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Synthesis and Structural Diversity of Mono-, Di- and Trinuclear Complexes with *N*,*N*′-Bis[(2-diphenylphosphanyl)phenyl]formamidine

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The synthesis, characterization, and coordination chemistry of a series of mono-, di-, and trinuclear homo-/heterometallic complexes with the dinucleating ligand, *N*,*N*′-bis[(2-diphenyl-phosphanyl)phenyl]formamidine (pnnp)[1] are reported. Treatment of (pnnp)PdMe (**1**) with $NiCl_2$(dme) forms the heterobimetallic (pnnp)PdMe(μ-Cl)NiCl (**3**) complex, whereas reaction of **1** with $Cu(CH_3CN)_4^+PF_6^-$ yields the Pd···Cu···Pd heterometallic trinuclear complex (pnnp)Pd(Me)CuPd(Me)(pnnp)·PF_6 (**8**). The reaction of pnnp with $NiCl_2$(dme) (dme = 1,2-dimethoxyethane) produces the Ni dimer $[(pnnp)NiCl(\mu\text{-}Cl)]_2$ (**5**) or the dinuclear (pnnp)NiCl(μ-X)NiCl (X = Cl or OH) (**4**) complexes, depending upon the stoichiometry. The reaction of pnnp with Co^{II} or Fe^{II} ions leads to the monometallic complexes (pnnp)$CoCl_2$ (**6**) or (pnnp)$FeCl_2$ (**7**), respectively. The dinuclear (pnnp)PdMe(μ-Cl)NiCl (**3**) and (pnnp)NiCl(μ-X)NiCl (X = Cl or OH) (**4**) complexes adopt A-frame structures with two square-planar d^8 metal complexes hinged by the bridging ligand; the angles between the square planes correlate to the covalent radii, in which the smaller homo-bimetallic Ni complex adopts a more coplanar arrangement of the two Ni square planes. The heterometallic trinuclear complex (pnnp)Pd(Me)CuPd(Me)(pnnp)·PF_6 (**8**) adopts an unusual structure around the Cu center, suggestive of a weak d^8–d^{10} interaction between the Pd and Cu atoms. All complexes have been characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, and their structural diversity is discussed.

Introduction

The placement of two metal centers in close proximity by an appropriate ligand can allow for cooperative effects, both improving their efficiency and selectivity in catalysis and promoting reactions that are not possible using a single metal center.[1–2] A variety of bridging ligands, such as bis(diphenylphosphanyl)methane, (diphenylphosphanyl)-pyridine, and various P_2N_2-type ligands have been developed extensively over the past decades.[3,4] In an effort to design novel bimetallic complexes, we recently explored a class of dinucleating N-heterocyclic carbene ligands spanned by pyrazoles (CNNC) and reported corresponding bimetallic complexes.[5] As an extension of these efforts, our attention was drawn to the *N*,*N*′-bis[(2-diphenylphosphanyl)phenyl]formamidine (pnnp) ligand recently disclosed by Tsukada for dinuclear Pt_2, Pd_2, and PtPd complexes.[1] Tsukada has investigated these complexes for a variety of organic transformations including arylation of alkynes and alkyne/alkene coupling reactions.[2m,6] An appealing feature of this ligand is the ability to introduce metal complexes in a stepwise fashion, enabling the synthesis of heterometallic multinuclear complexes. As a part of our ongoing investigation into potential bimetallic olefin polymerization catalysts,[2f,2j,2k] we have expanded the coordination chemistry of this ligand to a family of various metal complexes of Pd, Ni, Fe, Co, and Cu. Herein, we report the synthesis, characterization and crystal structures of homo-/heterometallic mono-, di-, and trinuclear complexes and describe the versatility of the pnnp ligand featuring various coordination modes for the transition metals.

