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Short-bite aminobis(phosphonite) containing olefinic functionalities, PhN{ $P(OC_6H_3(OMe-o)(C_3H_5-p))_2$ }₂: Synthesis and transition metal complexes

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Dedicated to Prof. Animesh Chakravorty on the occasion of his 75th birthday

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1. Introduction

There is an upsurge interest in designing complexes containing mixed-donor ligands or ligands with hemilabile donor functionalities due to their catalytic potential in various organic transformations [1]. In general, ligands containing additional donor functionalities are ideally suited to provide temporary coordinative saturation to the metal center through weak coordination bonds until it is necessary to furnish an active site at the metal center prior to the oxidative addition, an important step in homogeneous catalysis. In these situations, poor σ -donors with π -acceptor capability are preferred so that the oxidative addition is smooth after the metal is reduced using a base while generating an active catalytic species.

Among various mixed-donor ligands of the type P,O [2], P,N [3], and P,S ligands [4], phosphorus and sulfur donors are especially interesting due to the low ionization energy of sulfur and the existence of several lone pairs of electrons besides its π -acceptor nature, which can offer rich sulfur based coordination chemistry. Surprisingly, phosphine derivatives containing olefin functionalities are sparse [5] although they are expected to play a major role

ABSTRACT

Short-bite aminobis(phosphonite) containing olefinic functionalities, PhN{P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂}₂ (**1**) was synthesized by reacting PhN(PCl₂)₂ with eugenol in the presence of triethylamine. The ligand **1** acts as a bidentate chelating ligand toward metal complexes [M(CO)₄(C₅H₁₀NH)₂] forming [M(CO)₄{ η^2 -PhN{P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂}₂] (**M** = Mo, **2**; W, **3**). The reaction between **1** and [CpFe(CO)₂]₂ leads to the cleavage of one of the P–N bonds due to the metal assisted hydrolysis to give a mononuclear complex [CpFe(CO){P(O)(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂}{PhN(H)(P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂}] (**4**). Treatment of **1** with gold(1) derivative, [AuCl(SMe₂)] resulted in the formation of a dinuclear complex, [(AuCl)₂{PhN{P(O-C₆H₃(OMe-*o*)(C₃H₅-*p*))₂}] (**5**) with a Au…Au distance of 3.118(2) Å indicating the possibility of aurophilic interactions. An equimolar reaction between **1** and [Ru(η^6 -*p*-cymene)Cl₂]₂ afforded a *tri*-chloro-bridged bimetallic complex [(η^6 -*p*-cymene)Ru(μ -Cl)₃Ru{PhN(P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂)₂Cl] (**6**). The crystal structures of **1–3** and **5** were established by single crystal X-ray diffraction studies.

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in catalytic reactions. Besides their catalytic utility, olefin functionalities after phosphorus atoms are being coordinated to appropriate metal centers, can participate in photochemically/thermally induced cycloaddition reactions or olefin metathesis to produce interesting molecules. In view of this and also as an extension of our interest in functionalized phosphorus ligands and their metal chemistry [6] and catalytic applications [7], we have sought to prepare bisphosphine ligand system containing eugenol functionalities. Herein we report the synthesis and transition metal (Mo, W, Fe, Ru and Au) chemistry of aminobis(phosphonite) appended with eugenol substituents.

2. Results and discussion

The reaction of phenylaminobis(dichlorophosphine), PhN(PCl₂)₂ with eugenol in a 1:4 ratio in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine afforded the aminobis(diphosphonite), PhN{P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂}₂ (1) (Scheme 1). The ligand 1 is a low melting white crystalline solid and moderately stable to air and moisture. The elucidation of the structure of ligand 1 is based on NMR (¹H and ³¹P{¹H}) spectroscopic data and elemental analyses. The ³¹P NMR spectrum of ligand 1 exhibits a single resonance at 127.7 ppm. The molecular structure of 1 is confirmed by the single crystal X-ray structure determination.



