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THE FACILE SYNTHESIS OF CATIONIC Ru(II)-HYDRAZINE AND HYDRAZONE COMPLEXES CONTAINING ETHYLDIPHENYLPHOSPHINE AND METHYLDIPHENYLARSINE LIGANDS

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ABSTRACT

This report demonstrates a simple procedure for the preparation of three Ru(II) hydrazine and hydrazone complexes formulated as $[Ru(NH_2NH_2)_2L_4][BPh_4]_2$ (L = ethyldiphenylphosphine (3), and $[Ru(NH_2{:}CMe_2)_2L_4][BPh_4]_2$ (L = methyldiphenylarsine (4), L = ethyldiphenylphosphine (5). The complexes were characterized by IR, elemental analysis and ^1H NMR spectroscopy. All the three complexes show $\nu N{-}N$ absorption in the range between 1031 – 1029 cm^{-1} indicating the presence of coordinated hydrazine. Evidence of ethyldiphenylphosphine coordination to the Ru(II) centre was further established by ^{31}P NMR spectroscopic analysis of 3. The obtained complexes could have potential applications in other fields such as catalysis and synthesis of nanomaterials.

Keywords: Hydrazine, hydrazone, ruthenium(II), ethyldiphenylphosphine and methyldiphenylarsine

INTRODUCTION

The chemistry of hydrazine and its substituted derivatives is an area of continuous research over the years, this is due to the ease with which hydrazine forms a variety of mixed-ligand complexes with transition metals (Kumar and Murugesan, 2018; Bai and Vairam, 2021). The metal-coordinated hydrazine with other co-ligands have been variously applied as precursors for the synthesis of useful organometallic complexes (Fryzuk and Johnson, 2000; Barney *et al.*, 2006). Several metal complexes containing coordinated hydrazine have been reported with excellent catalytic and antimicrobial activities (Alibrahim *et al.*, 2022). A comprehensive review of the chemistry of coordinated hydrazines as well as neutral substituted hydrazines has been reported (Heaton *et al.*, 1996).

Nickel and cadmium nano powder have been generated from the thermal decomposition of their respective hydrazine complexes with homophthalic acid as a co-ligand (Banupriya *et al.*, 2019). Thermal decomposition of transition metal carboxylates with coordinated hydrazine have reported to easily yield high purity fine particles of the metal or metal oxides after combustion (Yasodhai *et al.*, 1999). Nanosized metal oxides were also obtained from the thermal treatment of 3-hydroxy-2-naphthoate complexes of a series of transition metals coordinated with hydrazine (Arunadevi and Vairam, 2009). Metal particles with less agglomeration and better dispersion were usually obtained when metal powders were prepared through reduction of the precursor of the hydrazine compound (Alibrahim *et al.*, 2022). Using this technique, the average particle size of metal powders can be controlled between 180 to 260 nm simply by adjusting the reaction molar ratio and concentration (Guo-yong *et al.*, 2009). Metal-hydrazine complexes have also been used as essential component in the manufacture of modern explosives and blasting agents (Wojewódka and Bełzowski, 2011).

In most of the previous reports, anhydrous hydrazine and its derivatives were used to prepare metal hydrazine complexes. Anhydrous hydrazine is an important raw material in the production of explosives and its procurement is therefore highly regulated, special security permit from the relevant authorities is normally required. This often takes a long time; the use of hydrated hydrazine was therefore investigated. Indeed, our studies have demonstrated that hydrated hydrazine, a commercially available reagent, can be used to make the Ru complexes (Owalude *et al.*, 2012; Owalude *et al.*, 2013).

In the present study, we report the synthesis and characterization of Ru(II) hydrazine and hydrazine complexes with ethyldiphenphosphine and methyldiphenylarsine co-ligands. Catalytic potential of these complexes in transfer hydrogenation of CO and CO_2 is currently under investigation.

MATERIALS AND METHODS

All the reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents were purified by standard procedures (Armanego and Perrin, 1996). $RuCl_3.xH_2O$ was purchased from Acros Organics. Ethyldiphenylphosphine and methyldiphenylarsine were commercially sourced from Aldrich. The starting materials $[\{RuCl_2(COD)\}_x]$ (**1**) (Albers *et al.*, 2007) and $[(COD)Ru(NH_2NH_2)_4][BPh_4]$ (**2**) (Owalude *et al.*, 2013) were synthesized according to literature methods. Elemental analyses were performed with an Elementar Vario EL analyzer at the Institute of Materials Science, University of Connecticut. High-resolution ^1H NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K and the chemical shifts were calibrated to solvent peaks, which are reported relative to TMS. ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4.