Results and Discussion

Treatment of the pnnp ligand with one equivalent of (tmeda)$PdMe_2$ (tmeda = tetramethylethyldiamine), as shown by Tsukuda, generates a stable square-planar (pnnp) PdMe complex **1**, a useful synthon for generating dinuclear (pnnp)$PdXMY_2$ complexes using a step-by-step reaction protocol.[1] Addition of THF to a 1:1 mixture of (pnnp) PdMe (**1**) and $NiCl_2$(dme) (dme = 1,2-dimethoxyethane) yielded the dark purple mixed-metal PdNi compound (**3**) (Scheme 1). Complex **3** was isolated as a purple solid in 98% yield. This bimetallic complex crystallized as prismatic crystals by vapor diffusion of pentane into a dichloromethane solution. The molecular structure is shown in Figure 1. The Pd ion is coordinated in a square-planar fashion by a P and a N atom of the chelating ligand, a methyl group, and a Cl atom that bridges to the nickel

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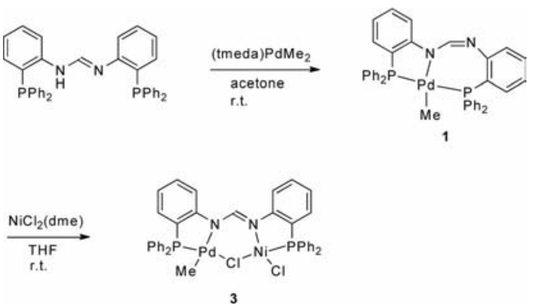
center. The methyl group is located *trans* to the N atom; the coordinating P and N atoms are necessarily in a *cis*-geometry. The Ni atom is also coordinated in a square-planar geometry by the other N and P atoms of the ligand and two Cl atoms, one of which forms the bridge (see Figure 1). The $\tau 4$ values {a measure of the coordination about a four-coordinate atom, given by $\tau 4 = [360 - (\beta + \alpha)]/141$}[7] for the Pd and the Ni ions are 0.026 and 0.116, respectively, indicating square planar geometries. As observed for the Pd_2 complex,[1] the solid structure of the PdNi complex **3** features an A-frame structure with the bridging Cl at the apex, where the angles of the two square planes are almost perpendicular to one another [angle formed by the mean planes is 89.07(10)°, see Table 1]. Whereas the Pd and the Ni ions are in close proximity, the Pd···Ni distance 2.9655(10) Å lies outside the sum of the covalent radii for these elements (approx. 2.63 Å).[8] Therefore, any direct interaction between the Pd and Ni centers is likely weak.



Scheme 1. Synthesis of heterodinuclear complex **3**.

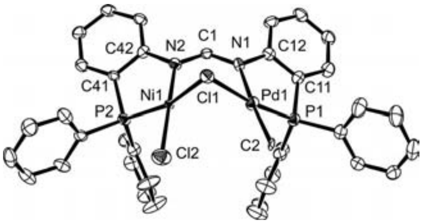
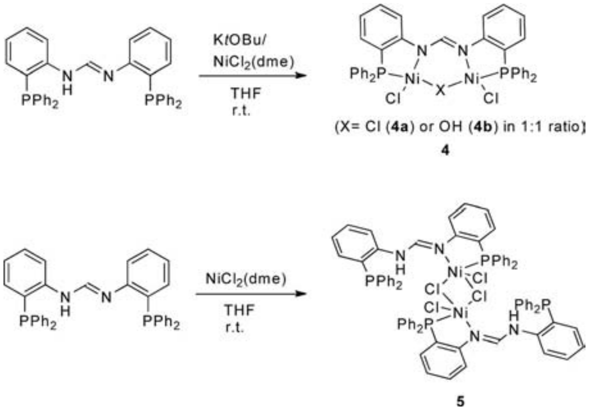


Figure 1. Molecular structure of **3** represented by thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; see Table 1.

To investigate the influence of the metal radii on the coordination geometry of these ligands, we prepared the corresponding Ni complexes **4** and **5** (Scheme 2). The addition of a THF solution of a 1:1 mixture of the pnnp ligand and KO*t*Bu to two equivalents of $NiCl_2$(dme) yielded the dinuclear NiNi complex (**4**), which crystallized as red plate-like crystals by vapor diffusion of diethyl ether into a dichloromethane solution. The ^1H NMR spectrum of **4** was consistent with a symmetrical dinuclear Ni complex, however, the micro-analytical data and X-ray analysis revealed that **4** was comprised of a 1:1 mixture of the bridging chloride **4a** and the bridging hydroxide **4b**. As the hydroxide-containing complex co-crystallizes with that of the chloride, we were unable to separate the two. We have not yet definitively assigned the source of hydroxide in the formation of **4**, but adventitious water in the KO*t*Bu is a likely source. Efforts to reproduce the synthesis of **4** yielded a similar mixture of **4a** and **4b**. The Ni centers are each coordinated in a square-planar geometry by a P and a N atom of the ligand. Completing the coordination sphere is a terminal Cl and a bridg-



Scheme 2. Synthesis of dinickel complexes **4** and **5**.