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The reaction of **1** with one equivalent of $M(CO)_4(C_5H_{10}NH)_2$ (M = Mo, W) in dichloromethane at room temperature afforded the chelate complexes, *cis*-[Mo(CO)₄{PhN(P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂)₂] (**2**) and *cis*-[W(CO)₄{PhN(P(OC₆H₃(OMe-*o*)(C₃H₅-*p*))₂)₂] (**3**), respectively in moderate yields as shown in Scheme 2. The IR spectrum of both the complexes **2** and **3** show four bands in the carbonyl region in the range of 1900–2035 cm⁻¹ as expected for a {M(CO)₄} moiety of $C_{2\nu}$ symmetry [8]. The ³¹P NMR spectrum of **2** shows a single resonance at 144.1 ppm with a coordination shift of 16.4 ppm, whereas the ³¹P NMR spectrum of complex **3** shows a single resonance at 117 ppm with a ¹J_{WP} coupling of 167.4 Hz. The structures of **2** and **3** were further confirmed by single crystal X-ray structure determination.

The reaction of **1** with $[CpFe(CO)_2]_2$ in a 1:1 ratio in toluene under reflux conditions for 24 h afforded a mononuclear complex $[CpFe(CO){P(O)(OC_6H_3(OMe-o)(C_3H_5-p))_2}{PhN(H)(P(OC_6H_5-p))_2}{PhN(H)(P(OC_6H_5$ $o(C_3H_5-p)_2)$] (4) (Scheme 3). The complex 4 is formed as a result of the moisture assisted cleavage of one of the P-N bonds during complexation to give the aminophosphine and phosphineoxide fragments which then bind to the metal center [9]. Similar reactions of $[CpFe(CO)_2]_2$ with aminophosphines of the type PhN(PX₂)₂ (X = F [10], OPh [11]) led to the isolation of dinuclear complexes containing PX₂ and RN=PX₂ fragments bridging the two metal centers with or without metal-metal bonds. The ³¹P NMR spectrum of complex 4 shows two doublets centered at 126.7 ppm and 167.2 ppm with a ${}^{2}J_{PP}$ coupling of 120.9 Hz due to the presence of two types of phosphorus centers. The low field resonance at 167.2 ppm is assigned to the $\{PhN(H)(P(OC_6H_3(OMe-o)(C_3H_5$ $p)_{2}$ unit whereas the resonance due to the covalently bound phosphorus fragment, $\{P(O)(OC_6H_3(OMe-o)(C_3H_5-p))_2\}$ appears at 126.7 ppm. The presence of a sharp band in the IR spectrum (\tilde{o}_{CO}) at 1982 cm⁻¹ indicates the presence of a terminal carbonyl group.

The reaction of **1** with [AuCl(SMe₂)] in a 1:2 molar ratio leads to the formation of a binuclear complex [(AuCl)₂{ μ -PhN(P(O-C₆H₃(OMe-o)(C₃H₅-p))₂)₂] (**5**) with the ligand exhibiting the bridging mode of coordination (see Scheme 4). The complex is soluble in solvents such as CH₂Cl₂ and CHCl₃ and is moderately stable towards moisture and air. The ³¹P NMR spectrum of the complex **5** consists of a single peak at 111.2 ppm. Further evidence for the structural composition of the complex comes from the elemental analyses, ¹H NMR data and single crystal X-ray diffraction study.





An equimolar reaction between the ligand **1** and $[Ru(\eta^6-p-cym$ $ene)Cl_2]_2$ in THF at 60 °C resulted in the formation of a *tri*-chlorobridged bimetallic complex $[(\eta^6-p-cymene)Ru(\mu-Cl)_3Ru{PhN(P(O C_6H_3(OMe-o)(C_3H_5-p))_2)_2]Cl]$ (**6**) in which one of the ruthenium(II) centers retains the cymene group. Similar type of *tri*-chlorobridged ruthenium complex containing an aminobis(phosphine) was reported by us earlier [12]. The ³¹P NMR spectrum of complex **6** shows a single resonance at 97.4 ppm. The presence of a cymene group on one of the ruthenium centers was confirmed by the ¹H NMR spectrum and elemental analysis. The ¹H NMR spectrum of **6** shows two doublets at 5.21 and 5.05 ppm with a ³J_{HH} coupling of 5.5 Hz for the aromatic protons of cymene. The methyl groups of isopropyl moiety appear as a doublet centered at 1.24 ppm with a ³J_{HH} coupling of 6.7 Hz. The chemical shift due to the *-CH* proton appears as a septet around 2.80 ppm.

