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Facile Formation of Stable Tris(imido)phosphate Trianions as Their Tri- and Hexanuclear Pd(II) Complexes in Protic Solvents

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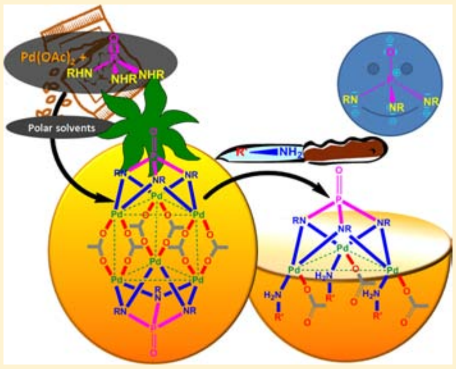
Supporting Information

ABSTRACT: Employing $Pd(OAc)_2$, a facile deprotonation route to access the highly basic tris(alkylimido)phosphate trianions, $[(RN)_3PO]^{3-}$ (R = ^{t}Bu, ^{c}Hex, or ^{i}Pr), analogous to the orthophosphate (PO_4^{3-}) ion in polar and in protic solvents has been achieved. Trinuclear and prismatic Pd(II) clusters of these imido trianions having the formula $\{Pd_3[(NR)_3PO](OAc)_3\}_n$ (n = 1 or 2) or as mixed-bridged clusters of the type $\{Pd_3[(N^iPr)_3PO](OAc)_2(OR')\}_2$ (R′ = Me or H) were isolated exclusively in all these reactions in which the trianionic species acts as a tripodal chelating ligand to the trinuclear Pd_3 unit. Reactivity studies aiming at the Pd(II) atoms in these clusters with nucleophilic reagents, such as primary amines (R″NH_2), have led to a new trimeric cluster with the formula $\{Pd_3[(NR)_3PO](OAc)_3(R''NH_2)_3\}$ in which the tripodal coordination of the Pd−N_{imido} moieties remained unaffected, exemplifying the robustness of the Pd_3 unit in all these clusters. We have also shown the catalytic activity of these Pd(II) complexes in Mizoroki−Heck type coupling reactions in the presence of $Cu(OAc)_2$.



■ INTRODUCTION

Imido analogues of common phosphorus oxo anions have been a topic of immense research interest in main group chemistry and are employed as ligands in coordination chemistry.[1] Metal complexes of several P(V)-imido anions were utilized as catalytic systems for olefin oligomerization and polymerization, ring-opening polymerization of lactides, hydroamination, transfer hydrogenation, etc.[2] Current synthetic procedures to access these imido-P(V) anions involve the use of highly reactive metal reagents in reaction with a phosphonium salt[3] like $[(NHPh)_4P]Cl$, phosphoramides[4] such as $[(RNH)_3P{=}E]$ (E = $NSiMe_3$, O, S, or Se), or preformed iminophosphoranes.[5] However, because of the highly reactive nature of the metal precursors employed in the reactions as well as the presence of residual metal−alkyl/aryl/halide/silylamide bonds in these complexes, their stabilities have largely been limited to anhydrous aprotic and nonpolar solvents. It has also been noticed that use of Lewis acidic transition metal ions such as Cu^{2+} ions in these deprotonation reactions has led to the cleavage of P−N bonds instead of the N-*H* deprotonation.[6] Hence, we started looking at using salts of soft transition metal ions as a source of a base to generate the P(V)-bound polyimido species in a polar medium, which would allow us to explore the potential of these species for broader synthetic applications. Spurred by the remarkable utility of palladium and its compounds in various organic bond-activation reactions,[7] we employed the salts of Pd(II) ions in deprotonation reactions with tris(alkylamido)phosphate ligands, $[(NHR)_3PO]$. Herein, we report on the facile syntheses of the fully deprotonated tris(imido)phosphate trianions of the type $[(RN)_3PO]^{3-}$ starting from $[(NHR)_3PO]$ and $Pd(OAc)_2$ in polar solvents such as CH_3OH, CH_3CN, $(CH_3)_2SO$, etc. These highly basic anions were isolated as their corresponding tri- and hexanuclear Pd(II) clusters of the type $\{Pd_3[(NR)_3PO](OAc)_3\}_n$ (**5**, R = ^{t}Bu, n = 1; **6**, R = ^{C}Hex, n = 2; **7**, R = ^{i}Pr, n = 2) or as mixed-bridged clusters of the type $\{Pd_3[(N^iPr)_3PO](OAc)_2(OR')\}_2$ (**7a**, R′ = Me; **7b**, R′ = H) depending upon the R and R′ groups and the reaction solvents (Scheme 1). All these complexes contain one or two triangular Pd_3 motifs in which the Pd(II) atoms are bound to three chelating N_{imido} moieties.

Further reactions at the Pd(II) atoms in the hexameric Pd_6 clusters with nucleophilic reagents such as primary amines (R″NH_2) lead to a trimeric species with the formula $\{Pd_3[(NR)_3PO](OAc)_3(R''NH_2)_3\}$ (**8**, R = ^{t}Bu, R″ = ^{C}Hex; **9**, R = ^{C}Hex, R″ = ^{C}Hex; **10**, R = ^{i}Pr, R″ = ^{C}Hex) obtained via the symmetrical cleavage of the hexamer. This suggests that the three Pd−N_{imido} moieties attached to the Pd_3 subunit exhibit a remarkable stability and remain unaffected during the cleavage reaction. To the best of our knowledge, the Pd(II) complexes reported here are the first examples of metal complexes isolated in protic solvents that feature the highly basic imido-phosphate trianions $[(RN)_3PO]^{3-}$ as ligands. Although the imido anions analogous to $H_2PO_4^-$ and HPO_4^{2-} ions can be generated using certain reactive Ag(I) salts from the P(V) moieties having fairly acidic N-*H* groups, the imido trianions corresponding to the orthophosphate (PO_4^{3-}) ion remain elusive in all these Ag(I)-mediated reactions.[8] In addition, we have explored the