Table 1. Selected bond lengths [Å] and bond angles [°] for dinuclear complexes **2**–**4**.

2a[1] (PdPd)		**3** (PdNi)		**4** (NiNi)	
Pd(1)–N(1)	2.04(1)	Pd(1)–N(1)	2.122(5)	Ni(1)–N(1)	1.921(3)
Pd(1)–P(1)	2.200(4)	Pd(1)–P(1)	2.1750(18)	Ni(1)–P(1)	2.1217(11)
Pd(1)–Cl(1)	2.405(4)	Pd(1)–Cl(1)	2.3928(18)	Ni(1)–Cl(3)	2.142(3)
Pd(1)–Cl(2)	2.285(5)	Pd(1)–C(2)	2.055(6)	Ni(1)–Cl(1)	2.1647(13)
Pd(2)–N(2)	2.05(1)	Ni(1)–N(2)	1.977(5)	Ni(2)–N(2)	1.911(3)
Pd(2)–P(2)	2.189(4)	Ni(1)–P(2)	2.1318(18)	Ni(2)–P(2)	2.1348(12)
Pd(2)–Cl(1)	2.398(4)	Ni(1)–Cl(1)	2.3077(17)	Ni(2)–Cl(3)	2.102(3)
				Ni(1)–O(1)	1.859(9)
				Ni(2)–O(1)	1.874(9)
Pd(2)–Cl(3)	2.276(5)	Ni(1)–Cl(2)	2.133(2)	Ni(2)–Cl(2)	2.1643(14)
N(1)–C(1)	1.32(2)	N(1)–C(1)	1.312(8)	N(1)–C(1)	1.328(5)
N(2)–C(1)	1.31(2)	N(2)–C(1)	1.327(8)	N(2)–C(1)	1.327(5)
Pd(1)···Pd(2)	3.24	Pd(1)···Ni(1)	2.9655(10)		
Pd(1)–Cl(1)–Pd(2)	84.8(1)	Pd(1)–Cl(1)–Ni(1)	78.21(6)	Ni(1)–Cl(3)–Ni(2)	116.0
N(1)–C(1)–N(2)	130(1)	N(1)–C(1)–N(2)	124.6(6)	N(1)–C(1)–N(2)	130.6
				Ni(1)–O(1)–Ni(2)	147.5
Angles formed by two square planes					
	78.67		89.07(10)		22.88(10)

ing Cl **4a** or OH **4b** (Figure 2). The Ni–O and Ni–Cl bond lengths are in the expected ranges for such bonds (see Table 1). Interestingly, the angle formed by the two Ni-containing square planes, 22.88(10)°, is considerably less than those of the analogous Pd homodimer **2a** (78.67°) and PdNi heterodimer **3** (89.07°) (see Table 1). This more planar arrangement is presumably due to the smaller covalent radii of the Ni ion relative to Pd,[1] reflecting that small variation within these complexes can lead to large structural differences in the solid state.

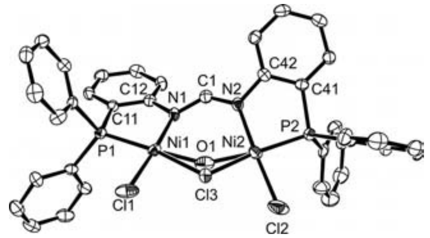


Figure 2. Molecular structure of **4** represented by thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; see Table 1.

