

Research | Vol 20 Iss 01

Iron(II) Coordination Complexes with PPh₂Py and DPEphos Ligands

Malabika Borah¹, Nabanita Saikia², Pankaj Das^{3*}

¹Department of Chemistry, B. N. College, Dhubri, Assam, India

²Department of Chemistry, New Mexico Highlands University, Las Vegas, United States

³Department of Chemistry, Dibrugarh University, Dibrugarh, Assam, India

*Corresponding author: Pankaj Das, Department of Chemistry, Dibrugarh University, Dibrugarh, Assam, India, Tel: 5054295536; E-mail: nsaikia@nmhu.edu

Received: November 29, 2023, Manuscript No. TSIC-24-121555; **Editor assigned:** December 04, 2023, PreQC No. TSIC-24-121555 (PQ); **Reviewed:** December 19, 2023, QC No. TSIC-24-121555; **Revised:** January 24, 2025, Manuscript No. TSIC-24-121555 (R); **Published:** January 31, 2025, DOI: 10.37532/0974-7419.2025.20(1).001

Abstract

Metal Iron(II) complexes [FeCl₂(η^2 -P,N-PPh₂Py)₂] (1) and [FeCl₂(η^2 -P,P-DPEphos)₂] (2), with PPh₂Py and DPEphos ligands were synthesized and characterized by elemental analysis, ESI-Mass, FTIR, UV-Vis, ¹H and ³¹P{¹H} NMR spectroscopy. The FTIR studies predicted cis-isomer to be the most stable form of complex 1 and trans-isomer as the most stable form of complex 2. Quantum chemical calculations using first-principles Density Functional Theory (DFT) in gas phase were performed on the two complexes at the B3LYP/LANL2DZ/6-31+G (d,p) level of theory. Theoretical calculations predicted the ground state of the complexes to be quintet spin state. However, in complex 1, quintet spin state led to a significant elongation in Fe–P bond length to ~3.55 Å. Thus, singlet (S=1/2) spin state was considered for complex 1 which showed reasonable agreement with calculated geometric parameters. Trans-configuration of complex 2 was shown to have a higher HOMO-LUMO energy gap (higher stability) than complex 1 which can be attributed to nature of ligand coordinated to Fe(II) ion.

Keywords: PPh₂Py ligand; P,P-chelate; Pyridylphosphine; Hydroformylation; Density Functional Theory (DFT)

Introduction

During the last few decades, transition metal complexes bearing hemilabile ligands have received substantial interest because of their structural diversity, unusual reactivity, and catalytic applications. In this regard, the bite angle of ligands plays an important role in determining their reactivity. The PPh₂Py ligand has been widely utilized as a bridging ligand because of its rigidity, that is induced by a small bite angle in a chelated mode, thereby, favoring the formation of a metal-metal bond [1-3]. The coordination modes of this ligand have been reported such as P-monodentate [4,5], P,N-chelate [5,6], P,N-bridging [7-9] and N-monodentate [10]. Several examples of pyridylphosphine coordinated homo- and hetero-binuclear complexes with transition metals were also reported [11-13]. The coordination chemistry of large bite angle diphosphine ligands find potential applications as catalysts in many organic transformation reactions [14]. DPEphos ligand with a large bite angle has been widely used because of its rich coordination modes of this ligand have been reported such as P-monodentate [15], P,P-chelate [15-17], P,O,P-chelate [17,18] and P,P-bridging [17,19]. Literature suggests that, this ligand can form coordination compounds with a variety of transition metals such as Cu(I) [15, 20-22], Ni(0) [23], Ni(II) [22], Rh(I) [24,25], Ru(II) [17], Ag(I) [19,26], Pd(0) [27], Pd(II) [16] and Re(II) [28-30]. Some of the complexes serve as excellent catalysts for hydrogenation [17,28], hydroformylation [31], carbonylation [24,25], aryl halide amination [32,33], and cross-coupling [34] reactions.

To the best of our knowledge, coordination compounds of iron with phosphine ligands, PPh₂Py and DPEphos is rather limited

[11,47]. This served as a motivation for our study to synthesize and characterize Fe(II) complexes with these two phosphine ligands. We synthesized Fe(II) complexes and characterized them by elemental analysis, ESI-mass, Fourier Transform Infrared spectra (FTIR), UV-Vis, 1H and 31P{1H} NMR spectroscopy. We performed computational calculations of both the cis- and trans-isomers using Density Functional Theory (DFT) method to compare the experimental findings of the synthesized complexes. DFT calculations in gas phase provided a detailed understanding on the most stable geometrical isomers and insights into the electronic properties.