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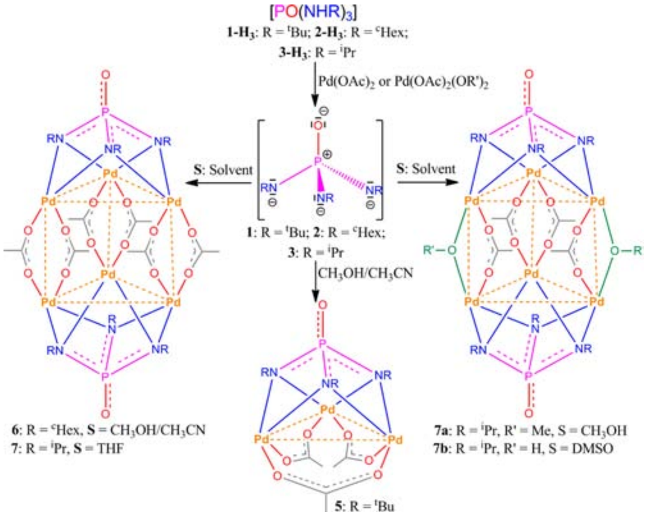
Scheme 1. Synthetic Routes To Access the Tri- and Hexanuclear Pd(II) Clusters of the Tris(alkylimido) Phosphate Trianions



preliminary catalytic activity of these Pd(II) complexes in the Mizoroki–Heck (M–H) type coupling reaction of phenylboronic acid with alkenes.

■ EXPERIMENTAL SECTION

General Remarks. All manipulations involving phosphorus halides were performed under dry nitrogen atmosphere in standard Schlenk glassware. Solvents were dried over potassium (thf, hexane) or sodium (toluene). The primary amines were purchased from Merck or from Aldrich and used as received. $POCl_3$ was purchased locally and was distilled prior to use. The ligands **1**-H_3 and **2**-H_3 were synthesized using literature methods.[9] NMR spectra were recorded on a Jeol 400 MHz spectrometer (^1H NMR 400.13 MHz, $^{13}C\{^1H\}$ NMR 100.62 MHz, $^{31}P\{^1H\}$ NMR 161.97 MHz) or on a Bruker 500 MHz spectrometer (^1H NMR 500.00 MHz, $^{13}C\{^1H\}$ NMR 125.725 MHz, $^{31}P\{^1H\}$ NMR 202.404 MHz) at room temperature using $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). The two-dimensional diffusion-ordered NMR spectroscopy (2D-DOSY) experiments were performed on a Bruker 500 MHz NMR with standard pulse program ledbpgp2S using bipolar gradient pulse pair and two spoiling gradients.[10a] The gradient strength was changed from 2 to 95% with a linear type of ramp. Other parameters, such as the diffusion time (Δ = 40–50 ms), sine-shaped pulse length (δ = 1.1–2.1 ms), and relaxation delay (D1 = 4–8 s), were employed as well.[10b] The electrospray ionization (ESI) mass spectra in the positive ion mode were recorded in a Waters-SYNAPT-G2 high-resolution spectrometer. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were obtained on an Applied Biosystems MALDI-TOF/TOF spectrometer. Fourier transform infrared (FT-IR) spectra were taken on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets. Melting points were obtained using an Electro thermal melting point apparatus and were uncorrected.

Synthesis. *3-H$_3$.* $POCl_3$ (5 mL, 8.23 g, 0.0536 mol) was added dropwise to an excess of isopropyl amine (23.12 mL, 16.69 g, 0.282 mol) in toluene (250 mL) at 0 °C. The resulting mixture was slowly brought to room temperature and stirred for 4 h. The precipitated isopropylammonium chloride was removed by filtration. The filtrate was reduced to 80 mL, and hexane (50 mL) was added to it. The mixture was kept at −15 °C for 2 days to yield a white impure solid. The impure solid was purified by sublimation at 120 °C/1 × 10^{-3} Torr. Yield: 75% (8.90 g, based on P). mp: 122–125 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 18H, CH_3), 2.15 (br, 3H, NH), 3.35 (septet, 3H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.00, 43.25. ^{31}P NMR (161 MHz, $CDCl_3$): δ 12.84. FT-IR data in KBr pellet (cm^{-1}): 3498, 3197, 1638, 1464, 1427, 1384, 1168, 1121, 933, 897, 794, 542. ESI(+): 222.17 $(M)^+$, 199.08 $(M - (C_3H_7NH))^+$. Anal. Calcd for $C_9H_{24}N_3OP$: C, 48.85; H, 10.93; N, 18.99. Found: C, 49.14; H, 10.76; N, 18.74.

5. To a solution of $[OP(NH^tBu)_3]$, **1**-H_3 (20 mg, 0.08 mmol), in methanol was added palladium acetate $Pd(OAc)_2$ (51 mg, 0.24 mmol) in acetonitrile. The resulting mixture was stirred for 1 h and kept for crystallization. Orange blocklike crystals were obtained after 5 days. Yield: 90% (52 mg, based on P). mp: 205–208 °C. ^1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.20 (s, 27H, CH_3), 2.04 (s, 9H, CH_3COO). ^{13}C NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 27.63, 32.20, 52.88, 179.19. ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 69.04. FT-IR data in KBr pellet (cm^{-1}): 3454, 1728, 1561, 1413, 1275, 1175, 1041, 976, 752, 634. ESI(+): 778 $(M + Na)^+$, 698 $(M - C_4H_9)^+$. Anal. Calcd for $C_{18}H_{36}N_3O_7PPd_3$: C, 28.57; H, 4.80; N, 5.55. Found: C, 28.60; H, 4.60; N, 5.38.