On the other hand, the bridging chloride dimer **5** was generated as a dark yellow solid in 94% yield by addition of a THF solution of $NiCl_2$(dme) to an equimolar amount of the pnnp ligand. The complex crystallized as yellow, prismatic crystals from a dichloromethane/hexane solution. The dimeric nature of **5** in the solid state was established by X-ray crystallography, revealing that the asymmetric unit consists of one Ni center coordinated by one P and one N (imide) atom of the ligand and two Cl atoms (Figure 3). Expansion of the asymmetric unit through the inversion center at [0, 0, 0] shows that the Ni ion is coordinated in a distorted square-pyramidal fashion by two bridging Cl atoms, one non-bridging Cl as well as N and P atoms. The P atom occupies the apical position of the square pyramid. The $\tau5$ value for the Ni center is 0.47 [given by $\tau5 = (\beta - \alpha)/60$], indicating that the geometry is intermediate between full square pyramidal ($\tau5 = 0$) and trigonal bipyramidal ($\tau5 = 1$).[9] The bridging chlorine Cl(1), has a slightly asymmetric bonding to the Ni centers, as reflected by the two Ni–Cl distances [2.3258(6) and 2.4524(7) Å]. The disposition of the uncoordinated amidine nitrogen N(2) and the N(2)···Cl(2) distance of 2.38(2) Å are suggestive of an intramolecular H-bond from N(2)–H to the non-bridging chlorine Cl(2).

Pd and Cu complexes exhibit a rich chemistry in a variety of oxidation reactions,[2e,10] and weak "metallophilic bonds" (d^8–d^{10} bonds) have been observed between the Pt group and the coinage metals.[11] To investigate the coordination chemistry of bimetallic PdCu complexes, an equimolar mixture of (pnnp)PdMe (**1**) and $Cu(NCCH_3)_4^+$ PF_6^- was dissolved in acetonitrile (Scheme 3). Crystallization of the resulting yellow complex from dichloromethane/diethyl ether yielded block-like crystals of the mixed-metal trinuclear complex **8**, instead of the expected heterometallic dinuclear complex. Selected bond lengths and angles for **8** can be found in Table 2. The coordination geometry of **8** around the Cu ion (Figure 4) features an unusual butterfly structure in which the two approximately square planar Pd centers are hinged by a Cu^I ion coordinated in a linear N–Cu–N arrangement from the amidine nitrogen atoms derived from two pnnp ligands. The Pd centers are ligated by two *trans*-phosphane moities derived from two pnnp ligands, an amidine nitrogen, and a terminal methyl group, but are distorted from a square-planar geometry, as evidenced by the P(1)–Pd(1)–P(3) and P(2)–Pd(2)–P(4) angles of 152.98(4)° and 153.79(4)°, respectively [the $\tau4$ values for the Pd(1) and Pd(2) square planes are 0.29 and 0.26, respectively]. This distortion may be a consequence of a weak

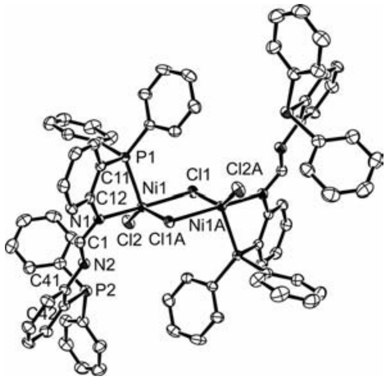
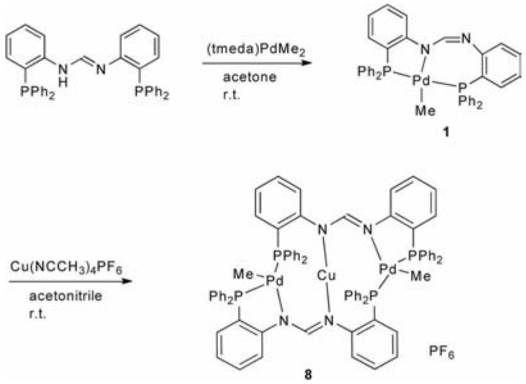


Figure 3. Molecular structure of **5** represented by thermal ellipsoids at 50% probability. Hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni(1)–N(1), 2.1161(16); Ni(1)–Cl(1), 2.4524(7); Ni(1)–Cl(2), 2.2450(7); Ni(1)–P(1), 2.2893(6); Ni(1)–Cl(1A), 2.3258(6); N(1)–C(1), 1.299(2); N(2)–C(1), 1.340(2); Ni(1)–Cl(1)–Ni(1A), 95.641(18); Cl(1)–Ni(1)–Cl(1A), 84.359(18); N(1)–C(1)–N(2), 125.59(17).



