Articles

Synthesis of a Library of Iridium-Containing Dinuclear Complexes with Bridging PNNN and PNNP Ligands (BL), [LM(μ-BL)M′L′]BF_4. 1. Specific Synthesis of Isomeric Heterodinuclear Complexes with Switched Metal Arrangements

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Specific synthesis of a series of Ir-containing homo- and heterodinuclear complexes with the PNNP (3,5-bis((diphenylphosphino)methyl)pyrazolato) and PNNN ligands (3-(diphenylphosphino)methyl-5-pyridylpyrazolato) is reported. Reaction of the PNNX-H precursors (X = P, N) with $[Ir(cod)_2]BF_4$ gives pale yellow precipitates, which are characterized as the cyclic dimers of the 1:1 adduct, [(μ-κ^1(*P*):κ^2(*N*,*X*)-PNNX-H)Ir(cod)]$_2$$(BF_4)_2$ (X = P, N). In the case of the PNNN system, subsequent sequential treatment of the 1:1 adduct with NEt_3 and a second metal reagent ([M(L)(cod)]BF_4: M(L) = Rh(cod), Pd(allyl)) (reaction 1) gives [(cod)Ir(PNNN)M(L)]BF_4, whereas the reversed addition of the reagents (reaction 2) furnishes [(L)M(PNNN)Ir(cod)]BF_4, the regioisomer with the switched metal arrangement. Selective preparation of the heterodinuclear PNNP complexes [(cod)Ir(PNNP)M(L)]BF_4 requires the addition according to reaction 1. In reaction 1 of the 1:1 dinuclear adduct of the PNNN system, deprotonation of the N−H part triggers interligand migration of the Ir(cod) fragment from the N,N site of one ligand to the P,N site of the other ligand to give [(cod)Ir(PNNN)]BF_4, which reacts with the second metal fragment at the N,N site to furnish [(cod)Ir(PNNN)M(L)]BF_4. On the other hand, reaction 2 involves dissociation of the dinuclear species into the mononuclear N,N-coordinated one, [(PNNN-H)Ir(cod)]BF_4, and subsequent interaction at the free P moiety followed by deprotonation and coordination gives the other regioisomer. These intriguing transformations result from the unique coordination properties of Ir (cationic vs neutral, hard vs soft, 5- vs 4-coordination, N,N vs P,N chelation), which are controlled by the deprotonation−protonation procedure. As a result of the present study, a library for Ir-containing homo- and heterodinuclear Ir(I) complexes with the PNNP and PNNN ligands has been constructed.

Introduction

Polynuclear complexes are expected to display unique chemical behavior through cooperative interaction of the metal centers, which cannot be realized by mononuclear species.[1] Furthermore, heteropolynuclear complexes consisting of metals of different kinds may realize more sophisticated functions through sharing the required functions by the metal centers of different characters, but selective synthesis of heteronuclear complexes is not always facile and frequently encounters problems such as formation of homonuclear complexes as byproducts.

When attention is turned to the structural motifs of polynuclear complexes, metal−metal-bonded cluster systems have been the major research subject of polynuclear organometallic chemistry, and little attention has been paid to the non-metal−metal-bonded systems.[1] This situation is in marked contrast to the relevant inorganic systems such as bioinorganic model systems[2] and polyoxometalates.[3] In the former systems, multiple metal centers are integrated by a well-designed bridging polydentate ligand mimicing the active site of the target metalloenzyme. To shed light on the non-metal−metal-bonded organometallic systems, we have been studying polynuclear complexes based on the PNNP ligand **1** (3,5-bis((diphenylphosphino)methyl)pyrazolato),[4] which separates the two metal centers beyond the metal−metal bonding interaction but is flexible enough to fit substrates of various sizes (Scheme 1). In previous papers, we reported that the dirhodium tetracarbonyl complex [(PNNP)-$Rh_2(CO)_4$]BF_4 was labile enough to release the two inner CO ligands trans to the P atoms and generated a coordinately unsaturated species (**A**) with cis-divacant coordination sites, which could bind a substrate with up to four donating electrons.[5]

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(2) See for example, the special issue for biomimetic inorganic chemistry: *Chem. Rev.* **2004**, *104*, 347−1200.

(3) (a) See, for example, the special issue for polyoxometalates: *Chem. Rev.* **1998**, *98*, 1−388. (b) Yamase, T: Pope, M. T. *Polyoxometalate Chemistry for Nano-Composite Design (Nanostructure Science and Technology)*; Kluwer Academic: New York; 2002.