Synthesis of the ruthenium(II) hydrazine and hydrazone complexes:

Bis(hydrazine)tetrakis(ethyldiphenylphosphine)ruthenium(II) bis(tetraphenylborate) **(3)**

The polymeric complex $[\{RuCl_2(COD)\}_x]$ (0.6 g, 2.15 mmol) was suspended in methanol (20 mL) and hydrazine hydrate (98%, 1.5 mL) was added. The solution obtained on shaking *(ca.* 30 seconds) was heated under reflux at 60°C for 5 minutes, and the solution was filtered. Ethyldiphenylphosphine (2.9 g, 13.6 mmol) was added to the pale red solution and the mixture heated under reflux for 24 hours. Addition of a solution of $Na[BPh_4]$ (1.0 g*)* in methanol (10 mL) and cooling to 0^oC gave the product as yellow precipitate. The yellow precipitate was collected by filtration and dried in air to give yellow powder. Yield: 1.79 *g,* 64%; m.p.: decomp > 180 ^oC; IR (cm^{-1}): v(N-H): 3296, v(N-N): 997, δ(HNH): 1597, $\delta_w(NH_2)$: 1330, $\delta_r(NH_2)$: 1033, v(M-N): 612; ^1H NMR ($CDCl_3$, ppm): 1.11(t, CH_3), 2.06(q, CH_2) 3.18(s) NH_2, 6.80-7.74 (phenyl protons); ^{31}P NMR ($CDCl_3$, ppm): -17.46; Anal. Calcd. (%) for $C_{104}H_{110}B_2N_4P_4O_2Ru$, C, 73.64; H, 6.49; N, 3.30. found (%): C, 74.28; H, 6.73; N, 3.54.

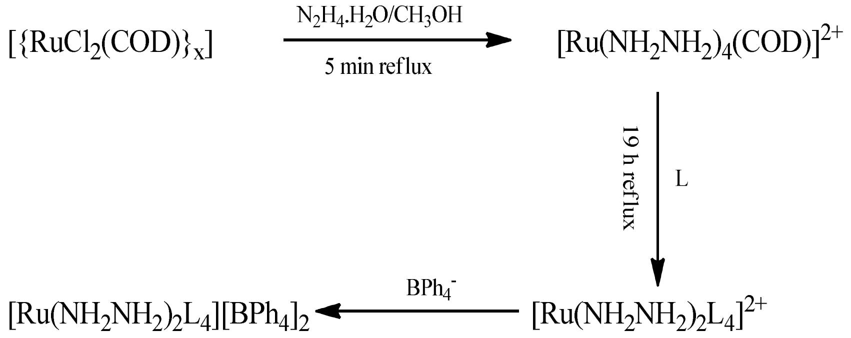
Bis(acetone hydrazone)tetrakis(ethyldiphenylphosphine)ruthenium(II) bis(tetraphenylborate) **(4)**

Ethyldiphenylphosphine (0.39 g. 1.78 mmol) was added to an acetone (15 mL) solution of **2** (0.22 g, 0.22 mmol) and the mixture was heated under constant stirring at 50°C for 24 hours. Ethanol (10 mL) was added to the orange solution and the acetone was removed under reduced pressure until a yellow precipitate formed. Complete precipitation was afforded by cooling the solution to 0^oC. The yellow precipitate was filtered and washed several times with acetone/ethanol (1:4) solution, then dried in air to give yellow powder. Yield: 1.78 *g,* 56%; m.p.: 175 – 178 ^oC; IR (cm^{-1}): v(N-H): 3271, v(N-N): 1031, v(C=N): 1663, v(M-N): 611; ^1H NMR ($CDCl_3$, ppm): 1.63 (s, 6H, $=CMe_2$), 2.04 (s, 6H, $=CMe_2$); 2.06 (CH_3), 2.84 (CH_2), 6.68 – 7.73 (m, C_6H_5). Anal. Calcd. (%) for $C_{110}H_{114}B_2N_4P_4Ru$, C, 75.83; H, 6.55; N, 3.22. found (%): C, 75.49; H, 6.85; N, 3.41.

