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A phosphomide based PNP ligand, 2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N) showing PP, PNP and PNO coordination modes

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A new class of PNP pincer ligand, pyridine-2,6-diylbis(diphenylphosphino)methanone, 2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N) (1) (hereafter referred as “bis(phosphomide)”) was prepared by the reaction of picolinoyldichloride with diphenylphosphine in the presence of triethylamine. The bis(phosphomide) 1 shows symmetrical PNP, unsymmetrical PNO and simple bidentate PP coordination modes when treated with various transition metal precursors. The reaction between 1 and [Ru(p-cymene)Cl\textsubscript{2}]\textsubscript{2} in a 1:1 molar ratio yielded a binuclear complex [Ru\textsubscript{2}Cl\textsubscript{4}(NCCH\textsubscript{3})(p-cymene){2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}]\textsubscript{2} (2) containing an unsymmetrical PNO pincer cage around one of the ruthenium centers, whereas the second ruthenium is bonded to the other phosphorus atom along with cymene and two chloride atoms. Symmetrical pincer complexes [RuCl(NCCCH\textsubscript{3})\textsubscript{2}{2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}][ClO\textsubscript{4}] (3), [Ru(\eta\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}){2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}][OTf] (4) and [RhCl{2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}]\textsubscript{2} (5) were obtained in the respective reactions of 1 with [RuCl(NCCCH\textsubscript{3})(p-cymene)][ClO\textsubscript{4}], [Ru(\eta\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})Cl(PPh\textsubscript{3})\textsubscript{2}] and [Rh(COD)Cl]\textsubscript{2}. Group 10 metal complexes [NiCl{2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}](BF\textsubscript{4}) (6), [PdCl{2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}][ClO\textsubscript{4}] (7) and [PtCl{2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)}][ClO\textsubscript{4}] (8) were
obtained by transmetallation reactions of \textit{in situ} generated Ag\textsuperscript{1} salts of \textbf{1} with Ni(DME)Cl\textsubscript{2} or M(COD)Cl\textsubscript{2} (M = Ni, Pd and Pt). The reactions between \textbf{1} and CuX or [Cu(NCCH\textsubscript{3})\textsubscript{4}](BF\textsubscript{4}) produced mononuclear complexes of the type [CuX\{2,6-\{Ph\textsubscript{2}PC(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{9}, X = Cl; \textbf{10}, X = Br; \textbf{11}, X = I), [Cu(NCCH\textsubscript{3})\{Ph\textsubscript{2}C(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{12} and [Cu\{Ph\textsubscript{2}C(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{13}. Similarly, the silver complexes [AgX\{2,6-\{Ph\textsubscript{2}PC(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{14}, X = ClO\textsubscript{4}; \textbf{15}, X = Br) were obtained by the treatment of \textbf{1} with AgClO\textsubscript{4} or AgBr in 1:1 molar ratios. Treatment of \textbf{1} with AuCl(SMe\textsubscript{2}) in 1:1 and 1:2 molar ratios produced mono- and binuclear complexes, [AuCl\{2,6-\{Ph\textsubscript{2}PC(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{16} and [Au\textsubscript{2}Cl\{2,6-\{Ph\textsubscript{2}PC(O)\}_2(C\textsubscript{5}H\textsubscript{3}N)\}](BF\textsubscript{4}) \textsubscript{17} in good yield. The structures of ligand \textbf{1} and complexes \textbf{2, 5} and \textbf{17} were confirmed by single-crystal X-ray diffraction studies. DFT calculations were carried to gain more insight into the structure and bonding features as well as feasibility of some key chemical transformations.

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**Introduction**

The last few decades have seen an enormous growth in the field of pincer ligands because of their importance in homogeneous catalysis and materials applications.\textsuperscript{1} Transition metal complexes of these ligands catalyze a plethora of reactions ranging from organic transformations such as Aldol and Michael addition reactions\textsuperscript{2} to olefin polymerization\textsuperscript{3}, alkane metathesis and alkane dehydrogenation.\textsuperscript{4} Of the various types of pincer ligands described in the literature, phosphorus based ligands have attracted special attention as these allow fine tuning of steric and electronic properties around the metal center thereby making them efficient catalysts. The PNP type of pincer ligands with a central pyridine moiety show diverse reactivity pattern and have
been extensively used in coordination chemistry. These are classified mainly into three types: PCNCP, POCOP and PN'NN'P, (N' = NR or NH) depending upon -CH2-, -O- or -NR- linkers (Chart 1). Milstein and coworkers and others have successfully employed the transition metal complexes of these ligands to activate C–H, C–C, O–H, N–H and S–H bonds as well as small molecules like N2, H2 and CO2. The facile dearomatization of the pyridine ring by the deprotonation in the sidearm introduces metal-ligand cooperativity which is less likely in the PCP analogues due to high dearomatization energy. This non-innocent behavior and charge switching character of the pyridine based PNP pincer ligands plays an essential role in a number of catalytic transformations such as hydrogenation of esters, amides and CO2, dehydrogenative coupling and other related reactions.

![Chart 1](image)

The synthesis and coordination chemistry of phosphomide based ligand system is scant which is mainly attributed to the sensitivity of the P–CO bond towards moisture and the difficulties involved in controlling their reactivity and isolation. We have recently reported the synthesis of bisphosphomide ligand [1,3-\{Ph2PC(O)\}2(C6H4)] and studied its coordination behavior in detail. The PCP pincer complexes of these ligands have been synthesized via C–H bond activation as well as by oxidative addition of the prefunctionalized ligand with zero-valent metal precursors. We envisioned that the similar carbonyl-linked PNP ligand system would be even more interesting since the presence of both phosphorus and oxygen donor atoms could
enable it to adopt variable coordination modes. As a continuation of our interest in designing new inexpensive ligands and studying their coordination behavior and catalytic applications\textsuperscript{13} we report the synthesis of a pyridine-based bisphosphomide ligand and its transition metal chemistry.

**Results and discussion**

**Synthesis of bisphosphomide ligand 2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N) (1)**

The reaction of picolinoyldichloride with two equivalents of diphenylphosphine in the presence of triethylamine at 0 °C afforded the tridentate PNP ligand 2,6-\{Ph\textsubscript{2}PC(O)\}\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N) (1) in quantitative yield (Scheme 1). The ligand 1 is a low-melting orange-yellow solid with moderate stability towards air and moisture.

![Scheme 1](image)

The \textsuperscript{31}P\textsuperscript{1}H NMR spectrum of 1 displays a single resonance at 17.5 ppm which is slightly deshielded in comparison with the corresponding PCP analogue (12.5 ppm) and is attributed to the electron withdrawing nature of the pyridine ring. In the \textsuperscript{1}H NMR spectrum, the pyridine protons appear as a broad singlet at 7.84 ppm. The IR spectrum of 1 exhibits a strong v\textsubscript{CO} band at 1656 cm\textsuperscript{-1}. The structure of ligand 1 was further confirmed by a single crystal X-ray structure determination. The molecular structure of 1 depicts that both the donor arms of bisphosphomide ligand are almost coplanar with the pyridine ring (Fig. 1). The distance between the two phosphorus atoms (P···P) is 4.429 Å while the distance between two carbonyl carbon atoms is
4.818 Å. The C—O and P—CO distances in 1 are 1.21 and 1.86 Å whereas the P1–C13–C14 and P2–C18–C19 bond angles are 115.20(10)° and 116.83(9)°, respectively.

