Inorganic Chemistry

H-Bonding Assisted Self-Assembly of Anionic and Neutral Ligand on Metal: A Comprehensive Strategy To Mimic Ditopic Ligands in Olefin **Polymerization**

Nilesh R. Mote,[†] Ketan Patel,[†] Dinesh R. Shinde,[‡] Shahaji R. Gaikwad,[†] Vijay S. Koshti,[†] Rajesh G. Gonnade,[§][©] and Samir H. Chikkali^{*,†,#}[©]

[†]Polyolefin Lab, Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008. India

[‡]Central NMR facility, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India

[§]Center for Materials Characterization, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India

[#]Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhawan, 2 Rafi Marg, New Delhi-110001, India

Supporting Information

ABSTRACT: Self-assembly of two neutral ligands on a metal to mimic bidentate ligand coordination has been frequently encountered in the recent past, but self-assembly of an anionic ligand on a metal template alongside a neutral ligand remains an elusive target. Such a self-assembly is hampered by additional complexity, wherein a highly negatively charged anion can form intermolecular hydrogen bonding with the supramolecular motif, leaving no scope for self-assembly with neutral ligand. Presented here is the self-association of anionic ligand 3-ureidobenzoic acid (2a) and neutral ligand 1-(3-(diphenylphosphanyl)phenyl)urea (1a) on a metal template to yield metal complex [$\{COOC_6H_4$ - $NH(CO)NH_2$ { $Ph_2PC_6H_4NH(CO)NH_2$ }PdMeDMSO] (4a).



The identity of 4a was established by NMR and mass spectroscopy. Along the same lines, 3-(3-phenylureido)benzoic acid (2b) and 1-(3-(diphenylphosphanyl)phenyl)-3-phenylurea (1b) self-assemble on a metal template to produce palladium complex $[COOC_6H_4NH(CO)NHPh]{Ph_2PC_6H_4NH(CO)NHPh}PdMePy]$ (5c). The existence of 5c was confirmed by Job plot, 1– 2D NMR spectroscopy, deuterium labeling, IR spectroscopy, UV-vis spectroscopy, model complex synthesis, and DFT calculations. These solution and gas phase investigations authenticated the presence of intramolecular hydrogen bonding between hydrogen's of 1b and carbonyl oxygen of 2b. The generality of the supramolecular approach has been validated by preparing six complexes from four monodentate ligands, and their synthetic utility was demonstrated in ethylene polymerization. Complex 4a was found to be the most active, leading to the production of highly branched polyethylene with a molecular weight of 55700 g/mol and melting temperature of 112 °C.

INTRODUCTION

Bidentate ligands play a prominent role in homogeneous catalysis¹⁻⁶ and perform better than their monodentate counterparts, with few exceptions.^{7–9} The enhanced regioand stereoselection can be attributed to the chelating ability of bidentate ligands and enforcement of a confined environment around the metal center.¹⁰ These attributes provide a better discrimination between the two faces of incoming substrate and lead to enhanced selectivities.^{11,12} However, synthesis of bidentate ligands is largely a tedious, multistep, and timeconsuming process. This is particularly inconvenient if a large ligand library has to be screened to meet the desired selectivity.¹³ Although combinatorial approaches have been designed to exactly address this bottleneck, they usually make use of covalently synthesized ligands and suffer from the lack of ligand libraries. $^{14-16}$ A supramolecular approach that can generate a large catalyst library using a small number of monodentate ligands was introduced by Reek, 17-22 Breit, 23-25 and others. $^{26-\widetilde{28}}$ It has been demonstrated that two supramolecular phosphine ligands with phosphorus as neutral-donor can self-assemble on a metal to produce a metal complex (Figure 1, left).^{29–31} The self-assembled metal complexes were found to be active in asymmetric hydrogenation,^{32–35} asymmetric hydroformylation,^{36,37} allylic amination,³⁸ nitro-aldol reaction,³⁹ and decarboxylative hydroformylation–hydrogenation,⁴⁰ and on many occasion these self-assembled complexes outperform their parent covalent metal catalysts.¹⁷⁻²² However, the success of supramolecular ligands has been so far limited to the self-assembly of two neutral-donor

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Figure 1. Classical supramolecular approach in homogeneous catalysis (left) and self-assembly of x-type and n-type ligands on a metal for olefin polymerization (right).

ligands only.^{41–43} To the best of our knowledge, self-assembly of an anionic and a neutral ligand to mimic ditopic ligand behavior generating a heterocomplex has never been reported.^{44,45} Although highly desirable, supramolecular catalyst designing strategies via the self-assembly of anionic and a neutral donor to mimic the ditopic ligand coordination have never been scouted and their application in olefin polymerization remains unexplored.⁴⁶ This may be due to the additional complexity of stabilization of the anion (from X-type ligand) by the supramolecular motif, which will hamper the self-assembly. Therefore, the choice of the anionic ligand and the supramolecular motif would be very crucial. A highly negatively charged anion may be stabilized by intermolecular interactions with the supramolecular motif, leaving no scope for selfassembly with neutral donor. In this context, we pondered if a monodentate supramolecular carboxylate and supramolecular phosphine unit can be self-assembled via secondary interaction on a metal template, which can then mimic the classical SHOP type catalyst^{47–49} (Figure 1, right) and might catalyze olefin oligomerization/polymerization. Apart from metal catalyzed polymerization, metal free organocatalytic approaches have been reported and an organo-catalytic ring opening polymerization of lactide has been reported in the recent past.⁵

RESULT AND DISCUSSION

In our pursuit to realize the supramolecular strategy, we attempted the synthesis of monodentate supramolecular ligands equipped with a hydrogen bonding motif (Scheme 1). The supramolecular phosphines **1a** and **1b** were prepared by treating iodourea with diphenylphosphine in almost quantitative yields (90%).⁵² The appearance of a ³¹P NMR resonance at

Scheme 1. Supramolecular Phosphine and Carboxylate Ligands



-6.05 and -5.96 ppm and disappearance of diphenylphosphine resonance clearly indicated formation of 1a and 1b. Along the same line, reaction of 3-aminobenzoic acid with potassium-cyanate produced 2a. Ligand 2b [3-(3-phenylureido)benzoic acid] was prepared by treating 3-aminobenzoic acid with phenylisocyanate in THF.^{53,54} Thus, the four ligands with an appended supramolecular motif were prepared in a single step in good to excellent yields.