Bis(acetone hydrazone)tetrakis(methyldiphenylarsine)ruthenium(II) bis(tetraphenylborate) **(5)**: Methyldiphenylarsine (0.43 g. 1.78 mmol) was added to an acetone (15 mL) solution of **2** (0.22 g, 0.22 mmol) and the mixture was refluxed for 24 hours. Ethanol (10 mL) was added to the orange solution and the acetone was removed under reduced pressure until a white precipitate formed. Complete precipitation was afforded by cooling the solution to 0 ^oC. The precipitate was collected through filtration, washed severally with acetone/ethanol (1:4) solution and then dried in air to give white powder. Yield: 0.96 *g,* 29%; m.p.: 155 - 158 ^oC; IR (cm^{-1}): v(N-H): 3285, v(N-N): 1031, v(C=N): 1578, v(M-N): 611; ^1H NMR ($CDCl_3$, ppm): 1.48 (s, CH_3), 1.93 (s, 6H, $=CMe_2$), 2.08 (s, 6H, $=CMe_2$); 6.89 – 7.82 (m, C_6H_5). Anal. Calcd. (%) for $C_{106}H_{106}As_4B_2N_4Ru$, C, 68.45; H, 5.70; N, 3.01. found (%): C, 68.85; H, 5.75; N, 3.08.

RESULTS AND DISCUSSION

The literature procedure for the preparation of phosphine complexes of ruthenium-hydrazine involved the reaction of the isolated salt **2** with the corresponding phosphine in ethanol at reflux (Singleton and Swanepoel, 1982). In the present study, the phosphine complex **3** was produced without first isolating **2** but from in-situ reaction of ethyldiphenylphosphine with the polymer $[\{RuCl_2(COD)\}_x]$ and hydrazine hydrate solution in methanol followed by the addition of BPh_4. This new route produced the required complex in good yield.



Scheme 1: Modified procedure for synthesis of the phosphine complex **3** (L = ethyldiphenylphosphine)

Infra-red absorption of the v(N-H) stretching vibration in **3** was observed as band of weak intensity around 3300 cm^{-1} (Albertin *et al.*, 2019). The asymmetric δ(N-H) bending vibrations were not observed in **3** as they were obscured by the BPh_4^- absorption bands (Singleton and Swanepoel, 1982). The v(N–N) stretching frequency was observed at 997 cm^{-1} indicating a monodentate coordination to the Ru(II) center (Bai and Vairam, 2021; Yasodhai *et al.*, 1999). The ^{1}H NMR spectra of **3** contained no resonances in the region expected for the cycloocta-1,5-diene protons, but the spectrum contained well defined resonance attributable to the hydrazine protons as a singlet at 3.18 ppm (Albers *et al.*, 2007). The CH_3 and CH_2 groups on the ethyl group in **3** were observed at 1.11 and 2.06 ppm respectively in the ^{1}H NMR spectrum. The ^{31}P NMR data for compound **3** revealed chemical shifts as expected for the coordinated phosphines ligands (Viswanathamurthi *et al.*, 2005). The chemical shift of -17.46 ppm present in the ^{31}P NMR spectra of **3** supports a coordinated ethyldiphenylphosphine molecule in agreement with the literature reports which revealed uncoordinated $EtPh_2P$ at +16 ppm (Grim and McFarlane, 1965). Elemental analysis indicate the presence of two molecules of water of crystallization in the complex.

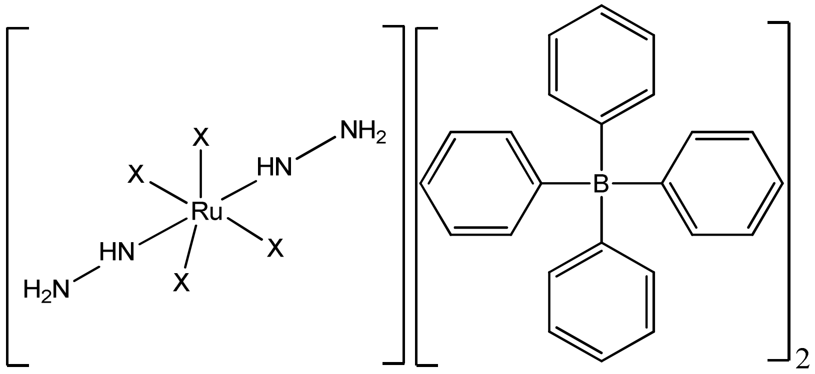


Fig. 1: Proposed chemical structure for complex **3** (X = Ethyldiphenylphosphine)

Separate treatment of **2** with four equivalents of ethyldiphenylphosphine or methyldiphenylarsine in boiling acetone under reflux resulted in the formation of the salt $Ru(NH_2NH{:}CMe_2)_2L_4][BPh_4]_2$ (**4**, L = ethyldiphenylphosphine; and **5**, L = methyldiphenylarsine) in good yields (Equation 1).