Fig. 1 Molecular structure of ligand, 2,6-\{Ph₂PC(O)\}_2(C₅H₅N) (1). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Compound 1 is essentially a trifunctional ligand with a combination of two soft phosphorus atoms, two oxygen atoms and a pyridyl N atom. Due to this, the coordination behavior of this ligand is interesting since the free rotation of donor arms can give a possible combination of PNP, ONO or PNO coordination modes. The choice of the metal ions/atoms can also influence the different coordinating modes.

Various possible coordination modes, as depicted in Chart 2, can be observed upon reacting 1 with transition metal precursors. Bidentate chelation of 1 to the metal center can be either symmetrical PP or OO or a hybrid OP coordination, whereas the tridentate coordination can lead to the formation of symmetrical PNP or ONO complex or a hybrid PNO complex. The transition
metal chemistry of this multi-functional ligand 1 was carried out in order to understand its coordination behavior.

In order to gain additional insights into the coordination properties of bisphosphomide ligand 1, density functional theory computations were performed using the M06 and B3LYP functionals (with 6-31G** basis set for C, H, O, N, P and Cl and SDD for heavier metals Rh, Ru and Au). A comparison of the computed geometric parameters with that obtained through X-ray crystallography for the free pincer ligand is provided in Table 2. The structural parameters showed generally good agreement.

![Chart 2 Possible coordinating modes of ligand 1](image)

**Chart 2** Possible coordinating modes of ligand 1

**Ruthenium(II) and Rhodium(I) complexes**

The reaction of 1 with [Ru($\eta^6$-cymene)Cl$_2$]$_2$ in a 1:1 molar ratio at room temperature afforded a binuclear complex, [Ru$_2$Cl$_4$(NCCH$_3$)($\eta^6$-cymene)\{2,6-\{Ph$_2$PC(O)\}$_2$(C$_5$H$_3$N)\}] (2) in 72% yield. One of the ruthenium centers is coordinated via the PNO mode whereas the other ruthenium is bonded to a phosphorus atom, two chlorine atoms and a $\eta^6$-cymene ligand as shown in Scheme 2. Similar reaction of the bis(phosphomide) ligand, 1,3-\{Ph$_2$PC(O)\}$_2$(C$_6$H$_4$), reported by our group recently, yielded a binuclear complex (I) of the type 2a showing two phosphorus arms independently coordinating to [Ru($\eta^6$-cymene)Cl$_2$] moieties with one of the ruthenium atoms
being closer to the pincer carbon atom at a bond distance of 3.311 Å. It is anticipated that such short distances can facilitate bonding interactions through the intermediates 2a and 2b thus facilitating the PNO pincer formation which requires simply the free rotation of the other ruthenium bound phosphorus arm to bring the carbonyl group closer to the metal center.

The reactions between [Ru(η⁶-cymene)Cl₂] and 1 or its PCP analog are facile as can be seen from the computed ΔG values for the formation of 2a (ΔG = -15.6 kcal/mol) and 1 (ΔG = -15.87 kcal/mol). Transformation of 2a to 2b (ΔG = -22.9 kcal/mol) and eventually to 2 (ΔG = -43.9 kcal/mol) are very facile due to the close proximity of pyridyl lone pair to the ruthenium center. Such transformation are less likely in the case of 1 as C–H activation requires drastic and prolonged reaction conditions.

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{PPh₂} & \quad \text{Ph₂P} \\
\text{O} & \quad \text{O} \\
\text{Ru} & \quad \text{Cl} \\
\end{align*}
\]

The ³¹P{¹H} NMR spectrum of 2 shows two doublets centered at 28.3 and 79.5 ppm with a \(^4\)J\(_{PP}\) coupling of 6.5 Hz indicating the presence of two different types of phosphorus centers. The chemical shift at 79.5 ppm was assigned to phosphorus center involved in PNO coordination, whereas the upfield signal at 29.5 ppm was due to the other phosphorus atom. The \(^1\)H NMR integration supports the presence of one cymene group in the molecule with two doublets centered at 5.63 and 5.47 (\(^3\)J\(_{HH} = 5.5\) Hz), the characteristic doublet and septet pattern for the isopropyl group was observed at 0.97 and 2.61 ppm and a singlet at 1.67 ppm for methyl group.
The central pyridine ring displays two doublets centered at 8.51 and 7.74 ppm corresponding to the protons ortho to the coordinated and uncoordinated carbonyl groups. There are some examples of PNO types of ligands described in literature, but with very different frameworks. The molecular structure of complex 2 is further confirmed by a single crystal X-ray diffraction study. The molecular structure consists of two ruthenium(II) centers coordinated in $\kappa^3PNO$, $\kappa^1P$ bonding modes. One of the ruthenium(II) atoms is coordinated in a terdentate PNO pincer fashion whereas the other ruthenium is surrounded by one phosphorus, with two chlorides and a cymene group (Fig. 2). The geometry around Ru1 is octahedral, whereas Ru2 is pseudo octahedral. The Ru1–P1 [2.2260(8) Å] bond distance is slightly shorter than that of Ru2–P2 [2.3486(9) Å] and the Ru1–O2 bond distance is 2.146(2) Å. One of the five membered chelate rings, formed because of P coordination, is larger in size and is exactly in the plane of the pyridine backbone with a C13–P1–Ru1 bond angle of 99.25(10)$^\circ$. The other chelate ring is
slightly out of the plane of the pyridine ring with a C19–O2–Ru1 bond angle of 113.12(19)°. The P1–C13 [1.896(3) Å] bond distance is slightly larger than that of P2–C19 [1.860(3) Å] whereas the O1–C13[1.211(4) Å] bond distance is slightly shorter than that of O2–C19[1.237(4) Å]. The Ru–C bond distances range from 2.179(3) to 2.242(3) Å with an average bond distance of 2.216 Å. The bond angle Cl3–Ru2–Cl4 is 87.69(3)° which compares well with the reported range of Cl–Ru–Cl bond angles (86.27–89.77°) for [Ru(p-cymene)Cl2(L)] type complexes.¹⁶

The calculated relative Gibbs free energies (at the M06/6-31G**, SDD level of theory) with respect to the separated reactants (1, [Ru(η⁶-cymene)Cl₂]₂ and CH₃CN) for complexes 2a and 2b (Scheme 2), which are found to be -15.5 and -22.8 kcal/mol, indicate that complex 2b enjoys an additional stabilization compared to complex 2a. More importantly, the formation of 2 is found to be exergonic by 44 kcal/mol, which is in line with the experimental observation and characterization of 2.

![Molecular structure of [Ru₂Cl₄(NCCH₃)(p-cymene){2,6-{Ph₂PC(O)}₂(C₅H₃N)}] (2). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.](image-url)
Fig. 3. Selected set of Kohn–Sham orbital contours for key orbitals of the Ru-PNO pincer complex 2.