With a set of four monodentate supramolecular ligands in hand, we set out to investigate the self-assembly between an anionic and a neutral ligand. A stoichiometric reaction between 1a. the sodium salt of 2a and [(COD)PdMeCl] in DMSO lead to a turbid mixture. The resultant reaction mixture was passed through Celite, and the volatiles were stripped off to obtain a gray solid. The ³¹P NMR of this solid revealed a broad resonance at 37.21 ppm, suggesting coordination of phosphine 1a. The corresponding proton NMR displayed a characteristic broad singlet at 0.35 ppm, which can be assigned to metal bound methyl protons (Pd-Me). The observed chemical shift of Pd-Me protons is similar to those reported previously.⁵⁵⁻⁶⁰ In addition, proton NMR of the complex displayed a downfield shift of NH protons to 8.99 and 9.23 ppm as compared to free ligands (1a: 8.56, 2a: 8.84). The phosphorus and proton NMR findings were further supported by ¹³C NMR, which revealed a 3 ppm downfield shift of the carboxylate carbon, suggesting that the carboxylate oxygen is covalently bound to the palladium. Additional evidence that supports the existence of complex 4a (formed per Scheme 2) was obtained from ESI-MS analysis. A

Scheme 2. Formation of Complexes 4a-c and 5a-c via Self-Association of an Anionic Donor and a Neutral-Donor Ligand on a Metal Template



positive mode ESI-MS revealed a molecular ion peak at m/z = 621.08 Da $[M - DMSO + H]^+$ and the corresponding sodium salt at m/z = 643.07 Da $[M - DMSO + Na]^+$, authenticating the identity of 4a. The observed and simulated isotopic patterns match exactly, confirming formation of 4a (SI Figure S21). Although DMSO complex 4a allowed characterization, it was found to be unstable in solution state and decomposes after a few hours. To prevail over this, we choose pyridine as a donor solvent with relatively small dielectric constant (≈ 12), and an alternate synthetic protocol was established. The three components of the self-assembly {1a:2a:[(TMEDA)PdMe₂]} were simultaneously mixed in pyridine at room temperature.⁶¹

treated with pyridine and washed with hexane to yield a powder. A single ³¹P resonance at 39.48 ppm, and the appearance of a methyl proton at 0.35 ppm indicated formation of self-assembled complex **5a**. Complex **5a** was found to be stable enough for full scale characterization, and identity of **5a** was established using a combination of 1-2D NMR and mass spectroscopy.

In a decisive through-bond direct C-H correlation spectroscopy (HSQC), metal bound methyl protons at 0.35 ppm revealed a cross peak to a carbon at 0.43 ppm (SI Figure S26). Similarly, pyridine protons at 8.58 ppm displayed a cross peak to a carbon at 150.1 ppm. The NOESY spectrum (SI Figure S27) unveiled a through space correlation between the methyl proton on palladium (Pd-Me) and the pyridine protons, which indicates that the methyl group and pyridine are placed cis to each other.^{62,63} As a consequence of this arrangement, phosphine (1a) and carboxylate ligand (2a) are situated *cis* to each other (Figure S27). A comparative proton NMR spectrum of the two ligands and the self-assembled complex 5a (Figure S29) revealed significant downfield shift of the internal NH protons, suggesting intramolecular hydrogen bonding in 5a. The deshielding of the urea protons after self-assembly is in line with the previous reports.⁶⁴ The solution structure of complex 5a was corroborated by positive mode electrosprav ionization mass spectrometry (ESI-MS). A methanol solution of 5a revealed pseudomolecular ion peaks at m/z = 621.08 [M – Py $(H^{+} + H)^{+}; 643.06 [M - Py + Na]^{+} (SI S28)$. To increase the solubility, complexes 4b-c and 5b-c were prepared by replacing one of the urea protons with a phenyl group. The thus prepared complexes 4b, 4c, 5b, and 5c were characterized using a combination of spectroscopic and analytical methods.⁶¹ The thus obtained data confirmed formation of 4b, 4c, 5b, and 5c. In our attempts to fully elucidate the self-assembly and map the molecular structure, we choose complex 5c as it was found to be soluble in nondonor solvents, such as dichloromethane and chloroform. The phosphorus resonates at 41.17 ppm as the only peak (SI Figure S44), and the urea protons were found to be deshielded to appear at 9.93 and 10.59 ppm (SI Figure S45). ¹³C NMR revealed a downfield shifted carbonyl carbon at 173.3 ppm, indicating covalent bonding with palladium.⁶⁵ The NOE experiment established a through space correlation between the methyl (Pd-Me) protons and pyridine protons, indicating that the two groups are cis to each other. This was further corroborated by a long-range P-H correlation (HMBC) experiment, which revealed a cross peak between a phosphorus and Pd-Me protons (Figure 2, SI Figure S50). The other two cross peaks can be attributed to minor equilibrium (pyridine coordination-decoordination) products that appear while recording 2D NMR. The NMR findings were supported by ESI-MS, which revealed a pseudomolecular ion peak at m/z =773.15 $[M - Py + H]^+$ (Figure S52).