6.H$_2$O. To a solution of $[OP(NH^cHex)_3]$, **2**-H_3 (20 mg, 0.06 mmol), in methanol was added palladium acetate $Pd(OAc)_2$ (40 mg, 0.18 mmol) in methanol. The resulting mixture was stirred for 1 h and kept for crystallization. Dark orange prismatic crystals were obtained after 10 days. Yield: 70% (69 mg, based on P). mp: 180–182 °C. ^1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.08 (m, 24H, CH_2), 1.60 (m, 12H, CH), 1.75 (m, 12H, CH_2), 2.25 (s, 18H, CH_3COO), 2.74 (m, 24H, CH_2). ^{13}C NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 113.23, 117.12, 139.15, 148.56, 154.24. ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 73.03. FT-IR data in KBr pellet (cm^{-1}): 3332, 1649, 1451, 1414, 1113, 1018, 647. ESI(+): 1694 $(M + Na)^+$, 836 $(^M/_2)^+$. Anal. Calcd for $C_{48}H_{84}N_6O_{14}P_2Pd_6$: C, 34.53; H, 5.07; N, 5.03. Found: C, 33.87; H, 5.04; N, 4.88.

7.2H$_2$O. A mixture of $[OP(NH^iPr)_3]$, **3**-H_3 (20 mg, 0.09 mmol), and palladium acetate $Pd(OAc)_2$ (60 mg, 0.27 mmol) in THF was stirred for 1 h and kept for crystallization. Platelike orange-colored crystals were obtained after 10 days. Yield: 75% (98 mg, based on P). mp: 198–200 °C. ^1H NMR (400 MHz, $\{(CD_2)_4O\}$): δ 1.19 (d, 36H, CH_3), 2.68 (septet, 6H, CH), 2.47 (s, 18H, CH_3COO). ^{13}C NMR (100 MHz, $\{(CD_2)_4O\}$): δ 22.53, 28.84, 52.20, 183.33. ^{31}P NMR (161 MHz, $\{(CD_2)_4O\}$): δ 78.87. FT-IR data in KBr pellet (cm^{-1}): 3338, 1611, 1552, 1425, 1261, 1140, 1019, 692. MALDI-TOF/TOF: 1423 $(M)^+$, 1365 $(M - C_3H_7NH)^+$. Anal. Calcd for $C_{30}H_{60}N_6O_{14}P_2Pd_6$: C, 25.21; H, 4.23; N, 5.88. Found: C, 25.35; H, 4.24; N, 5.77.

7a. A mixture of $[OP(NH^iPr)_3]$, **3**-H_3 (20 mg, 0.09 mmol), and palladium acetate $Pd(OAc)_2$ (60 mg, 0.27 mmol) in methanol was stirred for 1 h and kept for crystallization. Orange blocklike crystals were obtained in 12 h. Yield: 85% (105 mg, based on P). mp: 180–182 °C. ^1H NMR (400 MHz, CD_3OD): δ 1.12 (d, 36H, CH_3), 2.49 (s, 12H, CH_3COO), 2.69 (septet, 6H, CH), 3.12 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, CD_3OD): δ 24.59, 25.29, 42.87, 53.74, 173.88. ^{31}P NMR (161 MHz, CD_3OD): δ 73.60. FT-IR data in KBr pellet (cm^{-1}): 3335, 1603, 1550, 1420, 1257, 1140, 1019, 722, 690. MALDI-TOF/TOF: 1369 $(M)^+$. Anal. Calcd for $C_{28}H_{60}N_6O_{12}P_2Pd_6$: C, 24.49; H, 4.40; N, 6.12. Found: C, 24.08; H, 4.15; N, 5.94.

7b.2DMSO. A mixture of $[OP(NH^iPr)_3]$, **3**-H_3 (20 mg, 0.09 mmol), and palladium acetate $Pd(OAc)_2$ (60 mg, 0.27 mmol) in dimethyl sulfoxide (DMSO) was stirred for 1 h and kept for crystallization. Orange blocklike crystals were obtained after 5 days. Yield: 75% (101 mg, based on P). mp: 220–222 °C. ^1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.10 (d, 36H, CH_3), 2.68 (s, 12H, CH_3COO), 2.74 (septet, 6H, CH), 2.84 (s, 2H, OH). ^{13}C NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 25.67, 25.85, 50.03, 177.14. ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 73.67. FT-IR data in KBr pellet (cm^{-1}): 3677, 1646, 1532, 1426, 1255, 1143, 1025, 696. MALDI-TOF/TOF: 1423 $(M + DMSO)^+$, 671 $(M/2)^+$. Anal. Calcd for $C_{30}H_{68}N_6O_{14}P_2S_2Pd_6$: C, 24.00; H, 4.57; N, 5.60. Found: C, 24.83; H, 4.11; N, 5.88.