We have performed an AOMix analysis for ruthenium pincer PNO complex 2 using the B3LYP/6-31G**, SDD level of theory. In this method, the important Kohn-Sham orbitals are analyzed for its constituent atomic orbital contribution from different fragments in the molecule. We focus on two key fragments, namely [Ru(1)Cl₂(NCCH₃)] and the rest of the molecule considered as a ligand bound to the first fragment (See Fig. S1 in the Supporting Information). The orbital compositions are summarized in Table 1.

The HOMO of ruthenium complex 2 is identified as a primarily Ru(1) centered orbital (~90%). The LUMO consists of the PNO ligand and the Ru(2) center with only little contribution from Ru(1). In the case of HOMO-29, as shown in Fig. 3, Ru(1) interacts with the carbonyl
oxygen as well as with the phosphorus of the PNO ligand. The percentage composition of Ru(1) is about 80% and the remaining 20% is a combination of pincer ligand and Ru(2) as shown in Table 1. These orbitals indicate the donor-acceptor interactions between Ru(1) and carbonyl oxygen of the PNP ligand. The charge decomposition analysis further reveals that the charge donation from [RuCl$_2$(p-cymene)$_2$] to [RuCl$_2$(NCCH$_3$)] is 0.211 electrons whereas back donation from Ru(1) center-to-combination of PNP and Ru(2) center is found to be 0.257 electrons.

Attempts to obtain a symmetrical Ru($\kappa^3$-PNP) complex by the reaction of 1 with half an equivalent of [RuCl$_2$(p-Cymene)$_2$] have been unsuccessful and resulted in the formation of a mixture of products containing 2 as major product along with some unidentified species. However, the reaction of 1 with in situ generated [RuCl(NCCH$_3$)$_2$(p-cymene)](ClO$_4$) exclusively afforded the desired complex [RuCl(NCCH$_3$)$_2$]2,6-{Ph$_2$PC(O)}$_2$(C$_5$H$_3$N)-$\kappa^3$PNP] (3) as dark brown solid (Scheme 3). Similarly, treatment of 1 with [Ru($\eta^5$-C$_5$H$_5$)(PPh$_3$)$_2$](OTf) in 1:1 molar ratio afforded the [Ru($\eta^5$-C$_5$H$_5$)(2,6-{Ph$_2$PC(O)})$_2$(C$_5$H$_3$N)$_2$](OTf) (4) as yellow solid. The reaction of 1 with [Rh(COD)Cl]$_2$ in a 2:1 molar ratio afforded the [RhCl$_2$]2,6-
{Ph₂PC(O)}₂(C₅H₃N)} (5) as brown solid. The \(^{31}\)P{\(^{1}\)H} NMR spectra of complexes 3-5 exhibit a single resonances at 51.9, 42.3 and 37.6 ppm, respectively, with rhodium complex 5 showing \(^{1}J_{Rhp}\) coupling of 104.3 Hz. The structure of 5 has been confirmed by single crystal X-ray analysis. As depicted in the molecular structure of 5, the ligand is coordinated to rhodium metal in a typical mer-κ³-PNP fashion (Fig. 4). Similar to the known rhodium pincer complexes\(^{18}\) the phosphorus atoms are located above the plane of pyridine ring in the same side resulting in a distorted square planar geometry around rhodium with P1–Rh–P2 bond angle of 153.10(22)°. The two five membered fused rings are puckered with an N–Rh–Cl bond angle of 176.71(4)°. The P1–C13–C14 and P2–C19–C18 bond angles are 112.07(12) and 113.19(12)° which are slightly less than the same bond angles in 1 [115.20(10) and 116.83(9)°]. The Rh–N [2.0375(14) Å], Rh–P1 [2.2523(6) Å] and Rh–P2 [2.2611(6) Å] bond distances are in the range of typical bond distances reported for PNP-Rh complexes.\(^{18}\) The C13–O1 and C19–O2 bond distances are 1.209(2) and 1.211(2) Å.

Fig. 4. Molecular structure of [RhCl{2,6-{Ph₂PC(O)}₂(C₅H₃N)}] (5). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.
Group 10 metal PNP pincer complexes

The direct reaction between 1 and [Ni(DME)Cl₂] or M(COD)Cl₂ (M = Pd, Pt and Ni) in the presence of one equivalent of AgClO₄ or AgBF₄ resulted in the formation PNP–M complexes [MCl{2,6-\{Ph₂PC(O)\}₂(C₅H₃N)₂}]ClO₄ (6, M = Ni; 7, M = Pd; 8, M = Pt). Slow diffusion of diethyl ether into the dichloromethane solution of complexes 6, 7 and 8 gave brown, yellow and greenish-yellow crystalline solids in 90%, 73% and 69% yields, respectively. The ³¹P{¹H} NMR spectrum of nickel and palladium complexes 6 and 7 showed single resonances at 28.7 and 45.1 ppm which is slightly shielded in comparison to the PCP analogue (49.3 ppm)¹² while the platinum complex 8 also displayed a single resonance at 32.9 ppm with characteristic satellite peaks showing ¹Jₚₚ coupling of 2733 Hz. The IR spectra of 6, 7 and 8 exhibit strong νCO absorption bands at 1685, 1695 and 1678 cm⁻¹. The structures and molecular compositions of these complexes were further confirmed by ¹H NMR and microanalytical data.

Group 11 metal complexes

In comparison with other transition metals, the group 11 metal chemistry of PNP ligands has attracted less attention and has been recently examined by van der Vlugt and co-workers.¹⁹ They observed that the presence of bulky substituents on phosphorus plays a decisive role in the formation of N-coordinated CuBr complexes. However, replacement of halides with bulky anions produced the N-coordinated cationic T-shaped Cu¹ complexes in all cases (Chart 3).¹⁹b
The reactions between 1 and CuX (CuX, X = I, Br, Cl) or [Cu(NCCH₃)₄](BF₄) in dichloromethane/acetonitrile produced mononuclear complexes of type [CuX{2,6-\{Ph₂PC(O)\}₂(C₅H₃N)}] (9, X = Cl; 10, X = Br; 11, X = I), [Cu(NCCH₃){2,6-\{Ph₂PC(O)\}₂(C₅H₃N)}](BF₄) (12), and [Cu{2,6-\{Ph₂PC(O)\}₂(C₅H₃N)}₂](BF₄) (13) as shown in Scheme 4. The ³¹P{¹H} NMR spectra of complexes 9-13 showed single resonances in the range 0.1 to 6.0 ppm. In PNPᵗBu and PNPʰ complexes, N-coordination to metal was confirmed by the presence of two characteristic absorption bands around 1568 and 1603 cm⁻¹.²⁰,²¹ In the IR spectra of 9-11, strong absorptions were observed for carbonyl groups (1677-1683 cm⁻¹) and ring vibrations of pyridine (1430-1436 cm⁻¹) but the characteristic pattern for N-coordination was absent confirming the formation of tricoordinated Cu¹ complexes where the ligand exhibits bidentate (P,P) coordination mode.