In addition, the existence of self-assembled complex **5c** was demonstrated by deuterium labeling experiments, by NMR titration (Job plot), by IR and UV–vis spectroscopy, by synthesizing a model complex **6**, and by computational methods (SI section 4 and 5). A NMR titration experiment revealed that the chemical shift of the NH proton changes with increasing concentration of **1b**, indicating intermolecular hydrogen-bonding in **1b**.⁶⁶ On the contrary, the NH resonance in complex **5c** does not shift with increasing concentration of **5c**, a characteristic feature of a self-assembled complex with intramolecular hydrogen-bonding (SI Figure S62).⁶⁷ The change in CO stretching frequencies from 1645 to 1698



Figure 2. Expanded view of a long-range P–H correlation (HMBC) spectrum of 5c.

cm⁻¹ further corroborated the NMR data (Figure S63). A weak d–d transition band at $\lambda_{max} = 354$ nm indicates the existence of a covalent bond between the carboxylate anion and the metal center.⁶⁸ Multiple attempts to crystallize **5c** lead to glassy crystals (SI, Figure S54). To obtain detailed insights, we sought assistance of computational methods (DFT), and the energy optimized structures for complex *cis*-**5c** and *trans*-**5c** are depicted in Figure 3. The energy optimized structures revealed that complex *cis*-**5c** is lower in energy (by 7.63 kcal/mol) than complex *trans*-**5c**.⁶¹



Figure 3. Energy (in kcal/mol) optimized structure of *cis*-**5c** and *trans*-**5c** (H atoms on phenyl rings have been omitted for clarity).

A careful evaluation of the structural features of selfassembled complexes 4a-c and 5a-c suggested that these complexes meet all the requirements to be an active catalyst for olefin polymerization. Just to demonstrate the synthetic utility, performance of self-assembled complexes 4a-c was evaluated in ethylene polymerization and Table 1 presents the most important results. Complex 4a was found to be the most active and complex 4c revealed the lowest activity in the ethylene polymerization. The reduced activity in 4b and 4c can be ascribed to the decreasing strength of hydrogen bonding in 4band 4c. It is well documented in the literature that substituting NH protons of urea with an aryl substituent leads to reduced intermolecular hydrogen bonding due to (i) increased steric crowding around the remaining NH protons, (ii) and the remaining NH protons can form hydrogen bonding with *ortho*-

Table 1. Polymerization of Ethylene Catalyzed by $4a-c^{a}$

$//$ Cat. $\land \land \land$					
Entry	Cat.	Temp. (°C)	Yield (g)	TOF (mol of PE/mol of Pd/h)	$\stackrel{T_{\mathrm{m}}}{(^{\circ}\mathrm{C})}$
1	4a	60	0.014	14.2	ND
2	4a	70	0.103	105.1	109
3	4a	80	0.183	186.7	112
4	4a	90	0.053	54.04	99.8
5	4b	70	0.040	44.64	ND
6	4b	80	0.043	47.99	ND
7	4c	70	0.025	30.68	ND
8	4c	80	0.030	36.94	ND

^{*a*}Reaction conditions: Catalyst = $35 \mu mol$ (DMSO - 0.5 mL + DCM-2 mL), toluene = 100 mL; time = 1 h, ethylene pressure = 10 bar, ND = not determined, NO = not observed.

CH protons of the aryl ring.⁶⁹⁻⁷¹ Complex 4a catalyzes the polymerization of ethylene at 60 °C (Table 1, entry 1), and the activity increases with increasing polymerization temperature. The best polymerization activity was observed at 80 °C, and increasing the temperature to 90 °C lead to lower activity (Table 1, entry 4).⁵⁷ It is most likely that 4a becomes less active at 90 °C due to weak or no intramolecular hydrogen bonding. The same constraints are presumably responsible for the vanished activity of 5a-c (Table S3). This hypothesis was supported by variable temperature proton NMR of 5a, which revealed that the NH protons of the two ligands merge with each other at 90 °C, indicating collapse of intramolecular hydrogen bonding and ditopic behavior of 5a (SI Figure S75). This finding is in line with the common observation encountered in supramolecular catalysis for hydrogenation and hydroformylation. $^{29-31,72}$ However, there could be other reasons for the reduced activity at high temperature, which cannot be ruled out at this stage.

The resultant polyethylene revealed a molecular weight of 55700 g/mol with a polydispersity of 2.2 (SI Figure S76). The HT-GPC data was further corroborated by MALDI-ToF-MS data which displayed a repeat unit mass of 28 Da (SI Figure 77). High temperature NMR of the polymer displayed methyl and methylene resonances at 0.79 and 0.87 and 1.31 ppm, confirming the existence of highly branched polyethylene. This apart, the proton NMR revealed resonance at 1.71, 1.88, 2.13, and 2.23 ppm, which can be ascribed to internal double bonds in the polyethylene backbone and CH protons at branching points. Thus, comparison of the NMR data indicates that the polyethylene is highly branched with internal double bonds (SI, Figure S78–S79).^{74–76} In accordance with the branched structure, the melting temperature of polyethylene was found to be 112 °C (Figure S74).⁷

CONCLUSION

In conclusion, self-assembly of an anionic and a neutral supramolecular ligand on a metal template has been demonstrated for the first time. A supramolecular carboxylate (X-type) ligand, supramolecular phosphine (L-type) ligand, and metal precursor were found to self-assemble through deliberately installed urea motifs to generate a small library of palladium complexes 4a-c and 5a-c that mimic the bidentate coordination in SHOP-type catalysts. The existence of selfassembled complex 5c was demonstrated using 1-2D NMR spectroscopy, deuterium labeling, NMR titration, IR spectroscopy, UV-vis spectroscopy, model complex synthesis, and

DFT calculations. The synthetic utility of these complexes was demonstrated by employing 4a-c in ethylene polymerization. Complex 4a was found to be the most active and led to the production of highly branched polyethylene, whereas 5a-c could not catalyze the polymerization, indicating the limitation of the present method. The ideal polymerization condition was found to be 80 °C at 10 bar ethylene pressure, although the best activity under these conditions is an order of magnitude lower than that of the corresponding phosphine-sulfonate complex.57