8. To a solution of **5** (30 mg, 0.04 mmol) in methanol was added cyclohexylamine (12.0 mg, 14 μL, 0.12 mmol). The resulting mixture was stirred for 30 min and kept for crystallization. Pale yellow-colored solid was obtained upon slow evaporation. Yield: 80% (72 mg, based on P). mp: 143–145 °C. ^1H NMR (400 MHz, CD_3OD): δ 1.28 (m, 12H, CH_2), 1.33 (s, 27H, CH_3), 1.65 (m, 3H, CH), 1.88 (m, 6H, CH_2), 2.08 (br, 6H, NH_2), 2.63 (s, 9H, CH_3COO), 2.74 (m, 12H,

CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ 25.08, 25.79, 27.66, 32.50, 38.02, 40.86, 52.86, 179.35. ^{31}P NMR (161 MHz, CD_3OD): δ 72.05. FT-IR data in KBr pellet (cm^{-1}): 3477, 1718, 1619, 1568, 1408, 1283, 1145, 1032, 968, 748, 625. MALDI-TOF/TOF: 1077 (M + Na)$^+$. Anal. Calcd for $C_{36}H_{75}N_6O_7PPd_3$: C, 41.01; H, 7.17; N, 7.97. Found: C, 41.03; H, 7.83; N, 7.22.

9.2H$_2$O. *Method A*: To a solution of **6**.H_2O (30 mg, 0.017 mmol) in methanol was added cyclohexylamine (11 mg, 13 μL, 0.10 mmol). The resulting mixture was stirred for 30 min and kept for crystallization. Platelike pale yellow-colored crystals were obtained after 7 days. Yield: 80% (32 mg, based on P). *Method B*: To a mixture of [$PO(NH^cHex)_3$], **2**-H_3 (20 mg, 0.06 mmol), and palladium acetate $Pd(OAc)_2$ (40 mg, 0.18 mmol) in methanol was added cyclohexylamine (17 mg, 20 μL, 0.18 mmol). The resulting mixture was stirred for 30 min. Platelike pale yellow-colored crystals were obtained after 10 days. Yield: 80% (56 mg, based on P). mp: 198−200 °C. ^1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.08 (m, 24H, CH), 1.53 (m, 6H, CH), 1.73 (m, 24H, CH_2), 2.49 (s, 9H, CH_3COO), 2.19 (m, 6H, NH_2), 2.74 (m, 18H, CH_2). ^{13}C NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 25.19, 25.66, 31.21, 34.49, 36.15, 40.94, 50.02, 177.18. ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 73.50. FT-IR data in KBr pellet (cm^{-1}): 3463, 1629, 1448, 1281, 1103, 894, 845, 712. ESI(+): 1132 (M)$^+$, 955 (M − 3(OAc))$^+$. Anal. Calcd for $C_{42}H_{81}N_6O_7PPd_3$: C, 44.55; H, 7.21; N, 7.42. Found: C, 44.18; H, 7.97; N, 6.97.

10. *Method A*: To a solution of **7** (30 mg, 0.02 mmol) in methanol was added cyclohexylamine (12 mg, 14 μL, 0.12 mmol). The resulting mixture was stirred for 30 min and kept for crystallization. Platelike pale yellow-colored crystals were obtained after 5 days. Yield: 70% (28 mg, based on P). Note: **10** can also be obtained from a similar reaction of **7a** with cyclohexylamine. *Method B*: To a mixture of [$OP(NH^iPr)_3$], **3**-H_3 (20 mg, 0.09 mmol), and palladium acetate $Pd(OAc)_2$ (60 mg, 0.27 mmol) in methanol was added cyclohexylamine (27 mg, 30 μL, 0.27 mmol), the mixture was stirred for 30 min and kept for crystallization. Platelike pale yellow-colored crystals were obtained after 5 days. Yield: 80% (73 mg, based on P). mp: 215−217 °C. ^1H NMR (400 MHz, CD_3OD): δ 1.13 (d, 18H, CH_3), 1.29 (septet, 3H, CH), 1.51 (m, 3H, CH), 1.71 (m, 12H, CH_2), 2.41 (m, 18H, CH_2), 2.63 (s, 9H, CH_3COO), 3.12 (br, 6H, NH_2). ^{13}C NMR (100 MHz, CD_3OD): δ 22.39, 25.81, 29.32, 33.84, 34.67, 35.16, 52.91, 179.15. ^{31}P NMR (161 MHz, CD_3OD): δ 73.67. FT-IR data in KBr pellet (cm^{-1}): 3465, 1640, 1574, 1496, 1395, 1196, 1037, 849. ESI(+): 1035 (M + Na)$^+$, 856 (M − 3(OAc) + Na)$^+$. Anal. Calcd for $C_{33}H_{69}N_6O_7PPd_3$: C, 39.16; H, 6.87; N, 8.30. Found: C, 40.34; H, 7.00; N, 8.08.

General Procedure for the M−H Type Coupling Reaction of Phenylboronic Acid with Alkenes. In a typical reaction, a screw-capped pressure tube (15 mL) was charged with phenylboronic acid (1.2 mmol), 3 mol % of the Pd(II) catalyst (**5**/**6**/**7a**), and 2.0 equiv of $Cu(OAc)_2.H_2O$. To this mixture was added the alkene precursor in dimethylformamide solvent (7.5 mL), and the resulting mixture was purged under a flow of N_2 for 15 min and then refluxed at 100 °C for 4 h. The resultant dark brownish-green-colored mixture was filtered in a thick pad of Celite, and the filtrate was then extracted with ethyl acetate. The separated ethyl acetate layer was then dried and evaporated to get a crude mixture of the product which was purified by column chromatography using ethyl acetate/hexane as eluents. All these reactions proceeded smoothly to afford the corresponding phenylated products in reasonable yields (Table 1).