Materials and Methods

Starting materials like diphenyl-2-pyridylphosphine (PPh₂Py) and (bis-2-diphenylphosphinophenyl)ether (DPEphos) were purchased from M/S Aldrich, USA. FeCl₂.4H₂O was purchased from Acros chemicals. All other chemicals and solvents were purchased from different Indian firms. The solvent was distilled and dried prior to use.

Synthesis of complexes

Synthesis of $[FeCl_2(\eta^2-P, N-PPh_2Py)_2](1)$ complex: A solution of the ligand PPh_2Py (250 mg; 0.95 mmol) in DMF (15 ml) was added to a solution of FeCl_2.4H₂O (100 mg; 0.50 mmol) in 10 ml DMF. The reaction mixture was stirred and refluxed under continuous flow of N₂ for an hour. The resulting solution was then evaporated after cooling and washed several times with ether and DCM to get a reddish colored complex (69% yield).

Analytical values for C₃₄H₂8N₂P₂Cl₂Fe: C, 62.48; H, 4.29; N, 4.29; Found: C, 61.99; H, 4.14; N, 3.97%. ESI-Mass, m/z (%): [M-2Cl-1]⁺, 581(100%); [M-2Cl-PPh₂Py-1]⁺, 318(3%); [M-2Cl-PPh₂Py-Fe+1]⁺, 264(5%); [M-2PPh₂-3]⁺, 280(5%); [M-Cl-2PPh₂+2]⁺, 249(5%). Selected IR frequencies (cm⁻¹, KBr): 540(ν_{FeP}), 318, 293(ν_{FeCl}). UV-Vis (CH₃CN), λ_{max} (nm): 300, 536. ¹H NMR (δ ppm): 8.67(br, 8H, Py), 5.73-6.05(br, 20H, Ph). ³¹P{¹H} NMR (δ ppm): -7.57(s).

Synthesis of $[FeCl_2(\eta^2-P,P-DPEphos)_2](2)$ complex: 10 ml DMF solution of $FeCl_2.4H_2O$ (100 mg; 0.50 mmol) was added to 15 ml DMF solution of the ligand DPEphos (550 mg; 1.02 mmol). The resulting mixture was refluxed under N₂ for an hour. After cooling the solution was evaporated and the product was washed several times with ether and DCM to obtain a reddish-brown complex (with 38% yield).

Analytical values for C₆₄H₅6O₂P₄Cl₂Fe: C, 71.70; H, 4.65; Found: C, 71.26; H, 4.37%. ESI-Mass, m/z (%): [M-1]+, 1204(12%); [M-2Cl-Ph+2]⁺, 1059(32%); [M-2Cl-Ph-PPh₂]⁺, 872(5%); [M-2Cl-3Ph-PPh₂-O-1]⁺, 702(100%); [M-2Cl-3PPh₂-O-PPh-P-2]⁺, 593(45%). Selected IR frequencies (cm⁻¹, KBr): 567(ν_{FeP}), 318(ν_{FeCl}). UV-Vis (CH₃CN), λ_{max} (nm): 315. ¹H NMR (δ ppm): 5.13-5.29(br, 56H, Ph). ³¹P {¹H} NMR (δ ppm): 30.05(s).

Physical measurements

The IR spectra was recorded in KBr disc and in CHCl₃ using Shimadzu IR-prestige-21 (4000-250 cm⁻¹). The UV-Vis spectra of the complexes were recorded using Shimadzu, Graphicord UV-240 and Shimadzu UV 1700 spectrophotometers. The electrospray mass spectra of the synthesized complexes were recorded using Waters ZQ-4000 LC-Mass spectrometer. The ¹H and ³¹P NMR spectra of the complexes were recorded using TMS and 85% H_3PO_4 as reference by Bruker Avance 400 MHz spectrometer.

Theoretical calculations

Since repeated attempts to obtain diffraction quality crystals of the two Fe(II) complexes failed at the level of experiment, using an approach outlined in our previous studies [11,47], we modeled the cis- and trans-isomers of the Fe(II) complexes by substituting the two bulky phenyl groups in PPh₂ by hydrogen atoms (Figure 1), to make the computations more tractable and reduce both calculation time and cost. The initial geometries of Fe(II) complexes with hemilabile phosphine-based ligands were optimized in gas phase without any symmetry constraints using Gaussian 09 program package [35]. Spin states, namely, singlet (S=1/2), triplet (3/2) and quintet (5/2) were considered to determine the ground state of Fe²⁺ complexes. The hybrid GGA (generalized gradient approximation) exchange-correlation functional, B3LYP was employed without any symmetry constraint along with the non-relativistic Effective Core Potential (ECP) LANL2DZ (Los Alamos effective-core potential) basis set [36] for Fe and Cl atoms and a 6-31+G (d,p) basis set for C, H, O, and P atoms. The reliability of B3LYP functional for studying a wide range of molecular properties including electronic structures of biomolecules interacting with metal nanoclusters have been reported [37,38] and