EXPERIMENTAL SECTION

Materials and methods. Unless noted otherwise, all manipulations were carried out under an inert atmosphere of argon using standard Schlenk line techniques or an M-Braun glovebox. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone under argon atmosphere. Acetonitrile, dimethyl sulfoxide, and methylene chloride were distilled on calcium-hydride. Potassium cyanate and hydrochloric acid were purchased from Loba Chemie. 3amino benzoic acid and 3-iodo aniline were obtained from Alfa Aesar. Phenylisocyante was purchased from Spectrochem Pvt. Ltd. Ligands 1a and 1b were synthesized by modifying a literature procedure.²⁶ Ligands 2a and 2b were synthesized by improved literature protocols.^{53,54} Other chemicals, such as [Pd(COD)MeCl]⁷⁸ and [Pd(TMEDA)Me₂], were synthesized by following known procedures. Ethylene polymerization was carried out in a 250 mL stainless steel high pressure Buchi (glasuster cyclone 075) reactor equipped with a mechanical stirrer and a heating/cooling jacket. NMR was recorded on Bruker 400 and 500 MHz instruments. Chemical shifts are referenced to external reference TMS (¹H and ¹³C). Coupling constants are given as absolute values. Multiplicities are given as follows: s: singlet, d: doublet, t: triplet, m: multiplet. High temperature NMR was recorded on a Bruker Avance 500 MHz instrument at 130 °C in a C₆D₆ + TCB (10:90) mixture. Mass spectra were recorded on a Thermo scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150 \times 4.6 mm diameter 8 μ m particle size, and the mobile phase used is 90% methanol + 10% water + 0.1% formic acid. Chromatography: separations were carried out on Spectrochem silica gel (0.120-0.250 mm, 60-120 mesh). IR spectra were recorded on Bruker ALPHA spectrometer. UV-vis spectra were recorded using a Shimadzu UV-1800 spectrometer. The pictures of glassy crystal were captured using a Leica MC 170HD microscope. MALDI-ToF-MS was performed on AB SCIEX TOF/TOFTM 5800 and matrix used is dithranol. High-temperature gel permeation chromatography (HT-GPC) of the polymers was recorded in 1,2,4-trichlorobenzene at 160 °C on a Viscotek GPC (HT-GPC module 350A) instrument equipped with triple detector system. The columns were calibrated with linear polystyrene standards and the reported molecular weights are with respect to polystyrene standards. C, H, and N analyses were carried out using PerkinElmer 2400 instrument. Computational details.^{79–82} All the calculations have been

conducted using density functional theory (DFT), employing the Turbomole 7.0 suite of programs. Geometry optimizations were performed using the Perdew, Burke, and Ernzerhof (PBE) functional. The triple- ζ basis set augmented by a polarization function (Turbomole basis set TZVP) was used for all the atoms. The resolution of identity (RI) along with the multipole accelerated resolution of identity (marij) approximations were employed for an accurate and efficient treatment of the electronic Coulomb term.

1-(3-(Diphenylphosphanyl)phenyl)urea (1a). 3-Iodoaniline was dissolved in 2 M hydrochloric acid and then diluted with water. Potassium cyanate (KOCN) was dissolved in a minimum amount of water and was dropwise added to the above solution. The reaction mixture was stirred at room temperature for 12 h, filtration and washing with toluene lead to intermittent formation of 1-(3iodophenyl)urea. The resultant 1-(3-iodophenyl)urea was dissolved in a THF/DMF (3:1) mixture, and diphenylphosphine and triethylamine were successively added to it. 0.5 mol % of $[Pd(OAc)_2]$ was

added as a catalyst and the resultant mixture was refluxed overnight at 70 $^{\circ}$ C. Next, volatiles were evaporated, 10 mL of degassed water was added to the residue, and the organic compound was extracted with ethyl acetate. Ethyl acetate was stripped off; the resultant crude solid was dissolved in dichloromethane and filtered over a plug of silica. The silica plug was washed with dichloromethane to remove impurities, and then the product was pushed through with ethyl acetate. A faint yellow solid was obtained in 90% isolated yield.

³¹P NMR (500 MHz in DMSO-*d*₆): δ = -6.05. ¹H NMR (500 MHz in DMSO-*d*₆): δ = 8.56 (s, 1H, NH), 7.51 (s, 1H, Ar–H), 7.39 (s, 6H, Ar–H), 7.25 (s, 6H, Ar–H), 6.74 (s, 1H, Ar–H), 5.82 (s, 2H, NH₂). ¹³C NMR (125 MHz in CDCl₃): δ = 156.5 (C=O), 138.5, 136.7, 133.8, 133.6, 129.4, 128.8, 128.5, 125.4, 121.3. IR (cm⁻¹) = 3301 (NH), 1668 (C=O).

1-(3-(Diphenylphosphanyl)phenyl)-3-phenylurea (1b). Phenylisocyanate was dissolved in DCM to which 3-iodoaniline was dropwise added at 0 °C and the mixture was stirred at room temperature for 70 h. The reaction progress was monitored by TLC. Volatiles were stripped off to obtain off white solid, which was dried under vacuum for 6-7 h. The intermittent 1-(3-iodophenyl)-3-phenylurea was dissolved in THF/DMF (3:1), diphenylphosphine and triethylamine were successively added under argon. A catalytic amount of [Pd(OAc)₂] (0.5 mol %) was added as a catalyst, and the mixture was refluxed overnight at 70 °C. Solvent was evaporated, 10 mL of degassed water was added, and the organic compound was extracted with ethyl acetate. The thus obtained ethyl acetate was stripped off, and crude solid was dissolved in dichloromethane and filtered over a plug of silica. The silica plug was washed with dichloromethane to remove impurities, and then the product was pushed through a silica plug with ethyl acetate. A faint yellow solid was obtained in 90% isolated yield.

³¹P NMR (500 MHz in DMSO- d_6): $\delta = -5.96$. ¹H NMR (500 MHz in DMSO- d_6): $\delta = 8.69$ (s, 1H, NH), 8.57 (s, 1H, NH), 7.53 (m, 1H, Ar–H), 7.37 (m, 8H, Ar–H), 7.24 (m, 8H, Ar–H), 6.92 (t, 1H, Ar–H), 6.79 (t, 1H, Ar–H). IR (cm⁻¹) = 3301 (NH), 1644 (C=O). ESI-MS (+ve): for $[C_{25}H_{22}ON_2P]^+ m/z = 397.14 [M + H]^+$; 419.12 [M + Na]⁺.