(4) (a) Schenk, T. G.; Downs, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985,** *24*, 2334. (b) Schenk, T. G.; Milne, C. R. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985,** *24*, 2338. (c) Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554.

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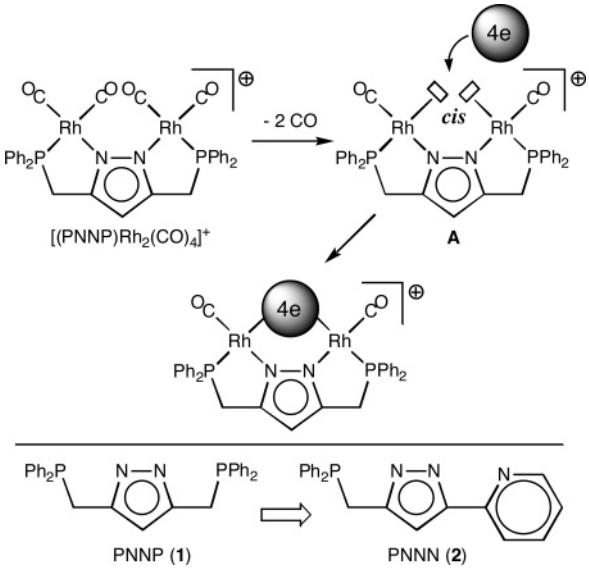
Scheme 1



Our study on the symmetrical homodinuclear PNNP system has been extended to a heterodinuclear one. As a first attempt, we have designed and synthesized a novel P,N-coordinating dinucleating ligand, PNNN (**2**; 3-((diphenylphosphino)methyl)-5-pyridylpyrazolato), having a P,N and an N,N coordination site, and studied its conversion to homo- and heterodinuclear complexes (Scheme 1). While pyrazolato-based bridging ligands with two coordinating tethers at the 3- and 5-positions of the ring such as **1** have been studied as dinucleating ligands for bioinorganic studies to a considerable extent,[6] unsymmetrical ligands such as **2** remain rare.[7]

As for the synthesis of dinuclear complexes, homonuclear species can be readily obtained by simply mixing the ligand and 2 equiv of the metal reagent. Selective preparation of heterodinuclear complexes, however, usually requires effort; otherwise, a mixture of homo- and heteronuclear complexes may be formed. In any event, for selective synthesis of a heterodinuclear complex, selective preparation of a mononuclear 1:1 adduct precursor is essential, and the 1:1 adduct can be accessible by addition of a first metal reagent to an excess amount of a dinucleating ligand. Subsequent treatment with a second metal reagent will furnish the heterodinuclear complex, as exemplified for a pyrazolato-based ligand system (**B**) leading to the heterodinuclear complex **D** (Scheme 2; addition of cationic fragments is shown, where addition of a base is needed). Simply changing the addition order of the metal reagents should form the regioisomer **D′** with the switched metal arrangement. This procedure, in principle, can be applicable to any system but is not always successful. For example, coordination of **B** to a cationic metal fragment causes labilization of the N−H proton (a decrease of its pK_a value), in part, to result in spontaneous deprotonation without addition of a base to give the neutral species **E**, which further reacts with the mononuclear reagent present in the reaction mixture to give the homodinuclear product **F** as a byproduct. If the deprotonation process, however, can be controlled by any method, the reaction sequence serves as an efficient synthetic method for a variety of dinuclear complexes.

Described herein are the results of our systematic synthetic study of homo- and heterodinuclear complexes with the PNNN ligand and relevant PNNP complexes as well.[8] We have found that a simple change of the experimental procedure leads to specific formation of regioisomeric pairs of heterometallic PNNN complexes. As a result of the present study, we have succeeded in construction of a library of homo- and heterodinuclear PNNN and PNNP complexes.

Results and Discussion

Preparation and Isolation of the Dinucleating Ligands PNNP-H (1-H) and PNNN-H (2-H). Preparation of the PNNP-H ligand (**1**-H) was first reported 20 years ago by Bosnich.[4a] Because of its sensitivity to air, **1**-H is stored as the nickel adduct, $[(PNNP)_2Ni_2](ClO_4)_2$, and before use the free ligand **1**-H is liberated by treatment with KCN and used as a benzene solution. This procedure, however, cannot be applied to the preparation of heterodinuclear complexes, because an exact 1:1 reaction is essential for selective preparation of a 1:1 adduct intermediate and the exact concentration of a benzene solution of **1**-H prepared as described above cannot be determined. Instead of trapping **1**-H as the Ni adduct, the crude product is subjected to column chromatographic purification (silica gel) under argon, and a spectroscopically pure sample of **1**-H is successfully obtained as a waxy solid.