2.1. The crystal and molecular structures of 1-3 and 5

Perspective views of the molecular structures of compounds **1– 3** and **5** with the atom numbering schemes are shown in Figs. 1–4, respectively. Crystal data and the details of the structure determinations are given in Table 1 while the selected bond lengths and the inter-bond angles appear in Tables 2 and 3.

Compound **1** crystallizes in the extended confirmation with a center of symmetry. The P1–N–P2 bond angle of $115.6(3)^{\circ}$ is larger than the average P–N–P bond angles (97–100°) observed in similar systems [13]. The Structure of compound **1** shows a distorted tetrahedral geometry about the phosphorus centers and a planar environment around the nitrogen center with the sum of angle around nitrogen is 360°. The two P–N bond distances in compound **1** are exactly the same, 1.717(5) Å.

The unit cell of both the complexes **2** and **3** contain two independent molecules with very similar bonding parameters. The crystal structures of **2** and **3** reveal typical octahedral environments around the molybdenum and tungsten centers surrounded by four carbonyl groups and two phosphorus centers. The two P–N bond distances in both the complexes are slightly different in contrast and shorter as compared to those in the free ligand, whereas the P–O bond distances decreases by a significant amount of 0.5–0.6 Å. The P–N–P bond angles shrink to 100.70(11)° in complex **2** and 100.52(13)° in complex **3** by ~15° when compared to the same in the free ligand [115.6(3)°] due to the formation of strained four-membered chelate rings. The sum of the angles around the nitrogen center ($\sum N$ 359.9°) in both the complexes **2**



Scheme 4.



Fig. 1. Molecular structure of 1. All hydrogen atoms have been omitted for clarity.

and **3** clearly indicate the planar geometry around the bridging nitrogen atoms. The non-bonded $P \cdots P$ distance in complex **2** [2.631 Å] and **3** [2.629 Å] are shorter than that in free ligand **1** [2.906 Å] which is expected due to the chelation.

The X-ray quality crystals are obtained from a mixture of dichloromethane and petroleum ether. The gold complex crystallizes in monoclinic crystal system with space group $P2_1/c$. The crystal structure of complex **5** reveals that, the P–N–P bond angle (123.68(19)°) is significantly larger compared to that of the free ligand (115.6(3)°). The coordination at each gold atom is only approximately linear, as evidenced by the P–Au–Cl bond angle [P1–Au1–Cl1 = 169.27 (4)° and P2–Au2–Cl2 = 175.59(4) °]. The intra molecular Au…Au distance is 3.118(2)Å, which falls in the range of the Au…Au distance considered to exhibit aurophilic interactions. In spite of increase in the P–N–P bond angle in complex **5**, which on the other hand results in the increase of P…P distance (2.943 Å) compared to the same in the free ligand **1** (2.906 Å), the short Au…Au distance is a result of attractive interaction between the two gold centers and just an approach imposed by the ligand. There is a slight twisting about the Au…Au vector as reflected by the Cl1–Au1…Au2–Cl2 torsion angle of 11.13°. There is no significant difference in the Au–P (Au1–P1, 2.203(1)Å; Au2–P2, 2.193(1)Å) and Au–Cl (Au1–Cl1, 2.280(1)Å; Au2–Cl2, 2.273(1)Å) bond distances.

3. Conclusions

The aminobis(phosphonite) **1** containing olefinic functionalities on phosphorus substituents reacts with molybdenum and tungsten carbonyl derivatives to give the corresponding tetracarbonyl chelate complexes in good yield. The reaction of **1** with $[CpFe(CO)_2]_2$ leads to the cleavage of one of the P–N bonds to give a Fe^{II} complex containing protonated aminophosphine and phosphineoxide fragments with later making a Fe–P σ -bond. Since the crystal structures have shown the presence of olefinic functionalities on adjacent groups in close proximity, it is possible to activate the aromatic substituted olefins to either participate in coordination to the metal centers or to undergo typical metathesis/cycloaddition reactions to form interesting molecules. The research works in this direction and also to understand the behavior of P–N bonds under various reaction conditions and in the catalytic reactions are under active investigation in our laboratory.



Fig. 2. Molecular structure of 2. All hydrogen atoms have been omitted for clarity.



Fig. 3. Molecular structure of 3. All hydrogen atoms have been omitted for clarity.