showed consistent results for complexes with gold and other transition metals [39,40]. The electronic properties, frontier molecular orbitals namely HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), HOMO-1, HOMO-2, LUMO+1, LUMO+2 and HOMO-LUMO energy gap of the complexes were calculated. GaussView 6.0 was employed for all structural analysis. The minimum energy structures of the complexes were visualized using GaussView and the frontier molecular orbitals were visualized using Avogadro software, version 1.2.0 [41].

Results and Discussion

Synthesis of complexes

The reaction of FeCl₂.4H₂O with two molar equivalent of PPh₂Py and DPEphos ligands in DMF solution yield hexa-coordinated $[FeCl_2(\eta^2-P,N-PPh_2Py)_2](1)$ and $[FeCl_2(\eta^2-P,P-DPEphos)^2](2)$ complexes where both ligands were coordinated in a bidentate fashion. The synthesis route of the complexes is shown in Figure 1.



The ESI-Mass spectrum of $[FeCl_2(\eta^2-P,N-PPh_2Py)_2](1)$ shows a base peak at m/z=581(100%) which correspond to the $[Fe(PPh_2Py)2+1]+$ fragment *i.e.* [M-2Cl-1]+ ion, formed by the removal of two Cl- ions from the complex. Low intense peaks are observed at m/z=318, 280, 264, 249, respectively which are due to $[M-2Cl-PPh_2Py-1]^+$, $[M-2PPh_2-3]+$, $[M-2Cl-PPh_2Py-Fe+1]^+$ and $[M-2PPh_2-Cl+2]^+$ ions respectively (Supporting Information, Figures 1 and 2). The ESI-Mass spectrum of $[FeCl_2(\eta^2-P,P-DPEphos)_2](2)$ show a low intense [M-1]+ peak at m/z=1204. The base peak at m/z=702 is due to the $[M-2Cl-3Ph-PPh_2-O-1]^+$ fragment. Peaks with moderate intensities are observed at m/z=1059 and 593 due to the $[M-2Cl-Ph+2]^+$ and $[M-2Cl-3PPh_2-O-PPh-2]+$ ions respectively. In addition, a peak at m/z=872 is observed for $[M-2Cl-Ph-PPh_2]^+$ fragment with a very low intensity (Supporting Information patterns of both the complexes are consistent with similar type of mononuclear dichloride complexes. The elemental analysis and ESI-mass spectra of the complexes are in clear agreement with the above formulation.

FTIR studies

The IR spectrum of $[FeCl_2(\eta^2-P,N-PPh_2Py)2](1)$ in KBr shows a characteristic band for M-P stretching at 540 cm⁻¹ consistent with coordination of the ligand through P–atoms (Figure 2A). In addition, the spectrum shows a pyridine ring deformation frequency $\{v(C=N)\}$ at 1614 cm⁻¹ which is shifted to higher frequency in comparison to the free PPh_2Py ligand (1567 cm⁻¹) indicating the presence of N–coordinated pyridine rings [6,42]. The far IR shows two M–Cl stretching bands at 318 and 293 cm⁻¹, respectively which are characteristic of the cis–arrangement of chlorides [43]. In the IR spectrum of $[FeCl_2(\eta^2-P,P-DPEphos)2](2)$, a very low intensity M–P stretching band is observed at 567 cm⁻¹ (Figure 2B). An intense M–Cl stretching peak in the far IR spectrum at 318 cm⁻¹ is consistent with the chlorides in a trans–arrangement [43]. The non-coordination of the ethereal oxygen is further confirmed by the presence of the band at 1122 cm⁻¹ [44].



FIG. 2. FTIR spectra of (A) complex 1 and (B) complex 2.

UV–Vis studies

UV–Vis spectrum of $[FeCl_2(\eta^2-P,N-PPh_2Py)_2](1)$ in methanol shows two intense bands at 300 and 536 nm (Figure 3A). The former is attributed to intraligand $n \rightarrow \pi^*$ transition which is slightly shifted to higher wavelength region compared to free ligand while the latter is due to LMCT transition. It may be noted that The UV–Vis spectrum of $[FeCl_2(\eta^2-P,P-DPEphos)^2](2)$ in DMSO shows a strong absorption band at 315 nm which can be assigned to intraligand $n \rightarrow \pi^*$ transition (Figure 3B). This band shifts about 46 nm in comparison to free ligand and is attributed to the coordination with Fe(II).