Crystallography. Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo Kα radiation (λ = 0.71073 Å) for **5**, **6**.H_2O, **7**.$2H_2O$, **7a**, **7b**.2DMSO, **9**.$2H_2O$, and **10** and on a Bruker Smart Apex II diffractometer at 273 K for **3**-H_3 (Table S1, Supporting Information). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).[11] All non-hydrogen atoms were refined aniostropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. Crystals of **7**.$2H_2O$ and **7a** were weakly diffracting at higher angles; hence, a 2θ = 50° cutoff was applied. Two of the three cyclohexyl groups in the asymmetric unit of **6**.H_2O were disordered. The cyclohexyl moiety of the primary amino group in the asymmetric unit of **9** was similarly disordered. Atom positions of the disordered C atoms were isotropically refined over two positions using similar distances and similar U-restraints. Five C atoms and one O atom in **7**.$2H_2O$ had slightly bad ellipsoids and hence were refined with partial isotropic parameters. The solvated DMSO molecule in the asymmetric unit of **7b** was disordered and is freely refined over two positions using similar distances and similar U-restraints. The water molecules in **6**.H_2O and **7**.$2H_2O$ were disordered as well and isotropically refined.

Table 1. M−H Type Reaction of PhB(OH)$_2$ with Alkenes

		% yield of the product		
starting material	coupled product	catalyst **5**	catalyst **6**	catalyst **7a**
11a	**12a**	90	90	95
11b	**12b**	90	92	90
11c	**12c**	92	90	95
11d	**12d**	95	95	98

RESULTS AND DISCUSSION

Synthesis and Spectra. The phosphoric triamide ligands, [$(NHR)_3PO$] (**1**-H_3, R = ^{t}Bu; **2**-H_3, R = ^{i}Pr; **3**-H_3, R = ^{c}Hex), were prepared by a slightly modified literature procedure.[4d,9] The reactivity of these ligands was further tested with $Pd(OAc)_2$ (**4**) in an appropriate polar solvent at room temperature with the view of obtaining various imido-P(V) derivatives. Crystals of $\{Pd_3[(N^tBu)_3PO](OAc)_3\}$ (**5**) and $\{Pd_3[(N^cHex)_3PO](OAc)_3\}_2$ (**6**) were obtained from the respective reaction of **1**-H_3 and **2**-H_3 with $Pd(OAc)_2$ in MeOH within 10 days. On the other hand, it has been observed that reaction of **3**-H_3 under similar conditions in MeOH gave $\{Pd_3[(N^iPr)_3PO](OAc)_2(\mathit{OMe})\}_2$ (**7a**) as a major compound. When the solvent system is changed to $(CH_3)_2SO$, crystals of $\{Pd_3[(N^iPr)_3PO](OAc)_2(\mathit{OH})\}_2.2(CH_3)_2SO$ (**7b**.2DMSO) were obtained. Formation of these mixed-bridged clusters **7a** and **7b** was attributed to the dynamic nature of bridging OAc groups in [$Pd_3(OAc)_6$] (**4**) where it exists as a mixture of **4** and [$Pd_3(OMe)_2(OAc)_4$] (**4a**) in MeOH, as observed by diffusion-ordered ^1H NMR spectroscopy (^1H-DOSY).[12] Similarly, in a solvent containing a large excess of water (such as DMSO), it exists as a mixture of **4** and [$Pd_3(OH)_2(OAc)_4$] (**4b**). Hence, it is evident that formation of **7a** and **7b** is mostly due to the reaction of **3**-H_3 with **4a** and **4b**, respectively. Finally, crystals of the all acetate-bridged species $\{Pd_3[(N^iPr)_3PO](OAc)_3\}_2$ (**7**) were exclusively obtained from the corresponding reaction in tetrahydrofuran. The ^{31}P NMR spectra of the reaction mixture of **3**-H_3 and $Pd(OAc)_2$ (**4**) after 12 h gave three signals at δ 77.7 (minor), 72.5 (major), and 65.8 (minor) in the cluster region, indicating that there are three species in solution having the anionic species **3**. The peaks at δ 77.7 and 72.5 indicate the presence of two hexameric clusters, while the minor peak at δ 65.8 is due to a trimeric species, suggesting that the formation of the hexameric cluster proceeds via a trimeric species similar to **5** (Figure S1, Supporting Information). The ^1H-DOSY measurements of the reaction mixture of **3**-H_3 and **4** in CD_3OD after 15 h at the acetate region show the presence of at least two major species in solution (Figure S2, Supporting Information). The first one, at a diffusion rate of log D = −8.98, shows the presence of an all acetate species (mostly **7**), and the second one, at log D = −9.33, corresponds to **7a** (similar to **4a** which gives more than one OAc peak in ^1H-DOSY).[12] On the other hand, the reaction mixture of **1**-H_3 and **4** and that of **2**-H_3 and **4** in methanol after 12 h show a single peak in the ^{31}P NMR spectra in the cluster region, indicating the formation of only **5** and **6** in their respective reactions. The absence of the mixed-bridged species in these reactions might be due to (a) the faster reactivity of **4** with the ligands **1**-H_3 and **2**-H_3 and (b) the stronger steric hindrance exhibited by the bulky ^{c}Hex and ^{t}Bu substituents for smaller bridging (methoxy or hydroxy) groups. The ^{31}P NMR spectra of all the isolated compounds gave a single peak in the range between δ 78.9 and 69.0 (Figure S3, Supporting Information). Further, the structure of all these clusters in solution has been confirmed by ESI(+) or MALDI-TOF mass spectra showing the isotopic distribution of peaks centered at the values corresponding to their $[M^+]$ or $[M + Na]^+$ ions along with other prominent fragment ion peaks (Figures S4−S12, Supporting Information).