![Chart 3](image)

Chart 3

Treatment of 1 with AgX (X = ClO₄, Br) in 1:1 molar ratio provided the mononuclear complexes, [AgX{2,6-\{Ph₂PC(O)\}₂(C₅H₃N)}] (14, X = ClO₄; 15, X = Br) in good yields. The ³¹P{¹H} NMR spectra of complexes 14 and 15 showed single broad resonances at 4.9 and 5.6 ppm. The presence of the molecular ion peak (m/z) at 708.9 confirmed the molecular structure of 14, whereas in the mass spectrum of 15, a (M⁺-Br) peak was observed at m/z 610.1. The reaction of 1 with [AuCl(SMe₂)] in 1:1 molar ratio resulted in the formation of a mononuclear complex,
[AuCl\{2,6-{Ph_2PC(O)}_2(C_5H_3N)\}] (16). Similar reaction of 1 with two equivalents of [AuCl(SMe_2)] afforded the binuclear complex, [Au_2Cl_2\{2,6-{Ph_2PC(O)}_2(C_5H_3N)\}] (17). The $^{31}$P ($^1$H) NMR spectra of complexes 16 and 17 exhibit single resonances at 24.6 and 38.5 ppm, respectively. In the mass spectrum of complex 16, a peak at 700.1 was observed for the ion corresponding to (M$^+$-Cl).

![Scheme 4](image)

The molecular structure of 17 was confirmed by a single crystal X-ray diffraction study. Complex 17 is a binuclear complex where each Au$^+$ center displays linear geometry with bond angles P1–Au1–Cl2 and P2–Au2–Cl1 of 167.58(4)$^\circ$ and 173.52(4)$^\circ$, (Fig. 6). The bond angles for C13–P1–Au1 and C19–P2–Au2 are 117.14(13)$^\circ$ and 110.45(14)$^\circ$, respectively. The bond lengths of C13–O1 and C19–O2 are 1.203(5) Å and 1.212(5) Å, respectively. Both the values are very close to that observed for the ligand [C13–O1 = 1.2114(17) and C19–O2 = 1.2108(17) Å] which
indicates that the coordination of the lone pair of electrons on phosphorus does not have any
effect on the C=O bond strength as predicted by theoretical calculation.\(^{22}\) The P1–C13 (1.881(4)
Å) and P2–C19 (1.893(4) Å) bond lengths are slightly longer than the same in the free ligand
(1.8195 and 1.8242 Å). The structure shows the presence of an intramolecular aurophilic
interaction with Au···Au distance of 3.1445(7) Å, which is less than the sum of the van der
Waals’ radii (3.6 Å).

![Molecular structure of complex, \([\text{Au}_2\text{Cl}_2\{2,6-\{\text{Ph}_2\text{PC(O)}\}_2\text{C}_5\text{H}_3\text{N}\}]\) (17). All hydrogen
atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.]

The interesting contact distance between the gold atoms in 17 prompted us to examine the
bonding in this compound in greater detail. The geometry of the digold complex 17 was first
optimized at the M06/6-31G**,SDD level of theory. The computed geometric parameters
showed a generally good agreement, including that of the Au-Au atom distance, with the X-ray
crystallographic data (Fig. 6/Table 2). Subsequently, an atoms-in-molecules (AIM) analysis for a
bimetallic gold PNP complex was carried out using the B3LYP/6-31G**, SDD level of theory.
Interestingly, the AIM analysis showed a distinct bond critical point between two gold atoms as
shown by the red dot in Fig. 7. It reveals the presence of an interaction between the two gold atoms in complex 17.

![Diagram showing bond paths and bond critical points in gold PNP pincer complex 17.]

**Fig. 7.** Topological map showing bond paths and bond critical points in gold PNP pincer complex 17.

**Conclusions**

Synthesis of a novel bisphosphomide PNP ligand and its low-valent late metal complexes are reported. The presence of three types of donor sites makes the ligand interesting and enables it to switch to different coordination modes. Symmetrical PNP–M complexes were obtained in the reaction of ligand 1 with Rh$^{I}$, Pd$^{II}$, Pt$^{II}$, Ni$^{II}$ and Cu$^{I}$ metal precursors. Both symmetrical (PNP–M) as well as unsymmetrical (PNO–M) coordination modes were observed in the case of Ru$^{II}$ complexes. With group 11 metal precursors (Cu$^{I}$, Ag$^{I}$ and Au$^{I}$) simple PP bidentate mode of coordination was observed. Although the utility of pincer complexes in catalytic applications is growing rapidly, mechanistic aspects are not too clear although it is presumed that the pincer framework remains intact during the catalytic process. The modified approach to incorporate a hard donor site to a typical low valent metal along with soft P enhances the possibility of the
reversible dissociation of M–L (hard) during oxidative addition thus bringing a new dimension to their versatile catalytic abilities in various organic transformations. Thus the bisphosphomide ligand 1 exhibits variable coordination behavior which is rarely observed in pincer type frameworks. Further synthesis of heterobimetallic complexes and catalytic studies of this class of ligands are in progress in our laboratory.

**Experimental**

**General Procedures**

All manipulations were performed using standard vacuum-line and Schlenk techniques under nitrogen atmosphere unless otherwise stated. All of the solvents were purified by conventional procedures and distilled prior to use. The compounds CuCl, CuBr, [Cu(NCCH₃)₄](BF₄), AuCl(SMe₂), [Ru(η⁶-p-cymene)Cl₂], [Rh(COD)Cl]₂, [Ru(η⁵-C₅H₅)Cl(PPh₃)₂] and M(COD)Cl₂, (M = Pd, Pt) were prepared according to the published procedures. The metal precursors CuI, AgBr and AgClO₄ were purchased from Aldrich chemicals and used as received. Other chemicals were obtained from commercial sources and purified prior to use.

**Instrumentation**

The NMR spectra were recorded at the following frequencies: 300 MHz (¹H), 121 MHz (³¹P), 400 MHz (¹H), 100 MHz (¹³C), 162 MHz (³¹P) using Varian VXR 300 or Varian VXR 400 or Bruker AV 400 spectrometers. ¹³C{¹H} and ³¹P{¹H} NMR spectra were acquired using broadband decoupling. The spectra were recorded in CDCl₃ solutions with CDCl₃ as an internal lock; chemical shifts of ¹H and ¹³C NMR spectra are reported in ppm downfield from TMS, used as an internal standard. The chemical shifts of ³¹P{¹H} NMR spectra are referred to 85% H₃PO₄ as external standard. The microanalyses were performed using a Carlo Erba Model 1112 elemental...
analyzer. Mass spectra were recorded using Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

**Synthesis of [2,6-{Ph₂PC(O)}₂(C₅H₅N)] (1)**

To a solution of diphenylphosphine (5.5g, 29.4 mmol) in diethyl ether (40 mL) was added dropwise a solution of picolinoyl dichloride (3.0 g, 14.7 mmol) in 15 mL diethyl ether over 10 minutes at 0 °C in the presence of Et₃N (2.9 g, 4.0 mL, 29.4 mmol) during which the color of the solution turned to orange-yellow. The reaction mixture was stirred for 4 h at room temperature and the amine hydrochloride was removed by filtration. The solution was dried under reduced pressure and the residue redissolved in CH₂Cl₂ (65 mL) followed by saturation with 12 mL of petroleum ether to give light orange-yellow crystals of 1. Yield: 95% (7.0 g). Mp: 173–175 °C. Anal. Calcd. for C₃₁H₂₃NO₂P₂: C, 73.95; H, 4.57; N, 2.78. Found: C, 73.63; H, 4.28; N, 2.75. FT IR (KBr disc) cm⁻¹: υ CO: 1656 vs, υ C=C: 1433 m. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (s, 3H, Ar), 7.48–7.43 (m, 8H, Ar), 7.34–7.33 (m, 12H, Ar). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 17.5 (s).