¹H and ³¹P{¹H} NMR studies

The ³¹P{¹H} NMR spectrum of [FeCl₂(η^2 -P,N-PPh₂Py)₂](1) shows a strong singlet at δ -7.57 ppm indicating the presence of only one type of P-atoms in the complex (Figure 4A). Compared to the ³¹P{¹H} NMR spectrum of free ligand [45], complex 1 shows an up field shift which is characteristic of a four–membered chelated ring [6]. However, it is important to mention here that a similar type of complex was reported by Ndifon et. al. [42] where they established using IR spectroscopy that each PPh₂Py ligand in the complex is η^1 -coordinated through N–atom and not through P–atom.

The ¹H NMR spectrum shows a broad peak for the pyridyl protons centered at δ 8.67 ppm, shifting downfield compared to free ligand which clearly indicate the coordination through N-atom (Supporting Information, Figure 5). Thus both ³¹P{¹H} and ¹H NMR spectra supports our proposed η^2 -P,N-structure of the complex.

The ³¹P{¹H} NMR spectrum of $[FeCl_2(\eta_2-P,P-DPEphos)_2](2)$ contains a singlet at about δ 30 ppm, shifting downfield compared to free ligand (δ -16.5 ppm) [46] confirming the coordination of P-atoms with the metal (Figure 4B). The ¹H NMR spectrum shows a slightly broad peak for aromatic protons in the region δ 5.29–5.13 ppm (Supporting Information, Figure 6).



FIG. 4. ³¹P{¹H} NMR spectra of (A) complex 1 and (B) complex 2

Structural properties of the complexes

In our theoretical calculations, we optimized the geometries of the two complexes in both cis- and trans-configurations. The cisisomer of complex 1 and trans-isomer of complex 2 are predicted to the minimum energy (stable) geometries (Figure 5). Geometry optimization of the complexes 1 and 2 in gas phase in the three spin states (S=1/2, 3/2 and 5/2) confirm the high-spin quintet (S=5/2) state to the minimum energy configuration. Structural parameters of the complexes such as bond length, bond angle, dipole moment and HOMO-LUMO energy gap is provided in Table 1. We calculated the relative stability of the complexes in terms of the total energy and quintet state is shown to be the ground state geometry for both complexes in their respective isomeric forms (Supporting Information, Table 1). However, the energy difference between cis- and trans-isomers is very small. For complex 1, though quintet spin state is shown to have favorable energy, it led to a significant elongation in Fe–P bond length to ~3.55 Å which was beyond the reported Fe–P bond length. Due to this reason, we consider singlet (S=1/2) spin state in this study which shows reasonable agreement in the calculated geometric parameters. The total energies and relative stability of the isomers of complexes 1 and 2 in spin states 1/2, 3/2 and 5/2 are provided in Supporting Information, Table 2.



FIG. 5. Minimum energy geometries of Fe(II) complexes 1 and 2 with hemilabile ligands. (A) Complex 1 in cisconfiguration and (B) complex 2 in trans-configuration. Frequency calculations confirmed the ground state of the optimized structures in gas phase.

	Bond length		Bond angle		Dipole moment (D)	Energy gap (eV)
	(Å)		(°)			
Complex 1	Fe-Cl1	2.38	Cl1-Fe-Cl2	128.92		
	Fe-Cl2	2.38	Cl1-Fe-P1	80.20		
	Fe–P1	2.39	Cl2-Fe-P2	80.25	8.97	3.79
	Fe–P2	2.39	N1-Fe-Cl1	102.80		
	Fe–N1	2.01	N2-Fe-Cl2	102.78		
	Fe-N2	2.01	P1-Fe-P2	75.47		
Complex 2	Fe-Cl1	2.42	Cl1-Fe-Cl2	180.0	0.07	4.80
	Fe-Cl2	2.37	Cl1-Fe-P1	92.66		
	Fe–P1	2.68	Cl2-Fe-P2	86.37		
	Fe–P2	2.70	Cl1-Fe-P3	93.63		
	Fe–P3	2.70	Cl2-Fe-P4	87.34		
	Fe–P4	2.68	P1-Fe-P2 P3-Fe-P4	89.45		

 Table 1. Geometrical parameters of the cis-isomer of complex 1 and trans-isomer of complex 2 calculated at the B3LYP/LANL2DZ/6-31+G(d,p) level of theory in gas phase.