Scheme 3. Synthesis of mixed-metal trinuclear complex **8**.

Table 2. Selected bond lengths [Å] and bond angles [°] for **8**.

Pd(1)···Cu(1)	2.8291(5)	Pd(2)···Cu(1)	2.8016(5)
Pd(1)–C(3)	2.075(4)	Pd(2)–C(4)	2.068(4)
Pd(1)–N(1)	2.180(3)	Pd(2)–N(4)	2.156(3)
Pd(1)–P(1)	2.2372(10)	Pd(2)–P(2)	2.3405(10)
Pd(1)–P(3)	2.3683(10)	Pd(2)–P(4)	2.2641(10)
Cu(1)–N(2)	1.880(3)	Cu(1)–N(3)	1.868(3)
P(1)–Pd(1)–P(3)	152.98(4)	P(2)–Pd(2)–P(4)	153.79(4)
Pd(2)–Cu(1)–Pd(1)	111.832(18)	N(3)–Cu(1)–N(2)	179.07(14)

d^8–d^{10} interaction between the Pd and Cu centers. The Cu···Pd(1,2) distances of 2.8291(5) and 2.8016(5) Å, respectively, fall outside the sum of the covalent radii (approx. 2.71 Å)[8] but are comparable to the bond lengths observed for heterodinuclear Pt^{II}···Cu^{I} [distance: 2.7368(4) Å], and Pd^{II}···Au^{I} [distance: 2.954(1) Å] complexes of $[M'M''(\mu\text{-dcpm})_2(CN)_2]^+$ {dcpm = bis(dicyclohexylphosphanyl)methane}, for which a d^8–d^{10} interaction was proposed.[12]

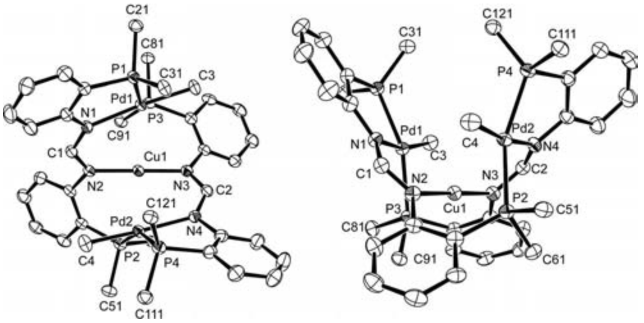
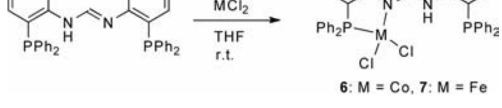


Figure 4. Molecular structure of **8** represented by thermal ellipsoids at 50% probability. Hydrogen atoms, counterions, solvent molecules, and phenyl groups attached to carbons 21, 31, 51, 61, 81, 91, 111, and 121 have been omitted for clarity. Selected bond lengths [Å] and angles [°]; see Table 2.

Further exploration into the coordination chemistry outside of Group 10 was also carried out with Co- and Fe-containing complexes. The monometallic cobalt compound (**6**) was prepared by reacting an equimolar quantity of pnnp with $CoCl_2$ in THF (Scheme 4). The product was obtained as a green solid in 89% isolated yield. The Co complex crystallizes as turquoise rod-like crystals from a dichloromethane/diethyl ether solution. The Co ion is coordinated in a distorted tetrahedral fashion by two Cl atoms, and one N and one P atom of the ligand (Figure 5). The $\tau 4$ value for this complex is 0.86.[9] The non-coordinating N atom is protonated and forms an intramolecular H-bond to one of the Cl atoms [N(2)···Cl(2) distance: 3.241(2) Å, see Table 3]. The second P atom of the ligand does not have any interactions with nearby atoms or molecules. It is also possible to synthesize the iron analogue of **6**; complex **7** was prepared by reacting an equimolar quantity of pnnp with $FeCl_2$ in THF (Scheme 4). The product was obtained as a yellow solid in 87% yield and single crystals of the Fe complex suitable for X-ray studies were obtained as colorless columnar crystals from a dichloromethane/diethyl ether solution. The iron is coordinated in a distorted tetrahedral fashion by one N and one P atom of the ligand and two Cl atoms (Figure 6) with the $\tau 4$ value of 0.82.[9] The bond lengths about the Fe center reflect its distorted nature (see Table 3).