$$[Ru(NH_2NH_2)_4(COD)][BPh_4]_2 \xrightarrow{4L/Acetone} [Ru(NH_2NH{:}CMe_2)_2L_4][BPh_4]_2 \qquad (1)$$

Further substitution of the hydrazone ligands with other groups such as CO, pyridine and CO_2 were not successful. In the IR spectra of **4** and **5**, an absorption band of medium intensity in the C=N double-bond stretching region expected for azomethines at 1663 and 1578 cm^{-1} respectively for **4** and **5** (Kargar *et al.*, 2021). The v(N-H) stretching vibrations were present in both complexes between 3050-3300 cm^{-1} (Fidder *et al.*, 2013).

The asymmetric δ(N-H) bending vibrations in these complexes were also not observed at the expected region in their IR spectra which is believed to be obscured by the $[BPh_4]^-$ vibrational absorption bands (Singleton and Swanepoel, 1982). In the ^{1}H NMR spectra of **4** and **5**, a pair of singlets typical of the azomethine methyls in acetone hydrazone were observed at 1.63 and 2.04 ppm in **4** while in **5** they were present at 1.93 and 2.08 ppm. The characteristic ethyl group protons in **4** were observed at 2.06 and 2.84 ppm while the methyl protons in **5** appeared as a singlet at 1.48 ppm. The protons of the $[BPh_4]^-$ and the phenyl rings were all observed at the expected regions in the two complexes. Resonances attributable to the NH protons could not be observed in the ^{1}H N.M.R. spectra of all the compounds as previously observed in the literature (Singleton and Swanepoel, 1982).

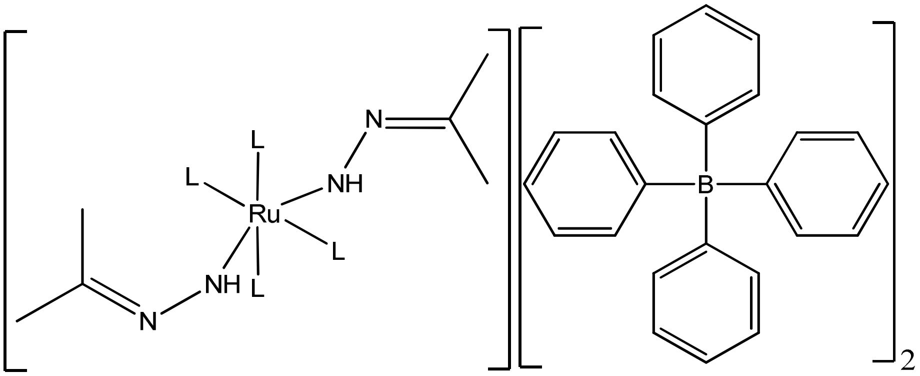


Fig. 2: Proposed chemical structure for **4** and **5** (**4**, L = Ethyldiphenylphosphine; **5**, L = Methyldiphenylarsine)

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CONCLUSION

The Ru-hydrazine complex with ethyldiphenylphosphine co-ligand (**3**) was produced by direct reaction of ethyldiphenylphosphine with the polymer $[\{RuCl_2(COD)\}_x]$ and hydrazine hydrate solution in methanol followed by the addition of BPh_4. The reaction of the ruthenium(II)-hydrazine precursor $[Ru(COD)(NH_2NH_2)_4][BPh_4]_2$ with ethyldiphenylphosphine and methyldiphenylarsine in acetone gave new Ru(II)-hydrazone complexes. The proposed stoichiometries of these hydrazine complexes agrees with the elemental, infrared and nuclear magnetic resonance spectroscopic analyses. All the complexes were isolated as air and moisture stable solids.

REFERENCES

Albers, M. O., Ashworth, T. V., Oosthuizen, H. E., Singleton, E., Merola, J. S. and Kacmarcik, R. T. (2007). (η^4-1,5-Cyclooctadiene)ruthenium(II) complexes, in: *Inorganic Syntheses*, John Wiley & Sons, Inc., pp. 68-77.

Albertin, G., Antoniutti, S., Castro, J. and Gasparetto, G. (2019). Pentamethylcyclopentadienyl half-sandwich hydrazine complexes of ruthenium: preparation and reactivity. *New Journal of Chemistry*, 43: 2676-2686.

Alibrahim, K.A., Alsuhaibani, A.M. and Refat, M.S. (2022). Synthesis and spectroscopic characterizations of manganese(II), iron(III), copper(II) and zinc(II) hydrazine complexes as catalytic activity agents. *Bulletin of the Chemical Society of Ethiopia*, 36(1): 33-44.