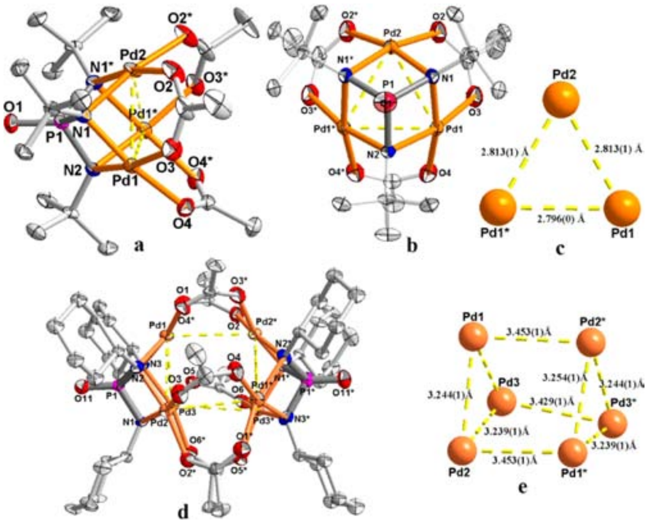


Figure 1. Molecular structure (a and b) and the triangular view of the Pd(II) atoms (c) in **5**. Molecular structure (d) and the prismatic assembly of the Pd(II) atoms (e) in **6**.

Crystal Structures. The trinuclear species **5** crystallized in the orthorhombic space group *Cmc*2(1) (Table S2, Supporting Information). The molecular core consists of one fully deprotonated ligand **1**, three Pd(II) atoms, and three charge-balancing acetate ions (Figure 1a,b). The imido ligand is hexadentate and is involved in bridging the three equilaterally arranged Pd(II) atoms in a chelating fashion. Each Pd(II) atom is located at a square planar coordination of two N-sites from **1** and two O-sites from the three bridging acetate units. It is interesting to compare the structure of **5** with the solid-state structure of the precursor $Pd(OAc)_2$.[13] In the solid state, $Pd(OAc)_2$ exists in the form of a trimer as $Pd_3(OAc)_6$ (**4**) with a central triangular Pd_3 unit sandwiched between three bridging carboxylate units on either side of it. In contrast, the molecular structure of **5** consists of three chelating N-sites of the trianionic ligand **1** on one side of the Pd_3 plane. The three acetate units on the other side of it remained intact and help to restore the charge balance in the molecule. Each imido nitrogen is bonded to two Pd(II) atoms at almost equal distances ranging from 2.052(3) to 2.061(3) Å, indicating the trianionic charge is equally delocalized on the three N-sites. Similarly, the Pd−O distances (av 2.053(3) Å) found in **5** are almost equal, pointing to the delocalized nature of the carboxylate charges. The molecules **6** and **7** are iso-structural and crystallized as **6**.H_2O and **7**.2H_2O, respectively. The molecular structure of **6**.H_2O was solved in the orthorhombic space group C222(1) with one-half of the molecule in the asymmetric unit (Figure 1d). The crystal structure of **7**.2H_2O was obtained in the monoclinic space group *C*2/*c* featuring the complete molecule in its asymmetric unit (Figure S14, Supporting Information). The molecular cores in **6**.H_2O and **7**.2H_2O consist of a hexameric Pd_6 cluster in a prismatic geometry sandwiched between two tris(imido)phosphate ligands (**2** or **3**). The prismatic Pd_6 cluster can be viewed as a pair of planar Pd_3 subunits (of the type found in **5** as well as in **4**) that are stacked upon each other in a nearly eclipsed manner. Each imidophosphate ligand acts as a hexadentate cisoidal ligand and is bonded in a chelating fashion to the triangular Pd_3 unit. These individual Pd_3 units are further connected by six carboxylate ligands (Harris notation: 2.1.1)[14] completing the hexameric structure. A closer look at these structures reveals that these six carboxylate ligands are interacting in *a set of two* and connect a pair of Pd(II) atoms from the adjacent triangular units. Thus, these prismatic Pd_6 cluster assemblies contain three such Pd_2 pairs, and each of them is held together by two bridging carboxylate ligands.

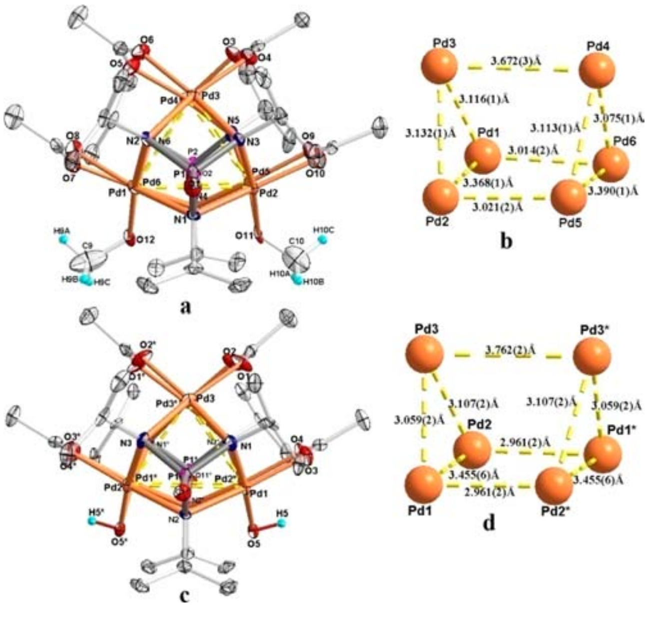


Figure 2. Molecular structures of **7a** (a) and **7b** (c) showing their two Pd_3 subunits stacked upon each other in an eclipsed manner. Prismatic view of the Pd(II) atoms in **7a** (b) and **7b** (d).