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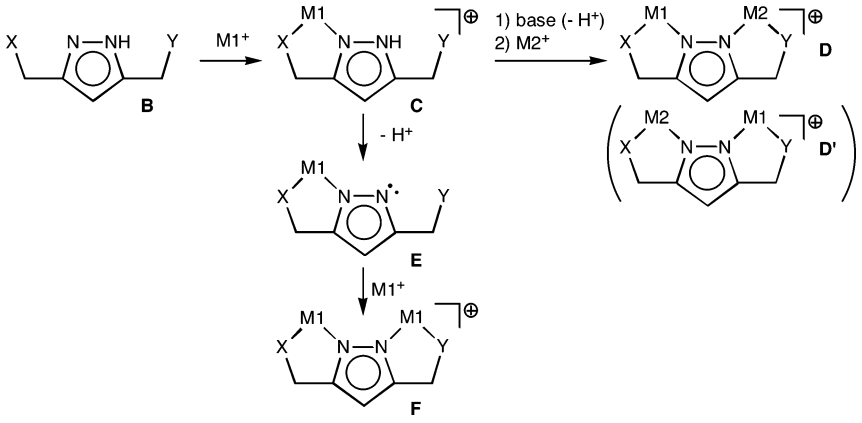
Scheme 2



The PNNN ligand **2**-H is prepared in a manner analogous to the synthetic route reported for **1**-H and can be isolated as a waxy solid after chromatographic separation under an inert atmosphere. Synthetic details are described in the Experimental Section (Scheme 11).

Preparation of Homodinuclear Complexes. Homodinuclear complexes with the PNNP ligand (**4**) are readily prepared by treatment of **1**-H with appropriate metal reagents **3** (2 equiv) in the presence of NEt_3, as reported by Bosnich,[4a] but better yields are obtained by the use of the isolated ligand (**1**-H) (Scheme 3). The corresponding PNNN complexes **5** are also readily obtained by similar procedures and have been characterized on the basis of their spectroscopic data: in particular, the presence of two sets of NMR signals for the two M(L) moieties

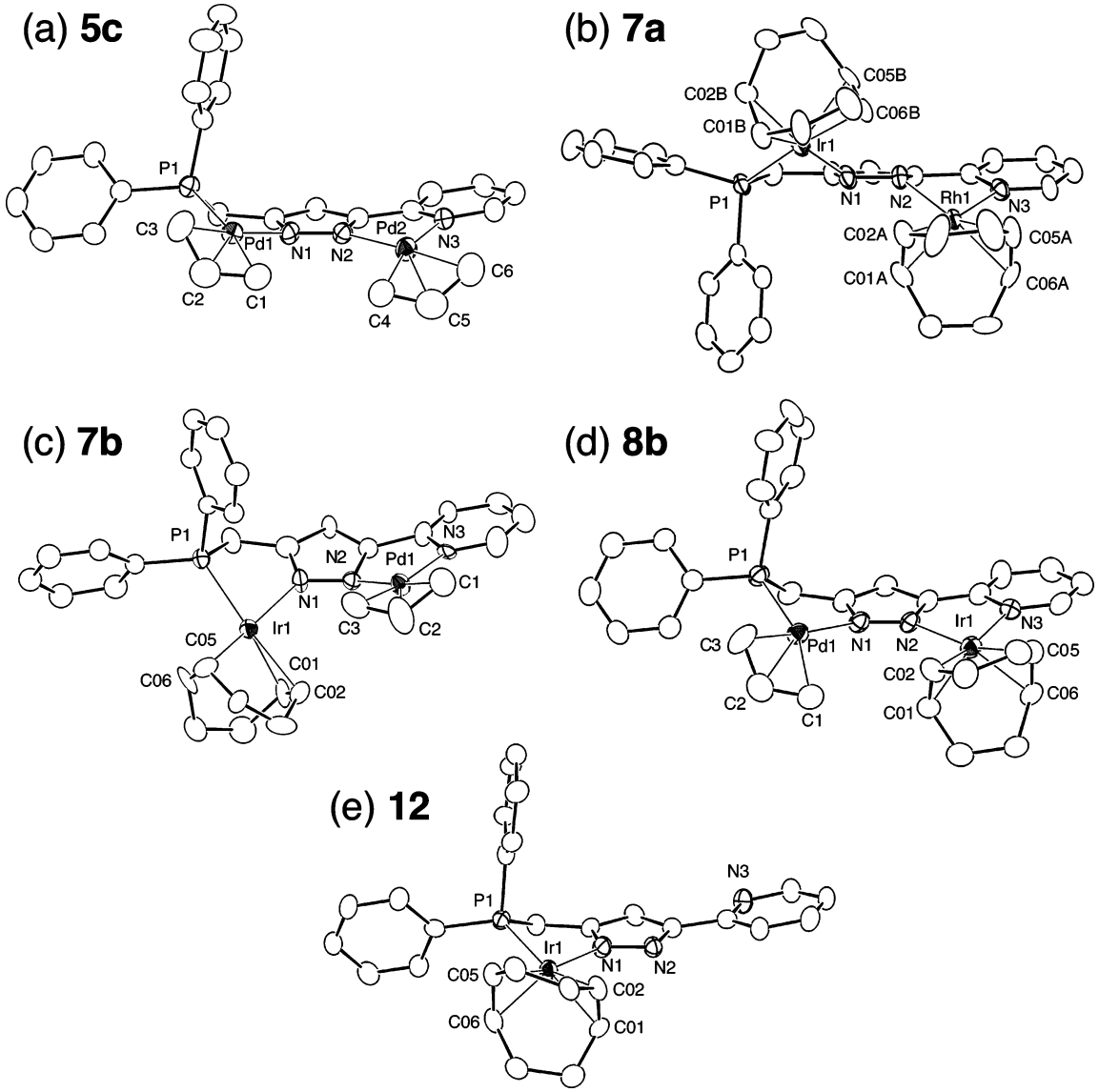
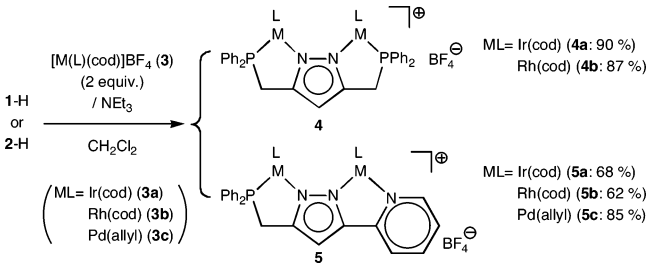