Fig. 4. Molecular structure of 5. All hydrogen atoms have been omitted for clarity.

4. Experimental

4.1. General consideration

All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use. PhN(PCl₂)₂ [14], M(CO)₄(C₅H₁₀NH)₂ (M = Mo, W) [15], [Ru(η^6 -cymene)Cl₂]₂ [16], [AuCl(SMe₂)] [17] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. The ¹H and ³¹P{¹H} NMR (δ in ppm) spectra were obtained on a Varian VRX 400 spectrometer operating at frequencies of 400 and 162 MHz, respectively. The spectra were recorded in CDCl₃ (or DMSO-*d*₆) solutions with CDCl₃ (or DMSO-*d*₆) as an internal lock; TMS and 85% H₃PO₄ were used as internal and external

Table 1Crystallographic information for compound 1, 2, 3 and 5.

	1	2	3	5
Empirical formula	$C_{46}H_{49}NO_8P_2$	C ₅₀ H ₄₉ NO ₁₂ P ₂ Mo	C ₅₀ H ₄₉ NO ₁₂ P ₂ W	C46H49Au2Cl2NO8P2
Formula weight	805.8	1013.78	1101.69	1270.64
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	ΡĪ	ΡĪ	PĪ	P2 ₁ /c
a (Å)	11.014(18)	10.9147(10)	10.9229(10)	14.7807(3)
b (Å)	11.36(2)	19.2977(6)	19.3001(2)	18.6060(3)
<i>c</i> (Å)	18.69(3)	23.2768(12)	23.2524(2)	18.5094(3)
α (°)	93.06(15)	96.959(4)	96.9510(10)	90
β(°)	92.53(14)	99.514(6)	99.9040(10)	111.625(2)
γ (°)	113.07(16)	95.347(5)	95.4330(10)	90
$V(Å^3)$	2142(6)	4767.5(5)	4759.81(8)	4732.02(14)
Ζ	2	4	4	4
$ ho_{ m calc}~(m Mg~m^{-3})$	1.249	1.412	1.537	1.784
μ (Mo K $lpha$) (mm $^{-1}$)	0.155	0.406	2.558	6.426
F(0 0 0)	852	2096	2224	2472
Crystal size (mm)	$0.32\times0.28\times0.22$	$0.33 \times 0.26 \times 0.21$	$0.23 \times 0.17 \times 0.13$	$0.33 \times 0.28 \times 0.23$
T (K)	120(2)	120(2)	120(2)	120(2)
2θ Range (°)	3.05-25.00	2.97-25.00	2.97-25.00	3.04-25.00
Total number of reflections	16 933	44 596	39 932	38 947
Number of independent reflections	7431	16 685	16 655	8316
	$[R_{int} = 0.0724]$	$[R_{int} = 0.0290]$	$[R_{int} = 0.0246]$	$[R_{int} = 0.0446]$
Goodness-of-fit (GOF) (F ²)	0.881	0.876	0.907	0.963
R_1^{a}	0.0911	0.0338	0.0265	0.0288
wR_2^{b}	0.2539	0.0752	0.0616	0.0460

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^b $R_w = \{ [\sum w(F_0^2 - F_0^2) / \sum w(F_0^2)^2] \}^{1/2}, w = 1 / [\sigma^2(F_0^2) + (xP)^2], \text{ where } P = (F_0^2 + 2F_c^2) / 3.$

Table 2	Та	ble	2
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Selected	bond	distances	(Å)	and	bond	angles	(°)	for	com	lexes	1	and 2
Julua	Dona	uistances	(11)	anu	Donu	angics	ີ	101	comp	JICACS		and 2.

