and G. Wu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202215938.
- J. Yount and D. G. Piercey, *Chem. Rev.*, 2022, **122**, 8809–8840.
- A. J. Timmons and M. D. Symes, *Chem. Soc. Rev.*, 2015, **44**, 6708–6722.
- V. Rosca, M. Duca, M. T. Groot and M. T. M. Koper, *Chem. Rev.*, 2009, **109**, 2209–2244.
- L. C. Seefeldt, Z.-Y. Yang, D. A. Lukoyanov, D. F. Harris, D. R. Dean, S. Raugei and B. M. Hoffman, *Chem. Rev.*, 2020, **120**, 5082–5106.
- A. J. Jasniewski, C. C. Lee, M. W. Ribbe and Y. Hu, *Chem. Rev.*, 2020, **120**, 5107–5157.
- K. Tanifuji, S. Ohta, Y. Ohki and H. Seino, *Coord. Chem. Rev.*, 2023, **475**, 214838.
- Y. Tanabe and Y. Nishibayashi, *Coord. Chem. Rev.*, 2022, **472**, 214783.
- M. J. Chalkley, M. W. Drover and J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582–5636.
- D. Singh, W. R. Buratto, J. F. Torres and L. J. Murray, *Chem. Rev.*, 2020, **120**, 5517.
- A. J. Kendall and M. T. Mock, *Eur. J. Inorg. Chem.*, 2020, 1358–1375.
- M. J. Chalkley and J. C. Peters, *Eur. J. Inorg. Chem.*, 2020, 1353–1357.
- Q. Zhuo, X. Zhou, T. Shima and Z. Hou, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218606.
- G.-X. Wang, Z.-B. Yin, J. Wei and Z. Xi, *Acc. Chem. Res.*, 2023, **56**, 3211–3222.
- S. J. K. Forrest, B. Schluschaß, E. Y. Yuzik-Klimova and S. Schneider, *Chem. Rev.*, 2021, **121**, 6522–6587.
- S. Kim, F. Loose and P. J. Chirik, *Chem. Rev.*, 2020, **120**, 5637–5681.
- M. D. Fryzuk, *Acc. Chem. Res.*, 2009, **42**, 127–133.
- J. J. Kiernicki, M. Zeller and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 18194–18197.
- Y.-H. Chang, P.-M. Chan, Y.-F. Tsai, G.-H. Lee and H.-F. Hsu, *Inorg. Chem.*, 2014, **53**, 664–666.
- M. Yuki, Y. Miyake and Y. Nishibayashi, *Organometallics*, 2012, **31**, 2953–2956.
- C. T. Saouma, C. E. Moore, A. L. Rheingold and J. C. Peters, *Inorg. Chem.*, 2011, **50**, 11285–11287.
- F. Hasanayn, P. L. Holland, A. S. Goldman and A. J. M. Miller, *J. Am. Chem. Soc.*, 2023, **145**, 4326–4342.
- B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385–401.
- Y. Gao, B.-F. Qiana, H.-T. Shi, A.-Q. Jia, Q.-B. Mei and Q.-F. Zhanga, *Inorg. Chim. Acta*, 2024, **570**, 122176.
- T. Toda, S. Suzuki and S. Kuwata, *Chem. Commun.*, 2019, 55, 1028–1031.
- K. Yoshimoto, T. Yatabe, T. Matsumoto, A. Robertson, H. Nakai, H. Tanaka, T. Kamachi, Y. Shiota, K. Yoshizawa, K. Asazawa, H. Tanaka and S. Ogo, *Chem. Lett.*, 2016, **45**, 149–151.
- M. Jiménez-Tenorio, M. C. Puerta and P. Valerga, *Organometallics*, 2016, **35**, 388–399.
- F. E. Fernández, M. C. Puerta and P. Valerga, *Inorg. Chem.*, 2013, **52**, 4396–4410.
- H.-F. Ip, X.-Y. Yi, W.-Y. Wong, I. D. Williamsa and W.-H. Leung, *Dalton Trans.*, 2011, **40**, 11043–11050.
- M. A. Rankin, K. D. Hesp, G. Schatte, R. McDonaldc and M. Stradiotto, *Chem. Commun.*, 2008, 250–252.
- M. A. Bennett, M. J. Byrnes, G. Chung, A. J. Edwards and A. C. Willis, *Inorg. Chim. Acta*, 2005, **358**, 1692–1708.
- D. Sellmann, A. Hille, A. Rösler, F. W. Heinemann, M. Moll, G. Brehm, S. Schneider, M. Reiher, B. A. Hess and W. Bauer, *Chem. – Eur. J.*, 2004, **10**, 819–830.
- D. Sellmann, A. Hille, F. W. Heinemann, M. Moll, A. Rösler, J. Sutter, G. Brehm, M. Reiher, B. A. Hess and S. Schneider, *Inorg. Chim. Acta*, 2003, **348**, 194–198.
- H. Aneetha, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga and K. Mereiter, *Organometallics*, 2002, **21**, 628–635.
- R. A. T. M. Abbenhuis, I. del Río, M. M. Bergshoef, J. Boersma, N. Veldman, A. L. Spek and G. van Koten, *Inorg. Chem.*, 1998, **37**, 1749–1758.