Figure 1. ORTEP views of the cationic parts of the cationic homo- and heterodinuclear complexes (a) **5c**, (b) **7a**, (c) **7b**, and (d) **8b** and of (e) the mononuclear neutral complex **12**, all drawn with thermal ellipsoids at the 30% probability level.

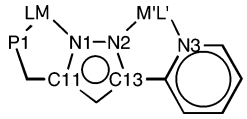
Scheme 3



incorporated into the P,N and N,N sites. NMR spectra reveal that the Pd(η^3-allyl) complex **5c** consists of two isomers, which turn out to be the supine and prone isomers[9] of the allyl ligand attached to the Pd(N,N) site, as characterized by X-ray crystallography. The envelope conformation of the five-membered metallacycle renders the two configurations diastereomeric, and the interconversion of the two isomers is slower than the ^{1}H NMR coalescence time scale. The isomer ratio is dependent on the solvent, and a single species is observed in DMSO-d_6. A single crystal obtained from $CH_2Cl_2-Et_2O$ contains the isomers in the ratio 0.53 (supine):0.43 (prone). An ORTEP view of the major species and selected structural parameters of **5c** are shown in Figure 1 and Table 1, respectively, and its structural features will be discussed later together with related compounds.

Specific Preparation of Isomeric Pairs of Heterodinuclear PNNN Complexes. Treatment of **2**-H with $[Ir(cod)_2]BF_4$ (**3a**; 1 equiv) in CH_2Cl_2 gives the pale yellow precipitate **6** in an almost quantitative yield (Scheme 4). Formation of a 1:1 adduct (**6**) has been confirmed by the relative intensities of the ^{1}H NMR signals for the PNNN and cod ligands. The low solubility and rather featureless NMR data of **6**, however, hamper its detailed spectroscopic characterization (e.g. ^{13}C NMR). A ^{31}P NMR spectrum contains a singlet signal (δ_P −5.5), which falls out of the range of the ^{31}P NMR signals for related compounds such as **4**, **5**, **7**, and **8**. Comparison of the structures and ^{1}H NMR data of the compounds reported herein reveals that the charac-