**Synthesis of [Ru₂Cl₄(NCCH₃)(p-cymene){2,6-{Ph₂PC(O)}₂(C₅H₅N)}] (2)**

A solution of 1 (0.050 g, 0.099 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of [Ru(η⁶-p-cymene)Cl₂]₂ (0.060 g, 0.099 mmol) in CH₃CN (3 mL) during which time the color of the solution turned from orange to deep blue. The reaction was allowed to stir for 4 h. The solution was dried under reduced pressure and the residue redissolved in CH₂Cl₂ (5 mL) followed by saturation with 2 mL of petroleum ether to obtain crystals of 2. 71.2% (0.072 g). Mp: 221–223 °C. Anal. Calcd. for C₄₃H₄₀Cl₄N₂O₂P₂Ru₂·CH₂Cl₂: C, 47.71; H, 3.82; N, 2.53. Found: C, 48.15; H, 3.62; N, 2.61. FT IR (KBr disc) cm⁻¹: υ CO: 1677 s, 1648 s, υ C=C: 1382 m. ¹H
NMR (400 MHz, CDCl₃): δ 8.51 (d, 1H, Ar, 3J_HH = 8.0 Hz), 8.32 (t, 4H, Ar, 3J_HH = 8.0 Hz), 7.83-7.78 (m, 5H, Ar), 7.75 (d, 1H, Ar, 3J_HH = 7.6 Hz), 7.44-7.35 (m, 12H, Ar), 5.63 (d, 2H, Cym, 3J_HH = 5.5 Hz), 5.47 (d, 2H, Cym, 3J_HH = 5.5 Hz), 5.23 (s, 2H, CH₂Cl₂), 2.67 (s, 3H, CH₃CN), 2.61 (m, 2H, CH), 1.67 (s, 6H, CH₃), 0.97 (d, 12H, CH₃, 3J_HH = 7.0 Hz).

31P{¹H} NMR (162 MHz, CDCl₃): δ 79.5 (d, 1P, 4J_PP = 6.5 Hz), 28.3 (d, 1P, 4J_PP = 6.5 Hz).

Synthesis of [RuCl(NCCH₃)₂{2,6-{Ph₂PC(O)}₂(C₅H₅N)}](ClO₄) (3)

A mixture of [Ru(η⁶-p-cymene)Cl₂]₂ (0.030 g, 0.049 mmol) and AgClO₄ (0.020 g, 0.099 mmol) was stirred for 1 h in 6 mL of CH₃CN. The reaction mixture was filtered and added to a solution of 1 (0.050 g, 0.099 mmol) in CH₃CN (8 mL) during which time the color of the solution turned to deep brown. The reaction was allowed to stir for 3 h. The solution was dried under reduced pressure and the residue redissolved in CH₂Cl₂ (4 mL) followed by saturation with 2 mL of petroleum ether to obtain analytically pure 3 as brown solid. 94.2% (0.077 g). Mp: 268-270 °C. Anal. Calcd. for C₃₅H₂₉Cl₂N₅O₆P₂Ru: C, 51.17; H, 3.56; N, 5.11. Found: C, 51.58; H, 3.74; N, 5.38. FT IR (KBr disc) cm⁻¹: νMeCN: 2346 m, νCO: 1681 s, νC=CH: 1434 m, νC-H: 1094 s. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 3H, Ar), 7.84-7.77 (m, 8H, Ar), 7.63–7.41 (m, 12H, Ar), 2.60(s, 3H, CH₃CN), 1.80(s, 3H, CH₃CN). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 51.9 (s).

Synthesis of [Ru(η⁵-C₅H₅){2,6-{Ph₂PC(O)}₂(C₅H₅N)}](OTf) (4)

A mixture of [Ru(η⁵-C₅H₅)Cl(PPh₃)₂] (0.029 g, 0.04 mmol) and AgOTf (0.0103 g, 0.04 mmol) was stirred for 4 h in 10 mL of CH₃CN. The reaction mixture was filtered throught celite and added to a solution of 1 (0.020 g, 0.04 mmol) in CH₃CN (10 mL) during which time the color of the solution turned to dark yellow. The reaction was allowed to stir for 6 h. The solution was
dried under reduced pressure and the residue redissolved in CH$_2$Cl$_2$ (2 mL) followed by saturation with 2 mL of petroleum ether to obtain analytically pure 4 as dark yellow solid. 61\% (0.019 g). Mp: 128-130 °C. Anal. Calcd. for C$_{37}$H$_{28}$F$_3$NO$_5$P$_2$RuS: C, 54.28; H, 3.44; N, 1.71. Found: C, 54.43; H, 3.19; N, 1.78. LRMS Calc for C$_{37}$H$_{28}$F$_3$NO$_5$P$_2$RuS (M+OTf+Na): 693.0536, Found: 693.1315. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.37-7.06 (m, H, Ar), 4.49 (s, 5H, Cp), 2.25 (s, 3H, CH$_3$CN). $^{19}$F{$^1$H} NMR (470 MHz, CDCl$_3$): $\delta$ -78.0 (s). $^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$): $\delta$ 42.37 (s).

**Synthesis of [RhCl{2,6-{Ph$_2$PC(O)}$_2$(C$_5$H$_3$N)}] (5)**

The ligand 1 (0.035 g, 0.069 mmol) and [Rh(COD)Cl]$_2$ (0.017 g, 0.035 mmol) were placed in a round bottom flask and CH$_2$Cl$_2$ (6 mL) was added. The resulting solution was allowed to stir for 4 h, upon which the solution turned deep brown in color. The solution was concentrated to small bulk (4 mL) and saturated with 2 mL of petroleum ether to get analytically pure 5 as brown solid. Yield: 79\% (0.035 g). Mp: 235-237 °C (dec). Anal. Calcd. for C$_{31}$H$_{23}$ClNO$_2$P$_2$Rh: C, 58.01; H, 3.61; N, 2.18. Found: C, 58.20; H, 3.60; N, 2.56. FT IR (KBr disc) cm$^{-1}$: $\nu$CO: 1692 vs, $\nu$C=C: 1436 m. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27 (m, 2H, Ar), 7.98 (m, 1H, Ar), 7.89-7.84 (m, 8H, Ar), 7.69-7.47 (m, 4H, Ar), 7.44-7.28 (m, 8H, Ar). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ 37.6 (d, $^1$J$_{RhP}$ = 104.3 Hz).