Arunadevi, N. and Vairam, S. (2009). 3-Hydroxy-2-naphthoate complexes of transition metals with hydrazine - Preparation, spectroscopic and thermal studies. *E-Journal of Chemistry*, 6(S1): S413-S421.

Bai, E.H.P. and Vairam, S. (2021). Coordination behaviour of hydrazine and isomers of acetoxy benzoic acids with transition metal ions. *Bulletin of the Chemical Society of Ethiopia*, 35: 337-350.

Banupriya, K., Parimalagandhi, K., Ranjithkumar, V., Mohanapriya, S. and Vairam, S. (2019). Metal-hydrazine homophthalic acid complexes as precursors of nanometal powder *Digest Journal of Nanomaterials and Biostructures*, 14: 271-277.

Barney, B.M., Lee, H.I., Dos Santos, P.C., Hoffman, B.M., Dean, D.R. and Seefeldt, L.C. (2006). Breaking the N_2 triple bond: insights into the nitrogenase mechanism. *Dalton Transactions*, 2277-2284**.**

Fidder, H., Yang, M., Nibbering, E.T.J., Elsaesser, T., Röttger, K., and Temps, F. (2013). N–H stretching vibrations of guanosine-cytidine base pairs in solution: Ultrafast dynamics, couplings, and line shapes. *The Journal of Physical Chemistry A*, 117(5): 845-854.

Fryzuk, M.D. and Johnson, S.A. (2000). The continuing story of dinitrogen activation. *Coordination Chemistry Reviews*, 200–202: 379-409.

Grim, S.O. and McFarlane, N. (1965). Phosphorus-31 chemical shifts in secondary and tertiary phosphines. *Nature*, 208: 995-996.

Guo-yong, H., Sheng-ming, X.U., Gang, X.U., Lin-yan, L.I. and Li-feng, Z. (2009). Preparation of fine nickel powders via reduction of nickel hydrazine complex precursors. *Transactions of Nonferrous Metals Society of China*, 19: 389-393.

Heaton, B., Jacob, C. and Page, P. (1996). Transition metal complexes containing hydrazine and substituted hydrazines. *Coordination Chemistry Reviews*, 154: 193-229.

Kargar, H., Aghaei-Meybodi, F., Elahifard, M. R., Tahir, M. N., Ashfaq, M. and Munawar, K. S. (2021). Some new Cu(II) complexes containing O, N-donor Schiff base ligands derived from 4-aminoantipyrine: synthesis, characterization, crystal structure and substitution effect on antimicrobial activity. *Journal of Coordination Chemistry*, 74: 1534-1549.

Kumar, K. and Murugesan, S. (2018). Synthesis, characterization and anti-bacterial activity of divalent transition metal complexes of hydrazine and trimesic acid. *Journal of Saudi Chemical Society*, 22: 16-26.

Owalude S.O., Eke U.B., Odebunmi E.O., Nesterov V.N., Meijboom R. and Coville N.J. (2012). Crystal Structure of (Cycloocta-1,5-diene)tris(hydrazine) hydridoruthenium(II) tetraphenylborate. *Analytical Sciences: X-ray Structure Analysis Online*, 28: 29-30.

Owalude, S. O., Odebunmi, E. O., Eke, U. B., Meijboom, R., Nesterov, V. N., Singleton, E. and Coville, N. J. (2013). Synthesis and X-ray studies of ruthenium(II) complexes containing hydrazine and benzyl isocyanide ligands. *Bulletin of the Chemical Society of Ethiopia*, 27: 405-411.

Singleton, E. and Swanepoel, H.E. (1982). Cationic hydrazine and hydrazone complexes of ruthenium(II) containing isocyanide ligands. *Inorganica Chimica Acta*, 57: 217-221.

Viswanathamurthi, P., Karvembu, R., Tharaneeswaran, V. and Natarajan, K. (2005). Ruthenium(II) complexes containing bidentate Schiff bases and triphenylphosphine *Journal of Chemical Sciences*, 117: 235-238.

Wojewódka, A. and Bełzowski, J. (2011). Hydrazine complexes of transition metals as perspective explosives. *CHEMIK*, 65: 20-27.

Yasodhai, S., Sivakumar, T. and Govindarajan, S. (1999). Preparation, characterisation and thermal reactivity of transition metal complexes of hydrazine with citric acid. *Thermochimica Acta*, 338: 57-65.