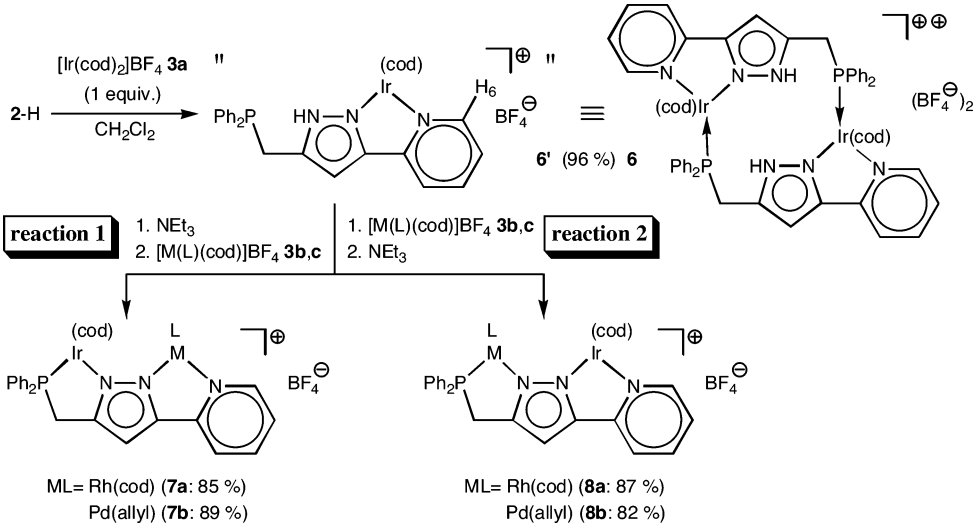
Table 1. Selected Structural Parameters for [LM(PNNN)M′L′]BF_4 (5c, 7a,b, and 8b) and (cod)Ir(PNNN) (12)[a]



	5c	7a	7b[c]		8b	12
ML	Pd(allyl)	Ir(cod)	Ir(cod)		Pd(allyl)	Ir(cod)
M′L′	Pd(allyl)[b]	Rh(cod)	Pd(allyl)		Ir(cod)	
M···M′	4.566(1)	4.444(1)	4.300(2)	4.292(2)	4.639(1)	
M−P1	2.280(2)	2.297(3)	2.290(6)	2.292(6)	2.290(3)	2.289(3)
M−N1	2.132(8)	2.095(9)	2.05(2)	2.07(2)	2.17(1)	2.07(1)
M′-N2	2.120(6)	2.10(1)	2.10(2)	2.11(2)	2.13(1)	
M′-N3	2.104(8)	2.129(8)	2.06(2)	2.09(2)	2.13(1)	
M−L	2.217(8) (C1)	2.14(1) (C01B)	2.12(3) (C01)	2.14(2) (C01)	2.27(1) (C1)	2.20(1) (C01)
	2.14(1) (C2)	2.17(1) (C02B)	2.21(2) (C02)	2.22(2) (C02)	2.17(2) (C2)	2.17(1) (C02)
	2.09(1) (C3)	2.19(1) (C05B)	2.10(3) (C05)	2.09(3) (C05)	2.09(2) (C3)	2.16(1) (C05)
		2.24(2) (C06B)	2.13(2) (C06)	2.18(2) (C06)	2.14(1) (C06)	
M′−L′	2.26(4) (C4)[b]	2.14(1) (C01A)	2.11(2) (C1)	2.12(3) (C1)	2.11(2) (C01)	
	2.16(2) (C5)[b]	2.17(1) (C02A)	2.09(3) (C2)	2.10(5) (C2)	2.15(2) (C02)	
	2.13(1) (C6)[b]	2.13(1) (C05A)	2.12(3) (C3)	2.10(4) (C3)	2.15(2) (C05)	
		2.16(2) (C06A)			2.10(1) (C06)	
∠P1−M−N1	82.0(2)	78.2(3)	77.3(5)	79.2(5)	83.0(3)	79.1(3)
∠N2−M′-N3	79.8(3)	77.4(4)	79.3(7)	77.0(8)	79.8(5)	
∠M−N1−N2−C13	162.0(6)	149.1(8)	168(1)	139(2)	166(1)	178.2(8)
∠M′−N2−N1−C11	178.2(5)	139.7(9)	172(2)	149(2)	177(1)	
∠M−N1−N2−M′	19(1)	71(1)	50(2)	41(3)	17(2)	

[a] Interatomic distances in Å and bond angles and dihedral angles in deg. [b] The Pd2(allyl) part was disordered.[12] [c] With two independent molecules.