**Synthesis of [NiCl{2,6-{Ph$_2$PC(O)}$_2$(C$_5$H$_3$N)}](BF$_4$) (6)**

A solution of [Ni(DME)Cl$_2$] (0.0088 g, 0.04 mmol) in 4 mL of dichloromethane was added dropwise to a solution of AgClO$_4$ (0.0078 g, 0.04 mmol) in acetonitrile (4 mL) and the reaction mixture was allowed to stir for 4 h to give a colorless solution. The solution was filtered through
a frit and the filtrate was added to the solution of 1 (0.02 g, 0.04 mmol) in CH₂Cl₂ (6 mL) and the reaction mixture was allowed to stir for 4 h. The solvent was removed under vaccum to obtain analytically pure product of 6 as dark brown solid. Yield: 90% (0.025 g). Mp: 155-160 °C. Anal. Calcd. for C₃₁H₂₃ClNO₂P₂NiBF₄: C, 54.40; H, 3.39; N, 2.05. Found: C, 54.13; H, 3.21; N, 1.73. HRMS Calc for C₃₁H₂₃ClNNiO₂P₂ (M+Cl+Na): 584.0450, Found: 584.0447. FT IR (KBr disc) cm⁻¹: υCO: 1685 m, υC=C: 1418 m, υC-H: 1083 m.¹H NMR (400 MHz, CDCl₃): δ 8.36 (t, 1H, Ar JHH = 7.6 Hz), 8.21 (d, 2H, Ar JHH = 7.6 Hz), 8.05 (br, s 8H, Ar), 7.66-7.63 (m, 4H, Ar), 7.57-7.54 (m, 8H, Ar). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 28.5 (s).

Synthesis of [PdCl{2,6-{Ph₂PC(O)}₂(C₅H₃N)}](ClO₄) (7)

A solution of 1 (0.056 g, 0.112 mmol) in 5 mL of dichloromethane was added dropwise to a solution of AgClO₄ (0.023 g, 0.112 mmol) also in dichloromethane (5 mL) and the reaction mixture was allowed to stir for 1 h to give a yellow solution. [Pd(COD)Cl₂] (0.032 g, 0.112 mmol) in CH₂Cl₂ (5 mL) was added dropwise and the reaction mixture was allowed to stir for 2 h. The solution was filtered through a frit, concentrated to 4 mL and saturated with 2 mL of petroleum ether to get yellow crystals of 7. Yield: 73% (0.060 g). Mp: 210-212 °C (dec). Anal. Calcd. for C₃₁H₂₃ClNO₂P₂Pd: C, 49.99; H, 3.11; N, 1.88. Found: C, 49.65; H, 3.51; N, 2.23. FT IR (KBr disc) cm⁻¹: υCO: 1695 m, υC=C: 1436 m, υC-H: 1092 m.¹H NMR (400 MHz, CDCl₃): δ 8.43 (br s, 1H, Ar), 8.37 (br s, 2H, Ar), 8.02-7.98 (m, 8H, Ar), 7.64-7.61 (m, 4H, Ar), 7.56-7.53 (m, 8H, Ar). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 45.2 (s).

Synthesis of [PtCl{2,6-{Ph₂PC(O)}₂(C₅H₃N)}](ClO₄) (8)
Compound 8 was synthesized by a procedure similar to that of 7 by using 1 (0.042 g, 0.084 mmol), AgClO₄ (0.017 g, 0.084 mmol) and [Pt(COD)Cl₂] (0.031 g, 0.084 mmol). Yield: 69% (0.048 g). Mp: 170-173 °C (dec). Anal. Caled. for C₃₁H₂₃Cl₂NO₆P₂Pt: C, 44.67; H, 2.78; N, 1.68. Found: C, 44.95; H, 2.61; N, 1.96. FT IR (KBr disc) cm⁻¹: υCO: 1678 vs, υC=C: 1434 m, υC-H: 1097 m. \(^1\)H NMR (300 MHz, CDCl₃): δ 8.17 (br s, 1H, Ar), 8.09 (br s, 2H, Ar), 7.96–7.89 (m, 8H, Ar), 7.69–7.63 (m, 4H, Ar), 7.51–7.48 (m, 8H, Ar). \(^{31}\)P\(^{1}\)H NMR (121 MHz, CDCl₃): δ 32.9 (s, \(^1\)J_{P-{H}} = 2733 Hz).

**Synthesis of [CuCl\{2,6-{Ph₂PC(O)}₂(C₅H₃N)\}] (9)**

A solution of 1 (0.08 g, 0.159 mmol) in dichloromethane (8 mL) was added dropwise to a solution of CuCl (0.016 g, 0.159 mmol) in CH₃CN (4 mL). The reaction mixture was stirred for 3 h to give a dark brown solution. The solution was concentrated to 6 mL and stored at -20 °C to obtain 9 as dark brown solid. Yield: 87.2% (0.069 g). Mp: 208-210 °C (dec). Anal. Caled. for C₃₁H₂₃ClNO₂P₂Cu·0.5 CH₂Cl₂: C, 58.66; H, 3.75; N, 2.17. Found: C, 58.79; H, 3.92; N, 2.25. FT IR (KBr disc) cm⁻¹: υCO: 1677 vs, υC=C: 1433 m, υC-H: 1258 s, 1093 vs, 1023 vs. \(^1\)H NMR (400 MHz, CDCl₃): δ 8.09 (br s, 3H, Ar), 7.49 (br s, 8H, Ar), 7.33–7.31 (m, 4H, Ar), 7.23–7.20 (m, 8H, Ar), 5.23 (s, CH₂Cl₂). \(^{31}\)P\(^{1}\)H NMR (162 MHz, CDCl₃): δ -0.08 (s). MS (EI): m/z 566.1, (M⁺-Cl).

**Synthesis of [CuBr\{2,6-{Ph₂PC(O)}₂(C₅H₃N)\}] (10)**

Compound 10 was synthesized by a procedure similar to that of 9 using CuBr (0.014 g, 0.099 mmol) and 1 (0.050 g, 0.099 mmol). Yield: 85% (0.084 g). Mp: 191-192 °C (dec). Anal. Caled. for C₃₁H₂₃BrNO₂P₂Cu·CH₂Cl₂: C, 52.52; H, 3.44; N, 1.91. Found: C, 52.98; H, 3.10; N, 2.37. FT
IR (KBr disc) cm⁻¹: ν₁CO: 1680 s, ν₁C=₁C: 1430 m, ν₂C-H: 1258 vs, 1093 vs, 1023 vs. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (br s, 3H, Ar), 7.50 (br s, 8H, Ar), 7.34 (t, 4H, Ar, 3 JHH = 7.3 Hz), 7.23-7.22 (m, 8H, Ar), 5.22 (s, CH₂Cl₂).

Synthesis of [CuI(2,6-{Ph₂PC(O)}₂(C₅H₃N))] (11)

Compound 11 was synthesized by a procedure similar to that of 9 using CuI (0.015 g, 0.079 mmol) and 1 (0.040 g, 0.079 mmol). Yield: 91% (0.072 g). Mp: 238-239 °C (dec). Anal. Calcd. for C₃₁H₂₃INO₂₇P₂Cu: C, 53.65; H, 3.34; N, 2.01. Found: C, 53.90; H, 2.97; N, 2.36. FT IR (KBr disc) cm⁻¹: ν₁CO: 1683 vs, ν₁C=₁C: 1436 m, ν₂C-H: 1258 m, 1093 vs, 1020 m. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (br s, 3H, Ar), 7.54 (br s, 8H, Ar), 7.40–7.38 (m, 4H, Ar), 7.29–7.27 (m, 8H, Ar). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -0.8 (s). MS (EI): m/z 566.1, (M⁺-Cl).