Complex 1				Complex 2			
Complex 1 P1-N1 P2-N1 P1-O1 P1-O3 P2-O5 P2-O7	1.717(5) 1.717(5) 2.203(11) 2.193(1) 2.280(1) 2.273(1)	P1-N1-P2 01-P1-03 01-P1-N1 03-P1-N1 05-P2-07 05-P2-N1 07-P2-N1	115.6(3) 97.0(2) 100.6(3) 98.3(2) 96.9(2) 100.3(2) 97.5(2)	Complex 2 P1-N1 P2-N1 P1-01 P1-03 P2-05 P2-07 M0-P1	1.705(2) 1.712(2) 1.618(2) 1.619(2) 1.610(2) 1.618(2) 2.434(1)	P1-N1-P2 N1-P1-M01 N1-P2-M01 01-P1-03 01-P1-N1 03-P1-N1 05-P2-07	100.70(11) 97.28(7) 96.72(7) 92.45(9) 103.51(10) 104.60(10) 95.12(10)
				Mo-P2 Mo-C1 Mo-C2 Mo-C3 Mo-C4	2.444(1) 2.045(3) 1.991(3) 2.052(3) 2.020(3)	05-P2-N1 07-P2-N1 P1-Mo-P2	102.59(9) 103.60(10) 65.29(2)

Table 3

Selected bond distances (Å) and bond angles (°) for complexes ${\bf 3}$ and ${\bf 5}.$

Complex 3				Complex 5			
P1-N1	1.706(2)	P1-N1-P2	100.52(13)	P1-N1	1.680(3)	P1-N1-P2	123.68(19)
P2-N1	1.712(2)	N1-P1-W1	97.39(8)	P2-N1	1.670(3)	P1-Au1-Cl1	169.27(4)
P1-01	1.613(2)	N1-P2-W1	96.68(9)	P1-01	1.579(3)	P2-Au2-Cl2	175.59(4)
P1-03	1.620(2)	01-P1-03	92.53(12)	P1-03	1.599(3)	P1-Au1-Au2	85.24(3)
P2-05	1.606(2)	01-P1-N1	103.97(12)	P2-05	1.595(3)	Cl1-Au1-Au2	105.08(3)
P2-07	1.616(2)	03-P1-N1	104.98(12)	P2-07	1.581(3)	P2-Au2-Au1	90.46(3)
W-P1	2.425(1)	05-P2-07	95.12(12)	Au1-P1	2.203(1)	Cl2-Au2-Au1	93.95(3)
W-P2	2.440(1)	05-P2-N1	102.86(12)	Au2-P2	2.193(1)	01-P1-03	100.18(16)
W-C1	2.042(4)	07-P2-N1	104.12(12)	Au1-Au2	3.118(2)	O1-P1-N1	98.85(15)
W-C2	2.005(4)	P1-W-P2	65.40(2)	Au1-Cl1	2.280(1)	O3-P1-N1	101.58(16)
W-C3	2.050(4)			Au2-Cl2	2.273(1)	O5-P2-O7	99.99(15)
W-C4	2.012(3)					O5-P2-N1	103.72(15)
						07-P2-N1	100.76(16)

standards for ¹H and ³¹P{¹H} NMR, respectively. Positive values indicate downfield shifts. Microanalyses were carried out on a Carlo Erba (model 1106) elemental analyzer. Melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected.

4.2. Synthesis of $PhN\{P(OC_6H_3(OMe-o)(C_3H_5-p))_2\}_2$ (1)

A mixture of eugenol (10.5 g, 0.064 mol) and triethylamine (6.98 g, 0.069 mol) in diethyl ether (10 mL) was added dropwise to a solution of phenylaminobis(dichlorophosphine) (4.74 g, 0.016 mol) in diethyl ether (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for overnight and Et₃N·HCl was separated by filtration through celite. The solvent was evaporated from the filtrate under vacuum to give an oily residue. The residue was dissolved in hot petroleum ether (bp: 60–80 °C) and kept at room temperature for crystalisation to give analytically pure product of **1** as colorless crystals. Yield: 73% (9.5 g). Mp: 60–62 °C. *Anal.* Calc. for C₄₆H₄₉NO₈P₂: C, 68.56; H, 6.13; N, 1.74. Found: C, 68.65; H, 6.23; N, 1.70%. ³¹P{¹H}NMR (CDCl₃) δ : 127.7(s). ¹H NMR (CDCl₃) δ : 3.63 (s, OCH₃, 12H), 3.31 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 5.056 (m, CH₂, 8H), 5.88–5.96 (m. CH, 4H), 6.6 (m, C₆H₃, 4H), 6.95 (d, C₆H₃, 4H, ³J_{HH} = 7.94 Hz), 6.67 (s, C₆H₃, 4H), 7.32–7.57 (m, C₆H₅, 5H).