The mixed-bridged cluster **7a** crystallized in the monoclinic space group *P*2(1)/*c* featuring the whole molecule in the asymmetric unit. The molecule **7b**.2DMSO crystallized in the monoclinic space group *C*2/*c* and contains one-half of the molecule and one solvated DMSO molecule in the asymmetric unit. The core structures of **7a** and **7b** resemble closely that of **7** and contain two μ^2-bridging methoxy and hydroxy groups, respectively, in place of two of the six acetate groups (Figure 2a,c). Two of the three Pd_2 pairs present in the prismatic cluster of **7a** and **7b** possess the mixed-bridged environment with one acetate moiety and one methoxy/hydroxy unit each, while the third pair contains only acetate bridges (Figure S15, Supporting Information). The two hydroxyl groups present in **7b** are hydrogen-bonded to two solvated disordered molecules of DMSO (Figure S16, Supporting Information). The Pd−N and Pd−O distances found in **6**.H_2O, **7**.2H_2O, **7a**, and **7b**.2DMSO are similar and comparable to those found in **5** (Table S2, Supporting Information).

It is interesting to compare the Pd−Pd distances found in these trimeric and hexameric assemblies. The two unique Pd−Pd distances of 2.796(0) and 2.813(1) Å, found in the trimeric assembly of **5** (Figure 1c), are considerably shorter than those found in the crystal structures of $Pd_3(OAc)_6$ (**4**, av 3.151(13) Å).[13] But in the hexameric assemblies of **6**, **7**, **7a**, and **7b**, the Pd−Pd distances found within the triangular segment are slightly longer than those found in **4** owing to the open bridging coordination of the acetate groups between the two Pd_3 subunits. A further look at the interplanar Pd−Pd distances found along the three rims of the prismatic assemblies reveals large deviations for the mixed-bridged clusters **7a** and **7b** in comparison with the all acetate-bridged clusters **6** and **7**. Thus, in **7a** and **7b**, two of the three rim distances are relatively much shorter (**7a**, 3.018(2) Å (average); **7b**, 2.961(2) Å) than the third (**7a**, 3.672(3) Å; **7b**, 3.762(2) Å), as the shorter ones are found at the Pd_2 pairs containing mixed (OAc and OR′) bridging groups (Figure 2b,d). All three interplanar Pd−Pd distances found in **6** (av 3.445(1) Å) and **7** (av 3.439(1) Å) are very similar to each other (Figure 1e and Figure S14). As a consequence, the mean plane deviation between the two triangular Pd_3 subunits in **7a** and **7b** is larger at 14 and 15°, respectively, while those found in **6** and **7** deviated minimally by an angle of 1°.

A Cambridge Structural Database (CSD) search on the structures of palladium-containing hexameric complexes indicates that the prismatic clusters observed in our reactions are rather unprecedented. Although a handful of octahedral structures are reported,[15] there are very few examples known for the prismatic arrangement of the six Pd(II) ions.[16] Hence, we presume that the key requirements for obtaining such prismatic Pd(II) clusters are the intact Pd_3 unit in its local structure and ligand sets which minimize the steric crowding between the two Pd_3 subunits in the eclipsed conformation. Even though crystalline $Pd(OAc)_2$ exists in the form of a discrete trimeric Pd_3 unit, most ligand displacement reactions tend to destroy this arrangement. In this regard, the tripodal nature of the ligand moieties in **2** and **3** proves to be compatible, sterically and electronically, with providing a structurally rigid triangular motif by tethering the Pd_3 unit together from one side of it. In addition, the acetate groups are well-suited at the bridging positions as the steric requirements for the two terminal imido-phosphate substituents are minimal in the prismatic arrangement.

Reactivity Studies of 5, 6, and 7. In order to test the robustness of tripodally chelated $(Pd{-}N_{imido})_3$ moieties in **5**, **6**, and **7**, we studied the reactivity of these complexes in the presence of a primary amine which acts as a nucleophilic reagent to the Pd(II) ions. Thus, the reaction of **5**, **6**, and **7** with stoichiometric equivalents of cyclohexylamine in MeOH proceeds spontaneously as observed by a visual color change in solution (from orange to yellow) from which yellow-colored crystalline solids of **8**, **9**, and **10**, respectively, were obtained (Figure 3). Single-crystal X-ray analysis of the crystals of **9** and **10** indicates the presence of a new trinuclear species of the formula $\{Pd_3[(NR)_3PO](OAc)_3(^{c}HexNH_2)_3\}$ (**9**, R = ^{c}Hex; **10**, R = ^{i}Pr), while a similar structure for **8** (R = ^{t}Bu) was confirmed by a combined ^{31}P NMR and mass spectral analysis. These new trinuclear assemblies were obtained via a nucleophilic attack on the Pd(II) ions by the amino groups, and in fact, **9** and **10** were obtained from a symmetrical cleavage of the hexanuclear assemblies in **6** and **7**, respectively. Although such an amine-triggered cleavage of a dinuclear Pd(II) species to a mononuclear complex has been observed previously,[17] formation of **8**, **9**, and **10** in the present instance is attributed to the rigid tripodal chelation of the imido-phosphate which provides the necessary stability to the Pd_3 units. In addition, formation of **9**/**10** has been observed in a direct reaction involving **2**-H_3/**3**-H_3, $Pd(OAc)_2$, and cyclohexylamine. The preferential deprotonation of **2**-H_3/**3**-H_3 over cyclohexylamine confirms that the trianionic species **2**/**3** provides a vital stability to keep triangular Pd_3 motifs intact. The ^{31}P NMR spectra of the compounds **8** (δ 72.05), **9** (δ 73.50), and **10** (δ 73.67) in CD_3OD gave a single peak in the cluster region. Furthermore, from the mass spectral data, their existence in solution has been confirmed. The single-crystal X-ray analysis of **9** and **10** reveals that these clusters are iso-structural in the solid state. The asymmetric unit of **9**.$2H_2O$ contains one-third of the molecule as it was crystallized in the trigonal space group *P*3-*c*1 (Figure S17, Supporting Information). The molecular structure of **10** was solved in the monoclinic space group *P*2(1)/*n*, in which the asymmetric unit contains the whole molecule (Figure 3, right). As observed before, one side of the Pd_3 plane in **9** and **10** was found with the tripodally chelating imido ligand, while the other side of it contains three hanging cyclohexyl amines and three acetate moieties. In addition, the H-bonding interactions between the acetate anions and the amino protons result in the formation of a two-dimensional hexagonal network for **9** and a one-dimensional zigzag chain for **10** (Figures S17 and S18 and Table S3, Supporting Information).