Scheme 4. Synthesis of mononuclear complexes **6** and **7**.

The hydrogen on the amide nitrogen N(2) forms an intramolecular H-bond to one of the Cl atoms [N(2)···Cl(1) distance: 3.2676(19) Å, see Table 3].

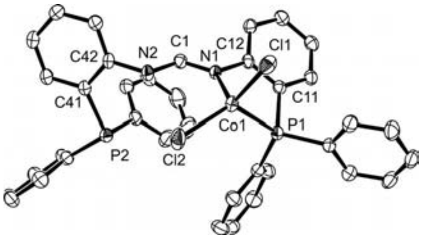


Figure 5. Molecular structure of **6** represented by thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; see Table 3.

Table 3. Selected bond lengths [Å] and bond angles [°] for complexes **6** and **7**.

6		7	
Co(1)–N(1)	2.029(2)	Fe(1)–N(1)	2.1046(17)
Co(1)–P(1)	2.3587(7)	Fe(1)–P(1)	2.4189(7)
Co(1)–Cl(1)	2.2232(7)	Fe(1)–Cl(1)	2.2357(7)
Co(1)–Cl(2)	2.2262(7)	Fe(1)–Cl(2)	2.2345(8)
N(1)–C(1)	1.306(3)	N(1)–C(1)	1.302(2)
N(2)–C(1)	1.333(3)	N(2)–C(1)	1.334(3)
N(2)···Cl(2)	3.241(2)	N(2)···Cl(1)	3.2676(19)
Cl(1)–Co(1)–Cl(2)	115.00(3)	Cl(1)–Fe(1)–Cl(2)	121.30(3)
N(1)–C(1)–N(2)	121.4(2)	N(1)–C(1)–N(2)	121.54(18)

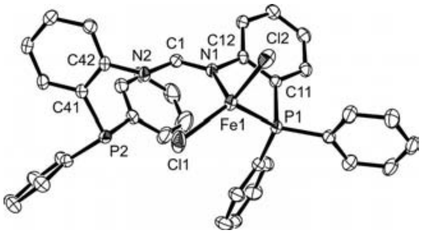
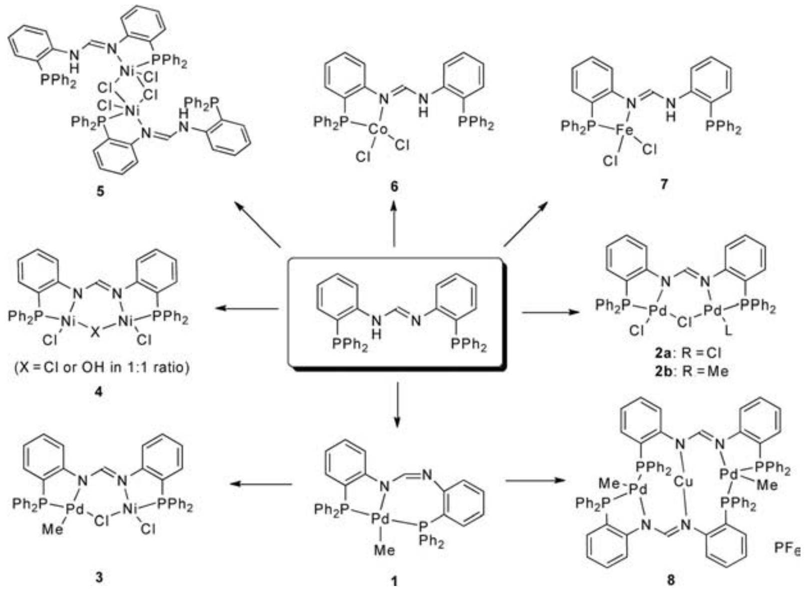


Figure 6. Molecular structure of **7** represented by thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; see Table 3.