In complex 1 and 2, the average Fe–P bond length is calculated to be ~2.39 Å and ~2.69 Å, respectively. These values of bond length are longer as compared to our previous reported value of ~2.3 Å [47]. An elongation in Fe–P bond is observed in complex 2 which may be accounted to the quintet spin state of the complex. The Fe–P bond in complex 1, cis-isomer, is shorter than complex 2, trans-isomer. In a previous study by Kneebone et. al. [48], Fe–P bond length in FeCl₂(bisphosphine) complexes were reported between 2.41–2.45 Å depending on the bisphosphine ligand coordinated to iron ion. The average Fe–Cl bond length is calculated to be 2.38 Å for complex 1 and ~2.39 Å for complex 2, which is in good agreement with our previous reported values [47]. However, the calculated values are slightly longer than the reported [FeCl₃{PPh2(p-C₆H₄NMe₂)-P}3] complex 1 and other known Fe-complex and these changes in the geometrical parameters may be attributed to electron delocalization [11,48,49]. The Fe–N bond length of 2.01Å in complex 1 is comparable to other known pyridyl complexes of Fe(III) [49]. Elongation in the calculated bond lengths, as shown in Table 1 is associated to the nature of ligand coordinated to Fe(II) ion, spin state of the complexes, electronic configuration, level of calculation and absence of intramolecular interactions e.g. van der Waals forces and hydrogen bond interactions in the gas phase DFT calculations [50,51].

Electronic properties of the complexes

HOMO-LUMO energy gap is an important molecular descriptor in comparing the stability of molecular complexes. Comparison of HOMO-LUMO energy gap suggests complex 2 to have a higher energy gap of 4.80 eV compared to complex 1 in gas phase (Table 1), that can be attributed to the nature of ligand coordinated to Fe(II) ion. The lower HOMO-LUMO energy gap in complex 1 explains the ultimate charge transfer interactions that take place within the complex. In terms of dipole moment, we find that a deviation from a perfectly octahedral geometry leads to an increase in the overall dipole moment of the complex, as shown in Figure 5. The significantly higher dipole moment in complex 1 compared to complex 2 point to the former being more polarizable than complex 2.



FIG. 6. Frontier molecular orbitals corresponding to HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 of complexes 1 and 2 in gas phase.

Frontier molecular orbitals suggests that in complex 1, HOMO is mainly localized on atoms of chlorine and Fe while LUMO is delocalized on the ligand except for chlorine atoms. In complex 2, both HOMO and LUMO orbitals are localized on atoms of chlorine and Fe along with some contributions from the ligand. The frontier molecular orbitals for HOMO-1, HOMO-2, LUMO+1, and LUMO+2 are depicted in Figure 6. In complex 1, like HOMO orbitals, HOMO-1 and HOMO-2 is concentrated on chlorine and Fe atoms. Thus, they act as sites for electron donors in the complex. In complex 2, both HOMO-1 and HOMO-2 is predominantly localized on chlorine atom and delocalized on the aromatic ring which suggest these sites to contribute as electron donors in the complex. The LUMO+1 and LUMO+2 orbitals in complexes 1 and 2 are predominantly delocalized on the ligand with some contributions on Fe and chlorine atoms.

Conclusion

Two Fe(II) chloride complexes with PPh₂Py and DPEphos ligands were synthesized and characterized by elemental analysis, ESI-Mass, FTIR, UV-Vis, ¹H, and ³¹P{¹H} NMR spectroscopy. Molecular geometries of the synthesized complexes were optimized in gas phase using Density Functional Theory (DFT) calculations to get better insights into their structural features. DFT calculations supported the experimental findings well establishing the cis- and trans-isomers of complexes 1 and 2, respectively. Further, spin state of the iron center is shown to play an important role in determining the stable geometry, isomeric forms, and interaction *via* the ancillary ligand. As synthesized complexes with Fe(II) are rather limited, the present study extends the scope of Fe(II) complexes with a large bite angle diphosphine ligand and a small bite angle PPh₂Py ligand and brings to our attention the importance of phosphine-based ligands in iron chemistry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The services of SAIF(NEHU), Shillong is gratefully acknowledged for the NMR and ESI-mass analysis.

Supporting Information

The analytical data of Fe(II) chloride complexes. The experimentally measured ESI-mass and ¹H NMR spectrum of complexes 1 and 2. The total energies and relative energies of complexes 1 and 2 in spin states 1/2, 3/2, and 5/2. The datasets generated during the current study are available from the corresponding authors on reasonable request.