3-Ureidobenzoic acid (2a). 3-Amino benzoic acid (7.2 mmol) was dissolved in 2 M hydrochloric acid (20 mL) and was diluted with water (100 mL). KOCN (29 mmol) was dissolved in a minimum amount of water and was dropwise added to the above solution with constant stirring at room temperature. After addition, the reaction mixture was stirred for 40 h. The formed precipitate was separated by filtration and the resultant solid was dried to obtain white powder in 51% isolated yield.

¹H NMR (500 MHz in DMSO- d_6): δ = 12.85 (s, 1H, COOH), 8.84 (s, 1H, NH), 8.05 (s, 1H), 7.59 (d, 1H, Ar–H), 7.47 (d, 1H, Ar–H), 7.32 (m, 1H, Ar–H), 5.94 (s, 2H, NH₂). ¹³C NMR (100 MHz in DMSO- d_6): δ = 167.4, 155.9, 140.8, 131.2, 128.8, 121.9, 118.4. IR (cm⁻¹) = 3310 (NH), 1673 (C=O). ESI-MS (+ve): for [C₈H₉O₃N₂]⁺ m/z = 181.06 [M + H]⁺; for [C₈H₈N₂NaO₃]⁺ m/z = 203.04 [M + Na]⁺.

3-(3-Phenylureido)benzoic acid (2b). 3-Amino benzoic acid (7.2 mmol) was dissolved in THF (100 mL), and phenylisocyanate (7.2 mmol) was dropwise added to the above solution with constant stirring. The reaction mixture was stirred at room temperature for 60 h. After the stipulated time, the formed precipitate was separated by filtration. The resultant white solid was dried and washed with diethyl ether (20 mL \times 2) and dichloromethane (20 mL \times 2) to obtain white powder in 92% yield, which was identified as 3-(3-phenylureido)-benzoic acid (2b).

¹H NMR (500 MHz in DMSO-*d*₆): δ = 12.91 (s, 1H, COOH), 8.88 (s, 1H, NH), 8.69 (s, 1H, NH), 8.14 (d, 1H, Ar–H), 7.64 (d, 1H, Ar–H), 7.56 (d, 1H, Ar–H), 7.47 (d, 2H, Ar–H), 7.40 (t, 1H, Ar–H), 7.29 (t, 2H, Ar–H), 6.98 (t, 1H, Ar–H). ¹³C NMR (125 MHz in DMSO-*d*₆): δ = 167.3 (C=O), 152.5 (C=O), 140.0, 139.5, 131.4 (C–Ar), 128.9 (C–Ar), 128.8 (C–Ar), 122.7 (C–Ar), 122.4 (C–Ar), 121.9 (C–Ar), 118.9 (C–Ar), 118.4 (C–Ar). IR (cm⁻¹) = 3312 (NH), 1688 (C=O). ESI-MS (+ve): for

 $[C_{14}H_{13}O_3N_2]^+ m/z = 257.09 [M + H]^+; \text{ for } [C_{14}H_{12}N_2O_3Na]^+ m/z = 279.07 [M + Na]^+.$

Palladium complex [PdMe(2a)(1a)DMSO] (4a). Ligand 2a (0.027 g; 0.150 mmol) was treated with sodium hydride (0.0043 g; 0.181 mmol) in THF for 24 h at room temperature. After evaporation of THF, the sodium salt of ligand 2a was dissolved in DMSO which was followed by addition of [Pd(COD)MeCl] (0.040 g; 0.150 mmol) and ligand 1a (0.048 g; 0.150 mmol). The reaction mixture was stirred at room temperature for 16 h. The resulting yellow brown solution was passed through the bed of Celite. After the evaporation of volatiles, a gray solid was obtained in 63% (0.094 mmol) isolated yield, which was identified as complex 4a. DMSO in 4a could not be accounted due to the overlapping resonance of DMSO- d_6 .

³¹P NMR (500 MHz in DMSO-*d*₆): δ = 37.21 (broad). ¹H NMR (400 MHz in DMSO-*d*₆): δ = 9.23 (s, 1H, NH), 8.99 (s, 1H, NH), 7.59 (s, 9H, Ar–H), 7.47 (s, 9H, Ar–H), 6.05 (s, 2H, NH₂), 5.99 (s, 2H, NH₂), 0.35 (s, 3H, Pd-Me). ¹³C NMR (100 MHz in DMSO-*d*₆): δ = 170.7, 156.4, 156.1, 140.9, 140.7, 139.8, 134.3, 130.4, 128.5, 128.2, 127.2, 126.6, 123.1, 122.0, 119.6, 118.9, 118.5, 0.9 (Pd-Me). ESI-MS (+ve): for [C₂₈H₂₈O₄N₄PPd]⁺ m/z = 621.08 [M – DMSO + H]⁺; for [C₂₈H₂₇O₄N₄NaPPd]⁺ m/z = 643.07 [M – DMSO + Na]⁺.

Palladium complex [PdMe(2a)(1a)Py] (5a). An equimolar mixture of 1a (0.177 g; 0.555 mmol), 2a (0.100 g; 0.555 mmol), and [(TMEDA)PdMe₂] (0.140 g; 0.555 mmol) was add to pyridine (8 mL) at room temperature and stirred for 2 h. The volatiles were evaporated, and pyridine (8 mL) was added to the solid. After 15 min volatiles were stripped off and the off white residue was washed with hexane (15 mL \times 3) to obtain 5a in 90% (0.351 g; 0.501 mmol) isolated yield.