Synthesis of [Cu(NCCH₃){2,6-{Ph₂PC(O)}₂(C₅H₃N)}](BF₄) (12)

A solution of 1 (0.05 g, 0.099 mmol) in acetonitrile (10 mL) was added dropwise to a solution of [Cu(NCCH₃)₄](BF₄) (0.0312 g, 0.099 mmol) in CH₃CN (5 mL). The reaction mixture was stirred for 4 h to give a dark brown solution. The solvent was evaporated by vacuum to obtain 12 as dark brown solid. Yield: 80% (0.054 g). Mp: 170-173 °C. Anal. Calcd. for C₃₃H₂₆N₂O₂P₂CuBF₄: C, 57.05; H, 3.77; N, 4.03. Found: C, 56.61; H, 3.58; N, 4.15. HRMS Calc for C₃₃H₂₆N₂O₂P₂Cu (M-NCCH₃): 584.0450, Found: 584.0447. FT IR (KBr disc) cm⁻¹: νMeCN:2281 ν₁CO: 1683 vs, ν₁C=₁C: 1436 m, ν₂C-H: 1261 s, 1061 vs. ¹H NMR (400 MHz, CDCl₃): δ 8.40 (t, 1H, Ar 3 JHH = 7.26 Hz), δ 8.33 (d, 2H, Ar 3 JHH = 7.3 Hz) 7.49-7.46 (br s, 12H, Ar), 7.38–
7.34 (m, 8H, Ar), 5.29 (s, CH₂Cl₂), 2.22 (s, 3H, CH₂CN). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 0.6 (s).

Synthesis of [Cu{2,6-{Ph₂PC(O)₂}₂(C₅H₅N)}₂](BF₄) (13)

A solution of 1 (0.05 g, 0.099 mmol) in acetonitrile (10 mL) was added dropwise to a solution of [Cu(NCCH₃)₄](BF₄) (0.0155 g, 0.05 mmol) in CH₃CN (5 mL). The reaction mixture was stirred for 3 h to give a dark brown solution. The solvent was evaporated by vacuum to obtain 13 as dark brown solid. Yield: 93% (0.053 g). Mp: 160-165 °C. Anal. Calcd. for C₆₂H₄₆CuN₂O₄P₄BF₄: C, 64.35; H, 4.01; N, 2.42. Found: C, 64.53; H, 3.76; N, 1.98. FT IR (KBr disc) cm⁻¹: υCO: 1682 vs, 1649 vs, υC=C: 1481 m, 1434 m, υC-H: 1056 vs. ¹H NMR (500 MHz, CDCl₃): δ 8.19 (br, s 2H, Ar), 7.96 (d, 4H, Ar ³JHH = 7.1 Hz), 7.32–7.29 (m, 8H, Ar), 7.07–7.06 (m, 32H, Ar), 2.003 (s, 3H, CH₃CN). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 6.0 (br, s).

Synthesis of [AgClO₄{2,6-{Ph₂PC(O)₂}₂(C₅H₅N)}] (14)

A solution of 1 (0.040 g, 0.079 mmol) in 5 mL of THF was added dropwise to a solution of AgClO₄ (0.016 g, 0.079 mmol) in THF (4 mL) and the reaction mixture was allowed to stir for 1 h to give a yellow solution. The solution was dried under reduced pressure and the residue redissolved in CH₂Cl₂ (4 mL) followed by saturation with 1 mL of petroleum ether to give 14 as yellow solid. Yield: 83% (0.066 g). Mp: 130-132 ºC (dec). Anal. Calcd. for C₃₁H₂₁ClNO₆P₂Ag: C, 52.38; H, 3.26; N, 1.97. Found: C, 52.44; H, 3.63; N, 2.31. FT IR (KBr disc) cm⁻¹: υCO: 1680 m, υC=C: 1436 m, υC-H: 1258 s, 1093 vs. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, 2H, Ar, ³JHH = 8.5 Hz), 8.16 (m, 1H, Ar), 7.56–7.51 (m, 8H, Ar), 7.48-7.45 (m, 4H, Ar), 7.37-7.34 (m, 8H, Ar). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 4.92 (br, s). MS (EI): m/z 708.9 (M⁺).
Synthesis of $[\text{AgBr}\{2,6-\text{Ph}_2\text{PC(O)}\}_2\text{(C}_5\text{H}_3\text{N)}]$ (15)

Compound 15 was synthesized by a procedure similar to that of 14 using AgBr (0.019 g, 0.099 mmol) and 1 (0.050 g, 0.099 mmol). Yield: 85% (0.085 g). Mp: 220-221 °C (dec). Anal. Calcd. for C$_{31}$H$_{23}$BrNO$_2$P$_2$Ag: C, 53.86; H, 3.35; N, 2.02. Found: C, 53.63; H, 3.73; N, 2.37. FT IR (KBr disc) cm$^{-1}$: $\nu$CO: 1674 vs, $\nu$C=C: 1433 m, $\nu$C-H: 1261 m. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.17 (br s, 3H, Ar), 7.50–7.48 (m, 8H, Ar), 7.38–7.34 (m, 4H, Ar), 7.26–7.22 (m, 8H, Ar). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ 5.56 (br, s). MS (EI): $m/z$ 610.1, (M$^+$-Br).

Synthesis of $[\text{AuCl}\{2,6-\text{Ph}_2\text{PC(O)}\}_2\text{(C}_5\text{H}_3\text{N)}]$ (16)

A solution of 1 (0.040 g, 0.079 mmol) in 5 mL of CH$_2$Cl$_2$ was added dropwise to a solution of AuCl(SMe$_2$) (0.023 g, 0.079 mmol) also in CH$_2$Cl$_2$ (3 mL) and the reaction mixture was stirred for 2 h to give a bright orange solution. The solution was concentrated to small bulk (3 mL) and saturated with 1 mL of petroleum ether to get analytically pure 16 as a bright orange solid. Yield: 88.2% (0.070 g). Mp: 165-167 °C (dec). Anal. Calcd. for C$_{31}$H$_{23}$ClNO$_2$P$_2$Au: C, 50.59; H, 3.15; N, 1.90. Found: C, 50.87; H, 2.95; N, 2.14. FT IR (KBr disc) cm$^{-1}$: $\nu$CO: 1680 vs, $\nu$C=C: 1435 m, 1384 s, $\nu$C-H: 1094 m. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (br s, 3H, Ar), 7.44–7.38 (m, 8H, Ar), 7.38–7.34 (m, 4H, Ar), 7.26–7.22 (m, 8H, Ar). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ 24.6 (s). MS (EI): $m/z$ 700.1, (M$^+$-Cl).

Synthesis of $[\text{AuCl}_2\{2,6-\text{Ph}_2\text{PC(O)}\}_2\text{(C}_5\text{H}_3\text{N)}]$ (17)

To a CH$_2$Cl$_2$ (3 mL) solution of 1 (0.030 g, 0.059 mmol) was added dropwise a solution of AuCl(SMe$_2$) (0.035 g, 0.119 mmol) also in CH$_2$Cl$_2$ (4 mL) and reaction mixture was stirred for 2 h to give a yellow solution. The solution was concentrated to 5 mL and saturated with 1 mL of
petroleum ether to get yellow crystals of 17. Yield: 86.4% (0.051 g). Mp: 178-180 °C (dec).