References

- Kuang SM, Zhang ZZ, Wu BM, et al. Synthesis of Fe-M complexes (M=Mo, Mn, Fe, Co, Ni, Zn, Cd, Hg) using trans-Fe(EtPhPpy)₂(CO)₃ as an organometallic tridentate ligand molecular structures of (CO)₃Fe(μ-EtPhPpy)₂Mo(CO)₃ and (CO)₃Fe (μ-EtPhPpy)₂Cd(SCN)₂(EtPhPpy=2-(ethylphenylphosphino) pyridine). J Organomet Chem. 1997;540(1-2):55-60.
- 2. Newkome GR. Pyridylphosphines. Chemical reviews. 1993;93(6):2067-2089.
- 3. Braunstein P, Knorr M, Strampfer M, et al. Synthetic, spectroscopic and structural studies on phosphinestabilised [PPh₃, Ph₂PCH₂PPh₂, Ph₂P(CH₂)₄PPh₂,(Ph₂P)C₅H₄N] main group element-iron-silicon chain complexes. J Chem Soc Dalton Trans. 1994(2):117-134.
- 4. Ang HG, Kwik WL, Lau PT. Coordinating properties of 2-pyridyldiphenylphosphine with some metal carbonyls. Polyhedron. 1990;9(12):1479-1482.
- 5. Nishide K, Ito S, Yoshifuji M. Preparation of carbonyltungsten (0) complexes of 2-pyridylphosphines showing a stepwise coordination pattern by way of monodentate to chelate mode. J Organomet Chem. 2003;682(1-2):79-84.
- 6. Wajda-Hermanowicz K, Ciunik Z, Kochel A. Syntheses and molecular structure of some Rh and Ru complexes with the chelating diphenyl (2-pyridyl) phosphine ligand. Inorg Chem. 2006;45(8):3369-3377.
- 7. Deeming AJ, Smith MB. Triosmium clusters with 2-pyridylphosphines as ligands. J Chem Soc Dalton Trans. 1993;(22):3383-33891.
- Franciò G, Scopelliti R, Arena CG, et al. IrPd, IrHg, IrCu, and IrTl Binuclear Complexes Bridged by the Short-Bite Ligand 2-(Diphenylphosphino) pyridine. Catalytic Effect in the Hydroformylation of Styrene Due to the Monodentate P-Bonded 2-(Diphenylphosphino) pyridine Ligands of trans-[Ir (CO)(Ph₂PPy) 2Cl]. Organometallics. 1998;17(3):338-347.
- Mak TW. A novel luminescent iridium (I)-cadmium (II) binuclear complex displaying a long-lived metal-toligand charge-transfer excited state. Synthesis and structural characterisation of I (CO)₂Ir (μ-Ph₂Ppy)₂CdI ₂[Ph₂Ppy=2-(diphenylphosphino) pyridine]. J Chem Soc Dalton Trans. 1997(19):3409-3410.
- 10. Carson EC, Lippard SJ. Dioxygen-Initiated oxidation of heteroatomic substrates incorporated into ancillary pyridine ligands of carboxylate-rich diiron (II) complexes. Inorg Chem. 2006;45(2):837-848.
- 11. Das P, Sarmah PP, Borah M, et al. Low-spin, mononuclear, Fe (III) complexes with P, N donor hemilabile ligands: A combined experimental and theoretical study. Inorganica Chimica Acta. 2009;362(14):5001-5011.
- Takahashi Y, Murakami N, Fujita KI, et al. Synthesis and reactivity of homo-and hetero-dimetallic complexes bridged by diphenyl-2-pyridylphosphine and hydrides: Regioselectivity of alkyne insertion into unsaturated M¹(μ-PPh₂Py)(μ-H)₂M² moieties. Dalton Trans. 2009;(11):2029-2042.
- 13. Deeming AJ, Smith MB. Cleavage of phosphorus-phenyl and phosphorus-2-pyridyl bonds in the reactions of mixed phenyl-(2-pyridyl) phosphines with [Ru₃(CO)₁₂]. J Chem Soc Dalton Trans. 1993;(13):2041-2046.
- 14. Birkholz MN, Freixa Z, van Leeuwen PW. Bite angle effects of diphosphines in C–C and C–X bond forming cross coupling reactions. Chem Soc Rev. 2009;38(4):1099-1118.
- 15. Venkateswaran R, Balakrishna MS, Mobin SM, et al. Copper (I) complexes of bis (2-(diphenylphosphino) phenyl) ether: synthesis, reactivity, and theoretical calculations. Inorg Chem. 2007;46(16):6535-6541.
- 16. Zuideveld MA, Swennenhuis BH, Boele MD, et al. The coordination behaviour of large natural bite angle diphosphine ligands towards methyl and 4-cyanophenylpalladium (II) complexes. J Chem Soc Dalton Trans. 2002;(11):2308-2317.
- 17. Venkateswaran R, Mague JT, Balakrishna MS. Ruthenium (II) complexes containing bis (2-(diphenylphosphino) phenyl) ether and their catalytic activity in hydrogenation reactions. Inorg Chem.