4.3. Synthesis of $[Mo(CO)_4 \{PhN\{P(OC_6H_3(OMe-o)(C_3H_5-p))_2\}_2\}]$ (2)

A solution of $[Mo(CO)_4(C_5H_{10}NH)_2]$ (0.042 g, 0.085 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **1** (0.069 g, 0.085 mmol) also in dichloromethane (5 mL) with constant stirring. The pale yellow colored reaction mixture was stirred for 12 h at room temperature and filtered through a frit. The solvent was removed under vacuum and the residue was washed with petroleum ether to give pale yellow colored solid product of **2**, which was dissolved in dichloromethane, layered with petroleum ether and kept for slow evaporation at room temperature to get colorless crystals suitable for X-ray analysis. Yield 54%. Mp: 135 °C (decomp). *Anal.* Calc. for C₅₀H₄₉NP₂O₁₂Mo: C, 59.24; H, 4.87; N, 1.38. Found: C, 59.38; H, 4.96; N, 1.37%. ³¹P{¹H}NMR (CDCl₃) δ : 144.1(s). ¹H NMR (CDCl₃) δ :, 3.63 (s, OCH₃, 12H), 3.31 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 5.056 (m, CH₂, 8H), 5.88–5.96 (m. CH, 4H), 6.6 (m, C₆H₃, 4H), 6.95 (d, C₆H₃, 4H, ³J_{HH} = 7.94 Hz), 6.67 (s, C₆H₃, 4H), 7.32–7.57 (m, C₆H₅, 5H). IR (nujol or KBr disk) ν_{CO} : 1914, 1934, 2033 cm⁻¹.

4.4. Synthesis of $[W(CO)_4 \{PhN(P(OC_6H_3(OMe-o)(C_3H_5-p))_2)_2\}]$ (3)

A solution of $[W(CO)_4(C_5H_{10}NH)_2]$ (0.037 g, 0.079 mmol) in dichloromethane (5 mL) was added dropwise to a solution of 1 (0.064 g, 0.079 mmol) in the same solvent (5 mL) with constant stirring. The yellow colored reaction mixture was stirred for 12 h at room temperature and filtered through a frit. The solvent was removed under vacuum and the residue was washed with petroleum ether (bp: 60-80 °C) to give pale yellow colored powder of 3. The solid residue was dissolved in dichloromethane and layered with petroleum ether and kept for slow evaporation at room temperature to get colorless crystals suitable for X-ray analysis. Yield 46%. Mp: 178 °C (decomp). Anal. Calc. for C₅₀H₄₉NP₂O₁₂W: C, 54.51; H, 4.48; N, 1.27. Found: C, 54.78; H, 4.46; N, 1.23%. ³¹P{¹H} NMR (CDCl₃) δ : 117.0 (s, ¹ J_{WP} = 167.4 Hz). ¹H NMR (CDCl₃) δ : 3.63 (s, OCH₃, 12H), 3.31 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 5.056 (m, CH₂, 8H), 5.88–5.96 (m. CH, 4H), 6.6 (m, C₆H₃, 4H), 6.95 (d, C₆H₃, 4H, ${}^{3}J_{HH}$ = 7.94 Hz), 6.67 (s, C₆H₃, 4H), 7.32–7.57 (m, C₆H₅, 5H). IR (nujol or KBr disk) v_{CO} : 1904, 1924, 2030 cm⁻¹.

4.5. Synthesis of $[CpFe(CO){P(O)(OC_6H_3(OMe-o)(C_3H_5-p)]}(4)$

A mixture of compound **1** (0.068 g, 0.084 mmol) and [CpFe(- CO_{2}]₂ (0.03 g, 0.084 mmol) in toluene (10 mL) was refluxed for

24 h to give a dark brown solution. The reaction mixture was filtered and the solvent was removed under reduced pressure to give a dark brown crystalline solid. The residue was washed with petroleum ether and dried under vacuum to get dark brown solid product of **4**. Yield 94%. Mp: 98–102 °C. *Anal.* Calc. for C₅₂H₅₄NP₂O₆Fe: C, 68. 87; H, 6.00; N, 1.54. Found: C, 68.52; H, 5.92; N, 1.50%. ³¹P {¹H} NMR (CDCl₃) δ : 123.6 (d, ²J_{PP} = 120.9 Hz), 167.2 (d, ²J_{PP} = 120.9 Hz). ¹H NMR (CDCl₃) δ :, 3.79 (s, OCH₃, 12H), 3.68 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 4.92–4.99 (m, CH₂, 8H), 5.90–5.96 (m. CH, 4H), 6.5–7.4 (m, Ph, 21H). IR (nujol or KBr disk): v_{CO}: 1982 cm⁻¹.