Scheme 4



teristic doublet H_6 signal of the pyridyl moiety (Scheme 4; the H_6 atom is denoted as H10 in the Experimental Section (Chart 2)) serves as a diagnostic for determination of the coordination site of the M(cod) fragment; the H_6 signals for the N,N-coordinated species ([X(PNNN)M(cod)$^+$] (X = none or a metal fragment: $\delta_H \sim 8$) appear at higher field compared to those of the P,N-coordinated regioisomers ([(cod)M(PNNN)X]$^+$; $\delta_H > 8.5$). On the basis of these diagnostics, the 1:1 adduct ($\delta_H(H_6)$ 7.98) was tentatively assigned as the N,N-coordinated species **6′**. It is notable, however, that an ESI-MS spectrum contains signals attributed to a dimeric species (*m*/*z* 1285.0 ([(PNNN-H)(PNNN)Ir$_2$(cod)$_2$]$^+$), and 1373.0 ([(PNNN)$_2$Ir$_2$(cod)$_2$(BF$_4$)]$^+$) in addition to the signal for a monomeric species (*m*/*z* 642.6 ([(PNNN)Ir(cod)]$^+$)). Although **6** cannot be characterized by the spectroscopic data mentioned above, comparison with the PNNP system described below leads to the conclusion that the 1:1 adduct is not the monomeric species **6′** but the dimeric species **6**.

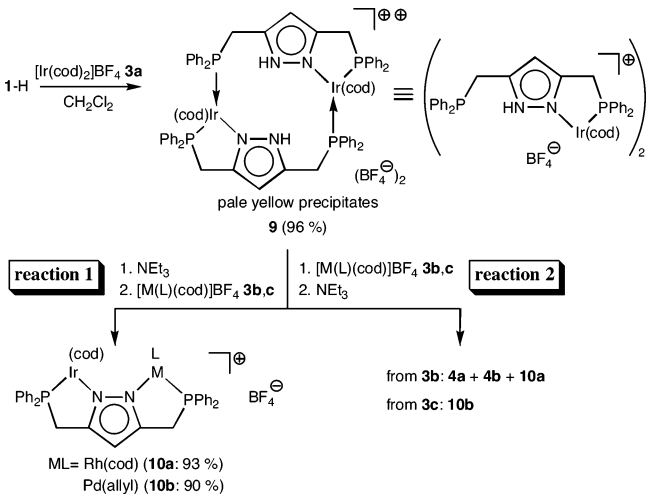
Then the 1:1 adduct **6** is converted into heterodinuclear complexes by treatment with a second metal fragment. Sequential treatment of **6** with a base (NEt_3) and [M(L)(cod)]BF$_4$ (**3**; M(L) = Rh(cod), Pd(allyl)) (reaction 1) results in selective formation of heterodinuclear complexes **7a**,**b**, where the Ir fragment sits on the P,N site and the second metal fragment is introduced to the N,N site. To our surprise, simple switching of the order of the addition of the second metal fragment and the base (reaction 2) leads to the formation of the regioisomeric heterodinuclear complexes **8a**,**b** with the switched metal arrangement. The selectivity is perfect, and neither the other isomeric species nor homodinuclear species can be detected. It is also remarkable that, in reaction 1, the Ir(cod) fragment is shifted from the N,N chelating site (**6**) to the P,N chelating site (**7**).

The formation of the heterodinuclear complexes [LM(μ-PNNN)M′L′]$^+$ is readily confirmed by the ^{1}H NMR data containing the signals for the two metal fragments (L and L′ in a 1:1 ratio) and the ESI-MS data, and the coordination sites of the metal fragments have been determined by spectroscopic analysis and verified by crystallography. For the Ir−Rh pair **7a**−**8a**, the ^{31}P NMR signal of **8a** appears as a doublet signal (δ_P (J_{Rh-P} = 155 Hz)) due to coupling with the Rh nucleus, while a singlet signal is observed for **7a**. On the other hand, for the Ir−Pd pair **7b**−**8b**, the allyl carbon signals of **8b** appear as doublet signals owing to coupling with the P nucleus indicating P,N coordination of the Pd(allyl) fragment, while **7b** shows the deshielded H_6 signal of the pyridyl moiety (δ_H 8.53) indicative of coordination of the Ir(cod) fragment to the P,N site according to the diagnostics mentioned above. The metal arrangements of the Ir−Rh complex **7a** and the Ir−Pd pair **7b**−**8b** have been verified by X-ray crystallography (Figure 1b−d).

It should be noted that this type of specific formation of regioisomeric species is observed only when the Ir(cod) fragment is introduced as the first metal fragment. For example, 1:1 reactions of **2**-H with the Rh (**3b**) and Pd reagents (**3c**) give mixtures of mono- and dinuclear complexes, presumably following the process discussed in Scheme 2. This result indicates that the specific reactions observed for the Ir system are thanks to the unique coordination properties of Ir.