Anal. Calcd. for C_{31}H_{23}Cl_{2}NO_{2}P_{2}Au_{2}: C, 38.45; H, 2.39; N, 1.45. Found: C, 38.20; H, 2.12; N, 1.66. FT IR (KBr disc) cm^{-1}: \nu_{\text{CO}}: 1678 \text{ vs}, \nu_{\text{C=C}}: 1434 \text{ m}, \nu_{\text{C-H}}: 1097 \text{ m}. ^{1}H \text{ NMR (400 MHz, CDCl}_{3}{}): \delta 7.99 \text{ (s, 3H, Ar), 7.46–7.38 (m, 12H, Ar), 7.35-7.31 (m, 8H, Ar).} ^{31}P^{(1}H\text{)} \text{ NMR (162 MHz, CDCl}_{3}{}): \delta 38.5 \text{ (s).}

**Computational Methods**

All geometries were optimized using the Gaussian 09\textsuperscript{30} suite of quantum chemical programs. All the geometries were optimized at the B3LYP\textsuperscript{31}, M06\textsuperscript{32} functional and characterized as true minima on the potential energy surfaces by evaluating the Hessian indices (Number of imaginary frequencies = 0). The 6-31G** basis set was used for all atoms except for the metal ion and iodine. The effective core potential basis set (SDD) is employed for metals (Rh, Ru and Au).\textsuperscript{33} Molecular orbital analysis has been done to find the HOMO-LUMO energy gap using the iop(6/7=3) at B3LYP/6-31G**, SDD level of theory. Molecular orbital compositions of metal and ligands were analyzed using AOMix–CDA program\textsuperscript{17} using the wave functions generated at the B3LYP/6-31G**, SDD level of theory and using Gaussian 03 suite of quantum chemical programs.\textsuperscript{34} Bader developed theory of atoms in molecules (AIM) which is applied to characterize weak interactions.\textsuperscript{35} Atoms in molecules (AIM) analysis calculations were carried out using AIM2000 software.\textsuperscript{36}

**X-Ray Crystallography**

Crystal of each of the compounds 1, 2, 5, and 17 suitable for X-ray crystal analysis were mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the
Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using combination of three sets of 400 scans in ω (0.5° per scan) at φ = 0, 90, and 180° plus two sets of 800 scans in φ (0.45° per scan) at ω = -30 and 210° using the SMART\textsuperscript{37} software package, or the APEX2\textsuperscript{38} program suite. The raw data were reduced to \( F^2 \) values using the SAINT software\textsuperscript{39} and a global refinements of unit cell parameters using \textit{ca.} 4575-9954 reflections chosen from the full data set were performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS\textsuperscript{40}). The structures were solved by Patterson or direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.\textsuperscript{41} The details of X-ray structural determinations are given in Table 3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1038055 (compound 1), 1038057 (compound 2), 1038058 (compound 5), and 1038056 (compound 17).

Associated content

Supporting Information

X-ray crystallographic files in CIF format for the structure determinations of and 1, 2, 5 and 17, and computational details. This material is available free of charge via the Internet at http://pubs.rsc.org.

Author information

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Acknowledgements
We are grateful to the Science & Engineering Research Board, New Delhi, for financial support of this work through grant No.SB/S1/IC-08/2014. P.K. thanks CSIR, New Delhi for Research Fellowship (JRF & SRF). We also thank the Department of Chemistry Instrumentation Facilities, IIT Bombay, for spectral and analytical data and J.T.M. thanks the Louisiana Board of Regents for the purchase of the CCD diffractometer and the Chemistry Department of Tulane University for support of the X-ray laboratory.

References


14. The optimized geometry obtained at the M06/6-31G**, SDD level of theory is provided in Fig. S6 in the Supporting Information.


38. APEX2 version 2.1-0, Bruker-AXS, Madison, WI, 2006.


41. G. M. Sheldrick, SHELXS97 and SHELXL97; University of Göttingen; Germany 1997.
Table 1. Composition and energies of important Kohn–Sham orbitals of ruthenium pincer complex 2 obtained using the Wave Function Generated at the B3LYP/6-31G**, SDD level of theory

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (in eV)</th>
<th>Orbital character</th>
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<td>LUMO</td>
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<td>HOMO</td>
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<td>HOMO-29</td>
<td>-8.720</td>
<td>79.99% d_z^2 Ru(1), 20.01% (PNO and Ru(2))</td>
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Table 2 Selected bond distances (Å) and bond angles (°) for compounds 1, 2, 5 and 17

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<tr>
<th>Parameter</th>
<th>2,6-{(Pb2PC(O))2}2(C5H3N) (1)</th>
<th>RuCl2(NCC(CH3)p-cymene)2,6-{(Pb2PC(O))2}2(C5H3N)] (2)</th>
<th>[RhCl{2,6-{(Pb2PC(O))2}2(C5H3N)}] (5)</th>
<th>[Au2Cl{2,6-{(Pb2PC(O))2}2(C5H3N)}] (17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond distances (Å)</td>
<td>Exp. Calculated</td>
<td>Exp. Calculated</td>
<td>Exp. Calculated</td>
<td>Exp. Calculated</td>
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<td>P1–C1</td>
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<td>Ru1–N1 1.981(3) 2.0053</td>
<td>Rh1–N1 2.0375(14) 2.0565</td>
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<td>P1–Au1–Cl2 167.58(4) 169.714</td>
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<td>C1–P1–C13</td>
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<td>N1–Ru1–O2 77.69(9) 76.794</td>
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<td>N1–Ru1–Cl1 85.46(7) 89.263</td>
<td>N1–Rh1–P2 85.10(4) 85.539</td>
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*aThe optimized geometrical parameters obtained at the M06/6-31G**, SDD level of theory.
Table 3 Crystallographic Data for 1, 2, 5 and 17

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<th>2</th>
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<th>17</th>
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<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
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<td>space group</td>
<td>P2(1)/n</td>
<td>P-1</td>
<td>P2(1)/c</td>
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<td>$a$, Å</td>
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<td>$c$, Å</td>
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<td>4</td>
<td>2</td>
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<td>1128</td>
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<td>100(2)</td>
<td>100(2)</td>
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<td>1.035</td>
<td>1.038</td>
<td>0.923</td>
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</tbody>
</table>

$^a$ $R = \sum ||F_o|| - |F_c|| / \sum |F_o||$.

$^b$ $wR_2 = \sqrt{[\sum w(F_o^2 - F^2_c)^2]/\sum w(F_o^2)}/2w = 1/[\sigma^2(F_o^2) + (xP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
A phosphomide based PNP ligand, 2,6-{Ph₂PC(O)₂(C₅H₃N)₃ showing PP, PNP and PNO coordination modes

Coordination chemistry of a versatile phosphomide ligand, 2,6-{Ph₂PC(O)₂(C₅H₃N)₃ is described.