4.6. Synthesis of $[(AuCl)_2 \{PhN\{P(OC_6H_3(OMe-o)(C_3H_5-p))_2\}_2\}]$ (5)

A solution of AuCl(SMe₂) (0.03 g, 0.1 mmol) in dichloromethane (5 mL) was added drop wise to a solution of **1** (0.041 g, 0.05 mmol) in dichloromethane (5 mL) with constant stirring. The reaction mixture was allowed to stir for 4 h, which was then concentrated to 2 mL, layered with petroleum ether, and cooled to $-20 \,^{\circ}$ C to give analytically pure white crystals of **5**. Yield 76% Mp: 141–142 $^{\circ}$ C. *Anal.* Calc. for C₄₆H₄₉NO₈P₂Au₂Cl₂: C, 43.48; H, 3.88; N, 1.10. Found: C, 43.37; H, 3.79; N, 1.13%. ³¹P{¹H}NMR (CDCl₃) δ : 111.2(s). ¹H NMR (CDCl₃) δ :, 3.63 (s, OCH₃, 12H), 3.31 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 5.056 (m, CH₂, 8H), 5.88–5.96 (m, CH, 4H), 6.6(m, C₆H₃, 4H), 6.95 (d, C₆H₃, 4H, ³J_{HH} = 7.94 Hz), 6.67 (s, C₆H₃, 4H), 7.32–7.57 (m, C₆H₅, 5H).

4.7. Synthesis of $[(\eta^6-p-cymene)(\mu-Cl)_3Ru\{PhN\{P(OC_6H_3(OMe-o)(C_3H_5-p))_2\}_2\}]$ (**6**)

A mixture of [Ru(η^{6} -cymene)Cl₂]₂ (0.03 g, 0.049 mmol) and **1** (0.039 mg, 0.049 mmol) in THF (15 mL) was stirred under reflux condition for 4 h. It was cooled to room temperature and filtered through celite. The reddish orange colored solution was concentrated to 5 mL under reduced pressure and layered with 1 mL of petroleum ether. Keeping this solution at -20 °C for one day afforded red crystals of **6**. Yield 73%. *Anal.* Calc. for C₅₆H₅₉NP₂O₈Cl₄Ru₂: C, 52.54; H, 4.64; N, 1.09. Found: C, 52.68; H, 4.62; N, 1.08%. ³¹P{¹H}NMR (CDCl₃) δ : 97.4 ppm; ¹H NMR (CDCl₃) δ : 3.63 (s, OCH₃, 12H), 3.31 (d, CH₂, 8H, ³J_{HH} = 6.4 Hz), 5.056 (m, CH₂, 8H), 5.88–5.96 (m, CH, 4H), 6.6 (m, C₆H₃, 4H), 6.95 (d, C₆H₃, 4H, ³J_{HH} = 7.94 Hz), 6.67 (s, C₆H₃, 4H), 7.32–7.57 (m, C₆H₅, 5H). 5.21 (d, C₆H₄, 2H ³J_{HH} = 5.5 Hz), and 5.05 (d, C₆H₄, 2H, ³J_{HH} = 5.5 Hz), 1.24 (d, CH₃, 6H, ³J_{HH} = 6.7 Hz), 2.8 (sept, CH, H).

4.8. X-ray crystallography

Single crystal X-ray structural studies were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo K α radiation ($\lambda_{\alpha} = 0.71073$ Å). The strategy for the data collection was evaluated by using the CRYSALISPRO CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CRYSALISPRO RED software. The structure was solved by direct methods using SHELXS-97 [18] and refined by full matrix least squares with SHELXL-97 [18], refining on F^2 . The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2 \times U_{eq}$ of their parent atoms.

Supplementary material

CCDC 761619, 761620, 761621, 761622 contain the supplementary crystallographic data for **1–3** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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