2007;46(3):809-817.

- 18. Kuang SM, Fanwick PE, Walton RA. Unsymmetrical Dirhenium Complexes that Contain [Re₂]⁶⁺ and [Re²]⁵⁺ Cores Complexed by Tridentate Ligands with P₂O and P₂N Donor Sets. Inorg Chem. 2002;41(2):405-412.
- 19. Freudenmann D, Feldmann C. Ionic liquid based synthesis of the dinuclear complex Ag₂I₂ (DPEphos)₂ with Ag–Ag interaction. Inorg Chim Acta. 2011;375(1):311-313.
- 20. Aslanidis P, Cox PJ, Tsipis AC. Structural and electronic properties of luminescent copper (I) halide complexes of bis [2-(diphenylphosphano) phenyl] ether (DPEphos). Crystal structure of [CuCl (DPEphos)(dmpymtH]. Dalton Trans. 2010;39(42):10238-10248.
- 21. Zhang L, Li B. A series of 4, 5-diazafluoren-9-one-derived ligands and their Cu (I) complexes: Synthesis, characterization and photophysical properties. Inorg Chim Acta. 2009;362(14):4857-4861.
- 22. Kuang SM, Cuttell DG, McMillin DR, et al. Synthesis and structural characterization of Cu (I) and Ni (II) complexes that contain the Bis [2-(diphenylphosphino) phenyl] ether ligand. Novel emission properties for the Cu (I) species. Inorg Chem. 2002;41(12):3313-3322.
- 23. Wilting J, Müller C, Hewat AC, et al. Nickel-catalyzed isomerization of 2-methyl-3-butenenitrile. Organometallics. 2005;24(1):13-15.
- 24. Guan ZH, Ren ZH, Spinella SM, et al. Rhodium-catalyzed direct oxidative carbonylation of aromatic C-H bond with CO and alcohols. J Am Chem Soc. 2009;131(2):729-733.
- 25. Wu XF, Neumann H. Ruthenium and Rhodium-Catalyzed Carbonylation Reactions. Chem Cat Chem. 2012;4(4):447-458.
- 26. Balakrishna MS, Venkateswaran R, Mobin SM. Silver (I) complexes of bis [2-(diphenylphosphino) phenyl] ether. Polyhedron. 2008;27(3):899-904.
- 27. Kranenburg M, Delis JG, Kamer PC, et al. Palladium (0)-tetracyanoethylene complexes of diphosphines and a dipyridine with large bite angles, and their crystal structures. J Chem Soc Dalton Trans. 1997;(11):1839-1850.
- 28. Dudle B, Rajesh K, Blacque O, et al. Rhenium in homogeneous catalysis:[ReBrH(NO)(labile ligand)(largebite-angle diphosphine)] complexes as highly active catalysts in olefin hydrogenations. J Am Chem Soc. 2011;133(21):8168-8178.
- 29. Dudle B, Rajesh K, Blacque O, et al. Rhenium nitrosyl complexes bearing large-bite-angle diphosphines. Organometallics. 2011;30(11):2986-2992.
- 30. Parr ML, Perez-Acosta C, Faller JW. Synthesis, characterization and structural investigation of new rheniumoxo complexes containing bidentate phosphine ligands: an exploration of chirality and conformation in chelate rings of small and large bite angle ligands. New J Chem. 2005;29(4):613-619.
- 31. Hanf S, Alvarado Rupflin L, Glaser R, et al. Current state of the art of the solid Rh-based catalyzed hydroformylation of short-chain olefins. Catalysts. 2020;10(5):510.
- 32. Hamann BC, Hartwig JF. Systematic variation of bidentate ligands used in aryl halide amination. Unexpected effects of steric, electronic, and geometric perturbations. J Am Chem Soc. 1998;120(15):3694-3703.
- 33. Sadighi JP, Harris MC, Buchwald SL. A highly active palladium catalyst system for the arylation of anilines. Tetrahedron Lett. 1998;39(30):5327-5330.
- 34. Dennis EG, Jeffery DW, Perkins MV, et al. Pd (DPEPhos) Cl₂-catalyzed Negishi cross-couplings for the formation of biaryl and diarylmethane phloroglucinol adducts. Tetrahedron. 2011;67(11):2125-2131.
- 35. Frisch MJEA, Trucks GW, Schlegel H, et al. "Gaussian 03, revision c.02, Gaussian." Inc., Wallingford, CT4 (2004).
- 36. Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J Chem Phys. 1985;82(1):299-310.
- 37. Wells Jr DH, Delgass WN, Thomson KT. Density functional theory investigation of gold cluster geometry and gas-phase reactivity with O₂. J Chem Phys. 2002;117(23):10597-10603.
- 38. Abdalmoneam MH, Waters K, Saikia N, et al. Amino-acid-conjugated gold clusters: Interaction of alanine and tryptophan with Au₈ and Au₂₀. J Phys Chem C. 2017;121(45):25585-25593.
- 39. Gronbeck H, Andreoni W. Gold and platinum microclusters and their anions: Comparison of structural and