³¹P NMR (400 MHz in DMSO- d_6): δ = 39.48 (s, broad). ¹H NMR (400 MHz, DMSO- d_6): δ = 9.23 (s, 1H, NH), 8.75 (s, 1H, NH), 8.58 (s, 3H, Ar–H), 7.78–7.74 (m, 2H, Ar–H), 7.67 (m, 2H, Ar–H), 7.58 (m, broad, 4H, Ar–H), 7.52 (m, 2H, Ar–H), 7.43 (m, 7H, Ar–H), 7.36 (m, 3H, Ar–H), 7.29 (m, 2H, Ar–H), 7.08 (s, 2H, Ar–H), 6.08 (s, 2H, NH₂), 5.91 (s, 2H, NH₂), 0.35 (s, 3H, Pd-Me). ¹³C NMR (100 MHz, DMSO- d_6): δ = 170.3 (COO), 156.1 (CO), 155.9 (CO), 150.1 (C-Py), 140.8, 139.7, 138.7, 137.0, 133.8, 130.5, 128.7, 128.4, 127.3, 124.4, 122.9, 122.0, 119.8, 118.8, 0.43 (Pd-Me). ESI-MS: for [C₂₈H₂₈O₄N₄PPd]⁺ m/z = 621.08 [M – Py + H]⁺; for [C₂₈H₂₇O₄N₄NaPPd]⁺ m/z = 643.06 [M – Py + Na]⁺. Elemental analysis (%) calculated for C₃₃H₃₂N₅O₄PPd: C 56.62, H 4.61, N 10.00; found: C 55.02, H 4.11, N 10.57.

Palladium complex [PdMe(2b)(1a)DMSO] (4b). Ligand 2b (0.100 g; 0.390 mmol) was treated with sodium hydride (0.010 g; 0.429 mmol) in THF (8 mL) for 24 h at room temperature. After evaporation of THF, the sodium salt of ligand 2b was dissolved in DMSO (8 mL) which was followed by addition of [Pd(COD)MeCl] (0.103 g; 0.390 mmol) and ligand 1a (0.125 g; 0.390 mmol). The above reaction mixture was stirred at room temperature for 16 h. The resulting brown solution was passed through a bed of Celite under argon. After the evaporation of volatiles, a gray solid was obtained in 71% (0.215 g; 0.277 mmol) yield, which was identified as complex 4b. DMSO in 4b could not be accounted due to the broad overlapping resonance of DMSO- d_{6r} .

³¹P NMR (500 MHz in DMSO-*d*₆): δ = 37.37. ¹H NMR (500 MHz in DMSO-*d*₆): δ = 11.18 (s, broad, 1H, NH), 10.70 (s, broad, 1H, NH), 9.00 (s broad, 1H, NH), 7.89 (s, broad, 2H, Ar–H), 7.64 (s, broad, 3H, Ar–H), 7.55 (s, broad, 6H, Ar–H), 7.45 (s, broad, 6H, Ar–H), 7.21 (s, broad, 4H, Ar–H), 7.04 (s, 1H, Ar–H), 6.87 (s, 1H, Ar–H), 5.95 (s, broad, 2H, NH₂), 0.40 (s, 3H, Pd-Me). ¹³C NMR (125 MHz in DMSO-*d*₆): δ = 170.8, 155.9, 153.6, 141.1, 140.0, 134.2, 130.6, 128.5, 127.3, 123.0, 122.4, 120.8, 119.9, 119.3, 118.0, 0.91 (Pd-Me). ESI-MS (+ve): for [C₃₄H₃₂O₄N₄PPd]⁺ *m/z* = 697.12 [M + H]⁺, for [C₃₄H₃₁O₄N₄PNaPd]⁺ *m/z* = 719.10 [M + Na]⁺.

Palladium complex [PdMe(2b)(1a)Py] (5b). A stoichiometric amount of 1a (0.125 g; 0.390 mmol), 2b (0.100 g; 0.390 mmol), and [(TMEDA)PdMe₂] (0.098 g; 0.390 mmol) was mixed in pyridine (20 mL) at room temperature and stirred for 2 h. Solvents were evacuated, and pyridine (12 mL) was added to the solid. After stirring for 15 min at room temperature, volatiles were stripped off to obtain an off white solid which was washed with hexane ($15 \text{ mL} \times 3$). The resultant residue was dried under vacuum to obtain a gray solid in 90% (0.271 g; 0.349 mmol) isolated yield, which was identified as compound **5b** (with an extra pyridine molecule) after analysis.

³¹P NMR (500 MHz in DMSO-*d*₆): δ = 42.61 (s, broad). ¹H NMR (500 MHz in DMSO-*d*₆): δ = 9.53 (s, 2H, NH), 8.93 (s, 1H, NH), 8.61 (s broad, 6H, Py-H), 7.78 (s, 2H, Ar–H), 7.60 (s, 10H, Ar–H), 7.54 (m, 10H, Ar–H), 7.741 (m, 3H, Ar–H), 6.93 (s, 2H, Ar–H), 5.99 (s, 2H, NH₂), 0.32 (s, 3H, Pd-Me). ¹³C NMR (125 MHz in DMSO-*d*₆): δ = 170.6, 155.9, 153.1, 149.9, 140.50, 139.5, 137.1, 133.8, 130.6, 128.6, 127.5, 124.5, 122.5, 121.2, 119.9, 119.3, 118.1, 0.76 (Pd-Me). ESI-MS (+ve): for [C₃₄H₃₂O₄N₄PPd]⁺ *m*/*z* = 697.11 [M – Py + H]⁺. Elemental analysis (%) calculated for C₃₉H₃₆N₅O₄PPd: C 60.35, H 4.68, N 9.02; found: C 60.42, H 4.68, N 10.29.

Palladium complex [PdMe(2b)(1b)DMSO] (4c). Ligand 2b (0.072 g; 0.281 mmol) was treated with sodium hydride (0.074 g; 0.309 mmol) in THF (8 mL) for 24 h at room temperature. THF was evaporated and the residue (sodium salt of ligand 2b) was dissolved in DMSO (1 mL), which was followed by the addition of [Pd(COD)-MeCl] (0.074 g; 0.281 mmol) and ligand 1b (0.111 g; 0.281 mmol). The reaction mixture was stirred at room temperature for 16 h. The resulting brown solution was passed through the bed of Celite under argon. Volatiles were stripped off to obtain a gray solid in 68% (0.163 g; 0.191 mmol) isolated yield. A combined spectroscopic and analytical characterization established that the above gray solid is compound 4c.