Specific Preparation of Heterodinuclear PNNP Complexes. The successful preparation of the heterodinuclear PNNN complexes prompted us to extend the preparation to the PNNP system. Formation of regioisomers is not applicable, because of the symmetric structure of PNNP. In this case, too, the addition order of the reagents turns out to be crucial for selective reactions.

Scheme 5



Treatment of **1**-H with [Ir(cod)$_2$]BF$_4$ (**3a**) gives the 1:1 adduct **9** as a pale yellow precipitate in a manner similar to that for **6** (Scheme 5). While **9** is also sparingly soluble in most organic solvents, the following spectroscopic data consistent with a dimeric structure have been obtained. ^{1}H and ^{31}P NMR spectra of **9** observed in DMSO-d_6 are shown in Figure 2a. Characteristic spectroscopic features are as follows. (1) The ^{31}P NMR spectrum contains a pair of doublet signals coupled with each other (δ_P −16.11, 4.37 (J_{P-P} = 42 Hz)), indicating coordination of two inequivalent phosphorus atoms to a single metal (Ir) center. This indicates that **9** is an oligomeric species, because the two P atoms in **1**-H separated by >4 Å cannot be chelated to a single metal center. (2) The sharp single ^{1}H NMR signals for the hydrogen atom for the 4-position of the pyrazolate ring (H_A; δ_H 5.10) and the N-H proton (δ_H 11.60) are in a 1:1 ratio, indicating formation of a symmetrical oligomer and retention of the protonated form. (3) The ^{13}C NMR data comparable to those of the reference compounds, **1**-H and the P,N-chelated species **10b** (Chart 1), support κ^1 and κ^2 coordination of the PNNP ligand, which bridges two metal centers. (4) An ESI-MS spectrum containing peaks at *m*/*z* 765.4 ([(PNNP-H)Ir(cod)]$^+$), 1529.1 ([(PNNP)(PNNP-H)Ir$_2$(cod)$_2$]$^+$), and 1615.0 ([(PNNP-H)$_2$Ir$_2$(cod)$_2$(BF$_4$)]$^+$) is consistent with a dimeric structure. On the basis of these results the yellow precipitate **9** can be characterized as a cyclic, dimeric species with five-coordinate Ir centers, as shown in Scheme 5. The notable differences in the δ_P values observed for **9** vs other complexes ($\delta_P \sim 30$; **4**, **5**, **7**, and **8**) mentioned above can be ascribed to the difference in the coordination number: 5 for **9** vs 4 for the others. Analogous 1:1 reactions of **1**-H with **3b**,**c** give mixtures of products, as noted for **2**-H (see above).

Upon subsequent introduction of the Rh fragment, treatment of **9** with NEt_3 followed by addition of **3b** (reaction 1) furnishes the heterodinuclear complex **10a** in an excellent yield, while the reversed addition of the two reagents (reaction 2) affords a mixture of the desired product **10a** and the homodinuclear complexes **4a**,**b**. In the case of the Ir−Pd complex **10b**, the desired product is obtained irrespective of the addition order.

The new heterodinuclear complexes **10a**,**b** are readily characterized by spectroscopic data, being consistent with a 1:1:1 adduct of the Ir and Rh/Pd fragments and the PNNP ligand.

(8) Some of the results have already been reported as a communication.[5d]