electronic properties. Chemical Physics. 2000;262(1):1-4.

- 40. Amiri MG, Golchoubian H. Solvatochromism, thermochromism and density functional theory studies of Copper (II) complexes containing hemilabile tetradentate ligand. J Mol Struct. 2018;1165:196-205.
- 41. https://avogadro.cc.
- 42. Ndifon PT, Agwara MO, Hayashi Y, et al. Synthesis and characterisation of some metal complexes of hybrid phosphorus-nitrogenligands: The crystal structure of 1-(diphenylphosphino)-2-(2-pyridyl) ethane cobalt (II) chloride. Bull Chem Soc Ethiop. 2008;22(2):253-260.
- 43. Nakamoto K. Infrared spectra of inorganic and coordination compounds. (No Title). 1970 Jan. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Second Ed., John Wiley & Sons, 1970.
- 44. Grim SO, Mitchell JD. Unsymmetrical bis-phosphorus ligands. 9. Group VI metal carbonyl complexes and other derivatives of various (phosphinomethyl) phosphine sulfides. Inorg Chem. 1977;16(7):1762-1770.
- 45. Rojas R, Valderrama M. Trimethylsilylcyclopentadienylchromium (III) complexes with diphenyl-2pyridylphosphine: Synthesis, structural characterisation and catalytic behaviour of [(C₆H₅)₂PC₅H₄NH][(η⁵-Me₃SiCp)CrCl₃]. J Org Chem. 2004;689(13):2268-2272.
- 46. Wong WK, Zhang L, Wong WT. Synthesis and X-ray crystal structure of a hexanuclear silver (I) complex with non-chelating tri-and tetra-dentate bridging o-(diphenylphosphino) benzoate ligands. Chem Comm. 1998(6):673-674.
- 47. Borah M, Saikia N, Das P. A combined computational and experimental study of Fe (II) complexes with hemilabile phosphine-based P, O donor ligands. J Mol Struct. 2021;1230:129661.
- 48. Kneebone JL, Fleischauer VE, Daifuku SL, et al. Electronic Structure and Bonding in Iron (II) and Iron (I) Complexes Bearing Bisphosphine Ligands of Relevance to Iron-Catalyzed C–C Cross-Coupling. Inorg Chem. 2016;55(1):272-282.
- 49. Mandon D, Nopper A, Litrol T, Goetz S. Tridentate Coordination of Monosubstituted Derivatives of the Tris (2-pyridylmethyl) amine Ligand to FeCl₃: Structures and Spectroscopic Properties of ((2-Bromopyridyl) methyl) bis-(2-pyridylmethyl) amine Fe^{III}Cl₃ and (((2-p-Methoxyphenyl) pyridyl) methyl) Bis (2-pyridylmethyl)] amine Fe^{III}Cl₃ and Comparison with the Bis (2-pyridylmethyl)] amine Fe^{III}Cl₃ Complex. Inorg Chem. 2001;40(18):4803-4806.
- 50. Shaghaghi Z, Bikas R, Tajdar H, et al. Iron (III) complexes with N₂O₂-donor salophen and azide ligands: Crystal structure, experimental and theoretical studies. J Mol Struct. 2020;1217:128431.
- Masoudiasl A, Montazerozohori M, Joohari S, et al. Structural investigation of a new cadmium coordination compound prepared by sonochemical process: Crystal structure, Hirshfeld surface, thermal, TD-DFT and NBO analyses. Ultrason Sonochem. 2019;52:244-256.