³¹P NMR (500 MHz in DMSO-*d*₆): δ = 37.21. ¹H NMR (400 MHz in DMSO-*d*₆): δ = 10.74 (s, broad, 1H, NH), 10.45 (m, broad, 2H, NH), 10.16 (s, broad, 1H, NH), 7.92 (s, broad, 1H, Ar–H), 7.86 (s, broad, 2H, Ar–H), 7.60 (m, 8H, Ar–H), 7.46 (m, 7H, Ar–H), 7.22 (m, 7H, Ar–H), 6.88 (m, 3H, Ar–H), 0.41 (s, 3H, Pd-Me). ¹³C NMR (100 MHz in DMSO-*d*₆): δ = 170.9, 153.5, 153.0, 140.9, 139.9, 134.2, 130.9, 130.5, 128.6, 128.4, 127.4, 123.4, 122.5, 121.4, 120.9, 120.3, 119.3, 118.1, 116.8, 0.82 (Pd-Me). ESI-MS (+ve): for [C₄₀H₃₆O₄N₄PPd]⁺ *m*/*z* = 773.15 [M – DMSO + H]⁺; for [C₄₀H₃₅O₄N₄PNaPd]⁺ *m*/*z* = 795.13 [M – DMSO + Na]⁺.

Palladium complex [PdMe(2b)(1b)Py] (5c). An equimolar mixture of 1b (0.156 g; 0.396 mmol), 2b (0.101 g; 0.396 mmol), and [(TMEDA)PdMe₂] (0.100 g; 0.396 mmol) was added to pyridine (8 mL) at room temperature and stirred for 2 h. Volatiles were evaporated, and a second batch of pyridine (6 mL) was added to the residue, and the mixture was stirred at room temperature for 15 min. Finally, volatiles were stripped off, and the remaining residue was washed with hexane (15 mL \times 3) to obtain a yellow solid in 86% (0.290 g; 0.340 mmol) isolated yield. Solid was crystallized from the mixture of chloroform:hexane at 0 °C. An extra molecule of pyridine was found to be trapped in the complex. No homocomplex could be observed by NMR.

³¹P NMR (500 MHz in CDCl₃): δ = 41.17. ¹H NMR (400 MHz in CDCl₃): δ = 10.59 (s, 1H, NH), 9.93 (s, 1H, NH), 9.75 (s, br., 1H, NH), 9.58 (s, br., 1H, NH), 8.57 (s br., 4H, Py-H), 8.18 (m, 2H, Py-H), 7.96 (s, 3H, Py-H), 7.60 (s, 6H, Ar-H), 7.40 (s, 4H, Ar-H), 7.23 (m, 9H, Ar-H), 7.10 (s, 4H, Ar-H), 7.01 (m, 2H, Ar-H), 6.78 (m, 4H, Ar-H), 0.48 (s, 3H, Pd-Me). ¹³C NMR (100 MHz in CDCl₃): δ = 173.3, 154.2, 150.1, 139.9, 137.1, 134.1, 131.0, 128.8, 125.4, 124.6, 123.2, 122.2, 121.5, 121.2; 120.4, 119.5, 119.2, 2.68 (Pd-Me). IR (cm⁻¹) = 3332 (NH), 1698 (C=O). ESI-MS (+ve): calculated for [C₄₀H₃₆O₄N₄PPd]⁺ m/z = 773.15 [M - Py + H]⁺; for [C₄₀H₃₅O₄N₄PNaPd]⁺ m/z = 795.13 [M - Py + Na]⁺. Elemental analysis (%) calculated for C₄₅H₄₀N₅O₄PPd: C 63.43, H 4.73, N 8.22; found: C 63.21, H 4.88, N 9.18.

Demonstration of self-assembled complex 5c. Deuterium labeling experiment. The purpose of deuterium labeling is to establish the identity of NH protons originating from ligand 1b when it self-assembles. If the NH protons belonging to 1b are labeled with deuterium (D), then these would be absent (or partially present if there is H/D exchange) after self-assembly with 2b. Those protons that remain absent (or partially present if there is H/D exchange) in a deuterium labeled self-assembled complex 5c' can therefore only belong to 1b. This exercise would establish the chemical shift of 1b

NH-protons after self-assembly. Then these **1b** NH protons in 5c can be tracked via NMR titration to establish the fate of inter- or intramolecular hydrogen bonding.

Thus, the deuterium labeled ligand 1b' was self-assembled with 2b to obtain a self-assembled complex $5c^\prime.$ As evident from SI section 4.1.2 and proton NMR (Figure \$59) of 5c', only 0.58 protons for the NH group of 1b' could be detected at 10.32 ppm. Similarly, instead of 2H only 1.36H were observed at 9.25 ppm, indicating that the remaining is ND belonging to 1b'. This observation indicates that the NH protons from 1b appear at 10.32 and 9.25 ppm after self-assembly. Having established the chemical shift of 1b NH protons after selfassembly, we performed NMR titration experiment as presented in SI section 4.2. The change in chemical shift as a function of concentration of 1b and concentration of 5c is presented in Table S1, and the same is plotted in Figure S62. As it is evident from this figure; the 1b NH proton shifts downfield with increasing concentration of 1b, suggesting intermolecular hydrogen bonding. Whereas, there was hardly any change in the chemical shift of 5c NH protons with increasing concentration of 5c, suggesting intramolecular hydrogen bonding.

Deuterium labeled 1-(3-(diphenylphosphanyl)phenyl)-3-phenylurea (1b'). Ligand 1b (0.120 g, 0.303 mmol) was dissolved in 2 mL of dichloromethane, and 1 mL of methanol- d_4 was added. After stirring at room temperature for 2 h, solvents were stripped off. The resultant solid was dried and was analyzed by NMR spectroscopy.