Conclusion

A series of homo-/heterometallic mono-, di-, and trinuclear complexes involving mid and late metals supported by the pnnp ligand was prepared as summarized in Scheme 5. The ability of this ligand to stabilize mononuclear metal species enables the facile synthesis of multinuclear structures by the stepwise introduction of different metal precursors. The heterometallic dinuclear PdNi complex adopts A-frame structures, whereas the homo-dinuclear Ni complex exhibits a more coplanar arrangement of the two Ni-containing square planes, reflecting the influence of the covalent radii of metal centers. The mixed-metal trinuclear complex **8** adopts the rare coordination geometry of the butterfly structure around Cu, probably as a consequence of a weak d^8–d^{10} interaction between the Pd and Cu ions. All the complexes have been characterized by NMR spec-



Scheme 5. Versatility of the pnnp ligand to chelate with various transition metals.

troscopy, elemental analysis, and X-ray crystallography. Reactivity investigations on multinuclear complexes are now underway.

Experimental Section

General: Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques or in an inert atmosphere glove box. Solvents were purchased from Sigma–Aldrich or Fisher Chemical and dried before use. All metal precursors were purchased from Strem Chemicals and used as received. CD_2Cl_2 was purchased from Cambridge Isotopes. CH_2Cl_2 was dried with CaH_2, vacuum transferred, and stored under a nitrogen atmosphere. THF was dried with sodium/benzophenone, vacuum transferred, and stored under a nitrogen atmosphere. *N*,*N′*-Bis[(2-diphenylphosphanyl)phenyl]formamidine (pnnp) and **1** were prepared as previously reported.[1] All NMR spectra were acquired on Inova 500 MHz or 600 MHz spectrometers. ^{1}H NMR spectra are referenced to the residual solvent peak. ^{31}P NMR spectra are referenced to phosphoric acid in D_2O.

(pnnp)PdMe(μ-Cl)NiCl (3): A mixture of (pnnp)PdMe (**1**, 37 mg, 0.0546 mmol) and $NiCl_2$(dme) (12 mg, 0.0546 mmol) was dissolved in THF (4 mL) and stirred for 15 min. A rapid color change from yellow to dark purple was observed. The reaction mixture was dried in vacuo to give a dark purple powder of **3** (yield 44 mg, 98%). ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): δ = 1.49 (s, 3 H, Pd CH_3), 6.29 (d, J = 7.5 Hz, 1 H, Ph), 6.66 (t, J = 7.5 Hz, 2 H, Ph), 7.03 (t, J = 7.5 Hz, 1 H, Ph), 7.22 (t, J = 7.5 Hz, 1 H, Ph), 7.27 (m, 1 H, Ph), 7.35–7.59 (m, 13 H, Ph), 7.78 (d, J = 7.5 Hz, 1 H, amidine CH), 7.97–8.07 (m, 9 H, Ph) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, CD_2Cl_2): δ = 25.7, 40.0 ppm. (pnnp)PdMe(μ-Cl)NiCl·$0.25CH_2Cl_2$: calcd. C 54.96, H 3.92, N 3.35; found C 55.11, H 4.15, N 3.14.

(pnnp)NiCl(μ-X)NiCl (X = Cl or OH in 1:1 ratio) (4): THF (8 mL) was added to a vial containing KO*t*Bu (33.7 mg, 0.3 mmol) and the pnnp ligand (169 mg, 0.3 mmol) and stirred. A color change from white to pale yellow was observed immediately. After 10 min, the pale yellow solution was added to $NiCl_2$(dme) (132 mg, 0.6 mmol). The reaction mixture was stirred for 15 min until no more solids were observed. The solvent was removed in vacuo, the residual solids were dissolved in CH_2Cl_2, filtered through celite, and the filtrate was dried in vacuo to give a deep wine-colored powder (yield 216 mg, 92%). ^{1}H NMR (600 MHz, –20 °C, CD_2Cl_2): δ = 6.87–7.98 (m, 29 H, Ph and amidine CH). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, CD_2Cl_2): δ = 26.4. As discussed in the X-ray crystal structure analysis section, this compound was found to be a 50:50 mixture of (pnnp)NiCl(μ-Cl)NiCl and (pnnp)NiCl(μ-OH)NiCl by the elemental analysis. a 50:50 mixture of (pnnp)NiCl(μ-Cl)NiCl and (pnnp)NiCl(μ-OH)NiCl: calcd. C 57.11, H 3.82, N 3.60; found C 57.11, H 3.82, N 3.60.