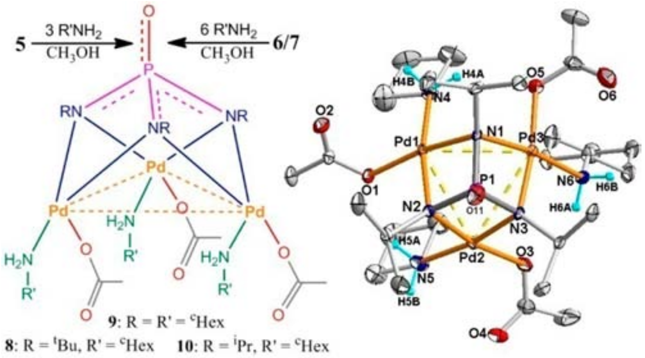
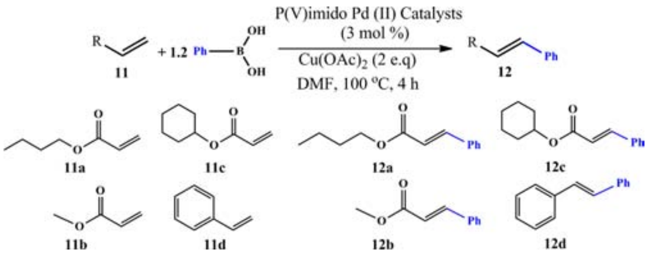


Figure 3. Syntheses of the new trinuclear clusters **8**, **9**, and **10** (left); molecular structure of the trinuclear cluster **10** (right).

Application in Catalytic Reactions. Inspired by their rigid $Pd{-}N_{imido}$ tripodal motifs, we were curious to see whether the Pd(II) atoms in these clusters are still active for catalytic reactions. As these imido motifs are strongly bound to the Pd(II) atoms, we thought a catalytic reaction that utilizes the Pd(II) ions as an active catalyst would be more suitable to examine (Figure S20, Supporting Information). Hence, we employed these complexes in the Mizoroki−Heck type reactions in which the Pd(II) species catalyzes the coupling reaction of phenylboronic acid with alkenes.[18,19]

Thus, the treatment of phenylboronic acid (1.2 equiv) with *n*-butyl acrylate (**11a**) in the presence of the trinuclear complex **5** (3 mol %) and $Cu(OAc)_2$ (2 equiv) in DMF at 100 °C for 4 h leads to the corresponding phenylated trans-alkene derivative (**12a**) in 90% isolated yield (Scheme 2). The reaction was also tested with the hexameric complexes **6** and **7a** under the same conditions which gave the alkene product **12a** in 90 and 95% yields, respectively. Similarly, we have tried the coupling reaction with a few more alkenes, such as methyl acrylate

Scheme 2. M−H Type Reaction of $PhB(OH)_2$ with Various Alkenes



(**11b**), c-hexyl acrylate (**11c**), and styrene (**11d**), in the presence of all three cluster motifs. Noticeably, **7a** acts as a better catalyst for all these substrates, yielding the coupled products **12b**−**d** in 90, 95, and 98% yields, respectively (Table 1). As observed before,[18c] the catalytic reaction presumably proceeds via the trans-metalation of the phenylboronic acid with Pd(II) complexes followed by insertion of the alkene substrate that subsequently undergoes β-hydride elimination in the presence of $Cu(OAc)_2$, which acts both as an acetate source and as an oxidant in the catalytic cycle.

■ CONCLUSIONS

In conclusion, we have shown that $Pd(OAc)_2$ provides a facile deprotonation route to access the highly basic tris(alkylimido) phosphate trianions, $[(RN)_3PO]^{3-}$, in polar and in protic solvents. Tri- or hexanuclear Pd(II) clusters of these trianions were isolated exclusively in all these reactions in which the trianionic species acts as a tripodal chelating ligand to the trinuclear Pd_3 unit. Reactivity studies on these clusters with primary amines have led to a symmetric cleavage of the prismatic assemblies in which the tripodally chelated $(Pd-N_{imido})_3$ moieties remained unaffected. The robustness of the Pd_3 unit in all these clusters is expected to offer a stable platform for catalytic reactions in which the trianionic ligand would act as a perfect spectator ligand, and the substrate will approach the Pd(II) ion from the side that is trans to the $Pd-N_{imido}$ sites. Also, the crystalline nature of these imido-Pd_3 motifs is an added advantage as it can assist in isolating various organic-intermediate species and thus would provide useful inputs for understanding reaction mechanisms. We have also demonstrated the catalytic activity of these complexes in M−H type coupling reactions, which proves that these clusters are worthy candidates for catalytic applications.

■ ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data for **3**-H_3, **5**, **6**.H_2O, **7**.$2H_2O$, **7a**, **7b**.2DMSO, **9**.$2H_2O$, and **10** in CIF format. NMR and mass spectra for all the compounds, additional figures, tables of bond lengths and angles, and H-bonding data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Prof. K. N. Ganesh on the occasion of his 60th birthday.

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