³¹P NMR (500 MHz in CDCl₃): δ = -5.11. ¹H NMR (500 MHz in CDCl₃): δ = 7.55 (d, 1H, Ar-H), 7.31 (s, 9H, Ar-H), 7.26 (m, 5H, Ar-H), 7.09 (m, 2H, Ar-H), 6.97 (m, 2H, Ar-H).

Deuterium labeled palladium complex [PdMe(2b)(1b)Py] (5c'). Ligand 1b' (0.100 g, 0.252 mmol), ligand 2b (0.064 g, 0.252 mmol), and [Pd(TMEDA)Me₂] (0.063 g, 0.252 mmol) were mixed in pyridine (8 mL) at room temperature and stirred for 3 h. Volatiles were stripped off, and pyridine (8 mL) was added to the residue. After stirring for 15 min, volatiles were evaporated and the resultant yellow solid was washed with diethyl ether (10 mL \times 2). The thus obtained solid was dried under vacuum to yield complex 5c' in 88.7% yield (0.190 g, 0.222 mmol).

³¹P NMR (500 MHz in DMSO-*d*₆): δ = 39.88. ¹H NMR (400 MHz in CDCl₃): δ = 10.32 (0.58H, NH/ND), 9.60 (1H, NH), 9.26 (1.36H, NH/ND), 8.56 (4H, Py), 7.93 (5H, Ar–H), 7.55 (7H, Ar–H), 7.33 (5H, Ar–H), 7.09 (8H, Ar–H), 6.73 (4H, Ar–H), 0.51 (s, 3H, Pd-Me).

NMR titration to establish self-assembly **5c**. NMR titration for 1-(3-(diphenylphosphanyl)phenyl)-3-phenylurea (**1b**). 0.0039 g (20 mM) of **1b** was taken in a NMR tube, and 0.5 mL CDCl₃ was added to the NMR tube. Proton NMR at 23 °C was recorded, and the chemical shift of NH protons was noted. Subsequently, the remaining quantity of ligand **1b** was added to the NMR tube to make a 40 mM and 60 mM solution of **1b** and proton NMR was recorded.

NMR titration for palladium complex (5c). 0.0085 g (20 mM) of 5c was taken in a NMR tube, 0.5 mL $CDCl_3$ was added to the tube, and a proton NMR at 23 °C was recorded. Subsequently, the remaining quantity of 5c was added to the above NMR tube to bring the concentration to 40 mM and 60 mM and the change in chemical shift was noted.

IR studies. The existence of hydrogen bonding was attested by the change in CO stretching frequencies from 1645 (free **1b**) to 1698 cm⁻¹(Figure S63). Similar frequencies have been accounted for hydrogen bonding interactions.³²

UV–vis studies. A weak d–d transition band at $\lambda_{max} = 354$ nm indicates formation of a covalent bond between the carboxylate group and the metal center. The UV–vis analysis is supported by literature data which reports a similar λ_{max} for a palladium complex, as well as a model complex **6** that we prepared (see SI section 4.5 for the synthesis and characterization of model complex **6**).

Synthesis of model complex 6. In our attempts to establish the covalent behavior of carboxylate ligand, we synthesized model complex 6. The molecular structure of complex 6 (Figure S67) unambiguously established the covalent bond between the carboxylate oxygen and palladium (Pd-O1 = 2.105 Å).⁸³ Triphenylphosphine (0.206 g, 0.790 mmol), benzoic acid (0.048 g, 0.395 mmol), and [Pd(TMEDA)Me₂]

(0.100 g, 0.395 mmol) were taken in a precooled (at -30 °C) Schlenk tube. A suitable quantity of DCM (6 mL) was added into the Schlenk tube, and the mixture was stirred overnight at 0 °C. Volatiles were evaporated at 0 °C, and crude solid was washed with hexane (5 mL × 3). The resultant residue after washing was dried under vacuum to yield complex 6 in 84.7% yields (0.255 g, 0.332 mmol). Recrystallization from dichloromethane:heptane at 0 °C afforded crystals suitable for single crystal X-ray measurement.

³¹P NMR (500 MHz, CDCl₃): δ = 29.23. ¹H NMR (500 MHz, CDCl₃): δ = 7.75 (s, 12H, Ar–H), 7.33 (s, 18H, Ar–H), 7.21 (s, 2H, Ar–H), 7.14 (t, 1H, Ar–H), 7.02 (t, 2H, Ar–H), -0.05 (s, 3H, Pd-Me).

Ethylene polymerization. Ethylene polymerization was carried out in a 250 mL stainless steel high pressure Buchi (glasuster cyclone 075) reactor equipped with a mechanical stirrer and a heating/cooling jacket. Prior to the experiment, the reactor was heated in vacuum to 90 °C for 30 min, cooled to room temperature, and filled with argon. Next, the reactor was flushed with ethylene (3 times, 12 bar) and was charged with an appropriate quantity of toluene under a positive ethylene stream. The reactor was then pressurized to 10 bar and saturated with ethylene for 30 min at the desired reaction temperature. After cooling at room temperature, catalyst solution (25 mg, 0.5 mL DMSO + 2 mL DCM) was introduced into the reactor at room temperature. The reactor was finally pressurized to 10 bar with stirring. The polymerization was generally carried out for 1 h, the excess ethylene was slowly vented off, and the reactor was allowed to cool down to room temperature. Solid was obtained after evaporating the volatiles which were further dried under reduced pressure at 60 °C for 10 h. Important polymerization experiments are summarized in Table \$3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01923.

Synthetic procedure, spectroscopic and analytical data, and polymer analysis. (PDF)

Accession Codes

CCDC 1550942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: s.chikkali@ncl.res.in.

ORCID 💿

Rajesh G. Gonnade: 0000-0002-2841-0197 Samir H. Chikkali: 0000-0002-8442-1480

Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Prof. Dietrich Gudat on the occasion of his 60th birthday.

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