- 36 J. P. Collman, J. E. Hutchison, M. A. Lopez and R. Guilard, *J. Am. Chem. Soc.*, 1992, **114**, 8066–8073.
- 37 M. E. Noss, N. L. Wieder, P. J. Carroll, M. J. Zdilla and D. H. Berry, *Inorg. Chem.*, 2018, **57**, 7036–7043.
- 38 Y. Tanabe, S. Kuriyama, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Organometallics*, 2014, **33**, 5295–5300.
- 39 K. Namura and H. Suzuki, *Organometallics*, 2014, **33**, 2968–2983.
- 40 N. L. Wieder, M. Gallagher, P. J. Carroll and D. H. Berry, *J. Am. Chem. Soc.*, 2010, **132**, 4107–4109.
- 41 M. Gallagher, N. L. Wieder, V. K. Dioumaev, P. J. Carroll and D. H. Berry, *Organometallics*, 2010, **29**, 591–603.
- 42 J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Dalton Trans.*, 2007, 107–113.
- 43 J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics*, 2004, **23**, 4026–4033.
- 44 L. Bonomo, C. Stern, E. Solari, R. Scopelliti and C. Floriani, *Angew. Chem., Int. Ed.*, 2001, **40**, 1449–1452.
- 45 D. G. Gusev, F. M. Dolgushin and M. Y. Antipin, *Organometallics*, 2000, **19**, 3429–3434.
- 46 K. Abdur-Rashid, D. G. Gusev, A. J. Lough and R. H. Morris, *Organometallics*, 2000, **19**, 1652–1660.
- 47 C. Creutz and H. Taube, *Inorg. Chem.*, 1971, **10**, 2664.
- 48 I. M. Treitel, T. Flood, R. E. Marsh and H. B. Gray, *J. Am. Chem. Soc.*, 1969, **91**, 6512–6513.
- 49 D. F. Harrison, E. Weissberger and H. Taube, *Science*, 1968, **159**, 320–322.
- 50 J. Li, X. Shi, F. Zhang, X. Lu, Y. Zhang, R. Liao and B. Zhang, *J. Am. Chem. Soc. Au*, 2025, **5**, 1812–1821.
- 51 S. Khan and S. Naskar, *Polyhedron*, 2022, **222**, 115898.
- 52 Y.-F. Xie, H. Zhu, H.-T. Shi, A.-Q. Jia and Q.-F. Zhang, *Inorg. Chim. Acta*, 2015, **428**, 147–153.
- 53 D. Sukanya, R. Prabhakaran and K. Natarajan, *Polyhedron*, 2006, **25**, 2223–2228.
- 54 J.-X. Wang, X.-T. Zhou, Q. Han, X.-X. Guo, X.-H. Liu, C. Xue and H.-B. Ji, *New J. Chem.*, 2019, **43**, 19415–19421.
- 55 Y. Zhang, L. Zhao, H. Zhang, R. Huang and J. Zhao, *Appl. Organomet. Chem.*, 2017, **31**, e3709.
- 56 T. Funaki, H. Funakoshi, N. Onozawa-Komatsuzaki, K. Kasuga, K. Sayama and H. Sugihara, *Chem. Lett.*, 2012, **41**, 647–649.
- 57 G. Wienhçfer, K. Schrçder, K. Mçller, K. Junge and M. Bellera, *Adv. Synth. Catal.*, 2010, **352**, 1615–1620.
- 58 L. Duan, Y. Xu, M. Gorlov, L. Tong, S. Andersson and L. Sun, *Chem. – Eur. J.*, 2010, **16**, 4659–4668.
- 59 V. W. Manner, A. G. DiPasquale and J. M. Mayer, *J. Am. Chem. Soc.*, 2008, **130**, 7210–7211.
- 60 F. Shi, M. K. Tse and M. Beller, *Chem. – Asian J.*, 2007, **2**, 411–415.
- 61 F. Shi, M. K. Tse and M. Beller, *J. Mol. Catal. A: Chem.*, 2007, **270**, 68–75.
- 62 M. K. Tse, S. Bhor, M. Klawonn, G. Anilkumar, H. Jiao, A. Spannenberg, C. Dçbler, W. Mågerlein, H. Hugel and M. Beller, *Chem. – Eur. J.*, 2006, **12**, 1875–1888.
- 63 H. Nishiyama, T. Shimada, H. Itoh, H. Sugiyama and Y. Motoyama, *Chem. Commun.*, 1997, 1863–1864.
- 64 *Handbook of Chemistry and Physics*, ed. R. D. Lide, CRC Press, New York, 76th edn, 1995, section 9, pp. 20.
- 65 *Mixed Valency Systems-Applications in Chemistry, Physics and Biology*, ed. K. Prassides, Kluwer Academic Publishers, Dordrecht, 1991.
- 66 H. P. Wang and J. T. Yates Jr., *J. Phys. Chem.*, 1984, **88**, 852–856.
- 67 (a) CCDC 2465787: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2nrvtj](https://doi.org/10.5517/ccdc.csd.cc2nrvtj); (b) CCDC 2465926: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2ns00h](https://doi.org/10.5517/ccdc.csd.cc2ns00h); (c) CCDC 2465788: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2nrkvk](https://doi.org/10.5517/ccdc.csd.cc2nrkvk).