[(pnnp)NiCl(μ-Cl)]$_2$ (5): A THF (5 mL) solution of the pnnp ligand (56.5 mg, 0.1 mmol) was added to a THF (5 mL) solution of $NiCl_2$(dme) (22 mg, 0.1 mmol). $NiCl_2$(dme) was consumed completely within 20 min while a rapid color change from green to dark red was observed. The solvent was removed in vacuo to give a dark yellow powder (yield 65 mg, 94%); in solution the complex is dark red. ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): δ = 6.33 (s, 2 H, NH), 7.21–7.72 (m, 56 H, Ph), 8.02 (s, 2 H, amidine CH) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ = 3.18, 5.4, 20.2, 22.5 ppm. [(pnnp)NiCl(μ-Cl)]$_2$·CH_2Cl_2: calcd. C 61.22, H 4.11, N 3.81; found C 60.89, H 4.39, N 3.74.

(pnnp)CoCl$_2$ (6): A THF (5 mL) solution of pnnp ligand (56.4 mg, 0.1 mmol) and $CoCl_2$ (13 mg, 0.1 mmol) was stirred for 2 h. A color change was observed from dark blue to a red-wine color in 10 min. After 2 h, the reaction mixture was dried in vacuo to give a paramagnetic green powder (yield 62 mg, 89%). (pnnp)$CoCl_2$·$0.5CH_2Cl_2$: calcd. C 61.12, H 4.24, N 3.80; found C 60.97, H 4.37, N 3.74.

(pnnp)FeCl$_2$ (7): A THF (5 mL) solution of pnnp ligand (56.4 mg, 0.1 mmol) and $FeCl_2$ (12.6 mg, 0.1 mmol) was stirred for 1.5 h. The $FeCl_2$ was completely consumed in 10 min. The resulting yellow solution was dried in vacuo to give a paramagnetic yellow powder (yield 60 mg, 87%). (pnnp)$FeCl_2$·$0.5CH_2Cl_2$: calcd. C 61.38, H 4.26, N 3.82; found C 61.11, H 4.12, N 3.72.

(pnnp)Pd(Me)CuPd(Me)(pnnp)·PF$_6$ (8): A mixture of (pnnp)PdMe (**1**, 34 mg, 0.050 mmol) and $Cu(CH_3CN)_4^+$ PF_6^- (19 mg, 0.050 mmol) was dissolved in acetonitrile (10 mL) and stirred for 10 min, the color of the mixture turned yellow. The volatiles were removed in vacuo from the resulting solution and the residue was washed with diethyl ether. The yellow powder remaining was dried in vacuo (yield 26 mg, 66%). ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): δ = 0.50 (t, J = 6 Hz, 6 H, Pd CH_3), 6.47–7.64 (m, 56 H, Ph), 8.34 (2 H, amidine CH) ppm. ^{31}P{^{1}H} = NMR (162 MHz, 25 °C, CD_2Cl_2): δ = –144.4, 4.3, 6.8, 27.5, 30.0 ppm. (pnnp)Pd(Me)-CuPd(Me)(pnnp)·PF_6·1.2CH_2Cl_2: calcd. C 55.18, H 3.98, N 3.33; found C 54.98, H 3.81, N 3.46.

CCDC-825816 (for **3**), -825817 (for **4**), -825818 (for **5**), -825819 (for **6**), -825820 (for **7**), -825821 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic data of **3**–**8**, ^{1}H NMR spectra of **3**–**6** and **8**, ^{31}P NMR spectra of **4**, **5**, and **8**.

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