(9) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410

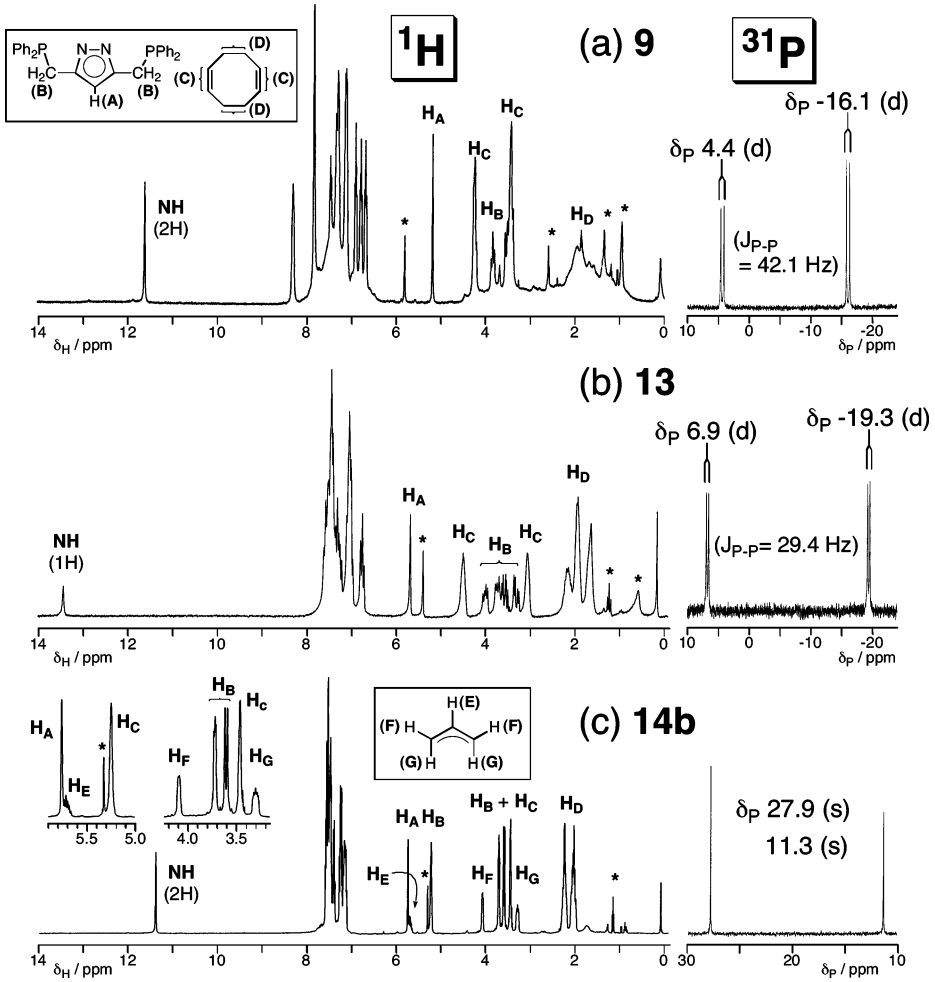
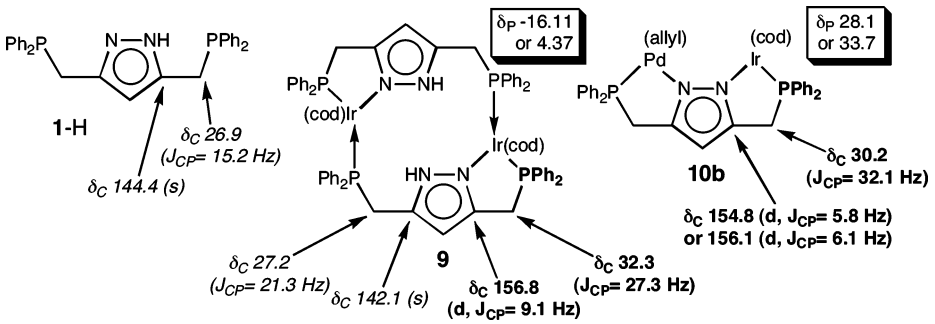


Figure 2. ^{1}H (400 MHz) and ^{31}P NMR spectra (81 MHz) for (a) **9** (in DMSO-d_6), (b) **13** (in CD_2Cl_2), and (c) **14b** (in CD_2Cl_2). Residual solvents (CH_2Cl_2, $CHDCl_2$, hexane) and impurities are denoted by asterisks.

Chart 1

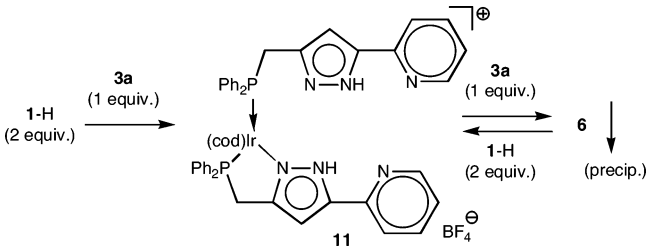


No homonuclear complex has been detected for the products obtained from reaction 1.

Mechanism of the Metal Switching Process. (i) 1:1 Adducts 6 and 9. The key intermediates of the present unique transformations are the 1:1 adducts **6** and **9**. The low solubility of **6** and **9** hampers detailed spectroscopic characterization and recrystallization. However, for the PNNP adduct **9**, the dimeric structure is consistent with the spectroscopic data as discussed above. The single set of NMR signals suggests a cyclic oligomeric structure, and the dimeric structure is supported by the ESI-MS data. The PNNN adduct **6** has also been characterized as the dimeric species on the basis of (1) the ESI-MS data and (2) the δ_P signals different from those of the 4-coordinate square-planar species.

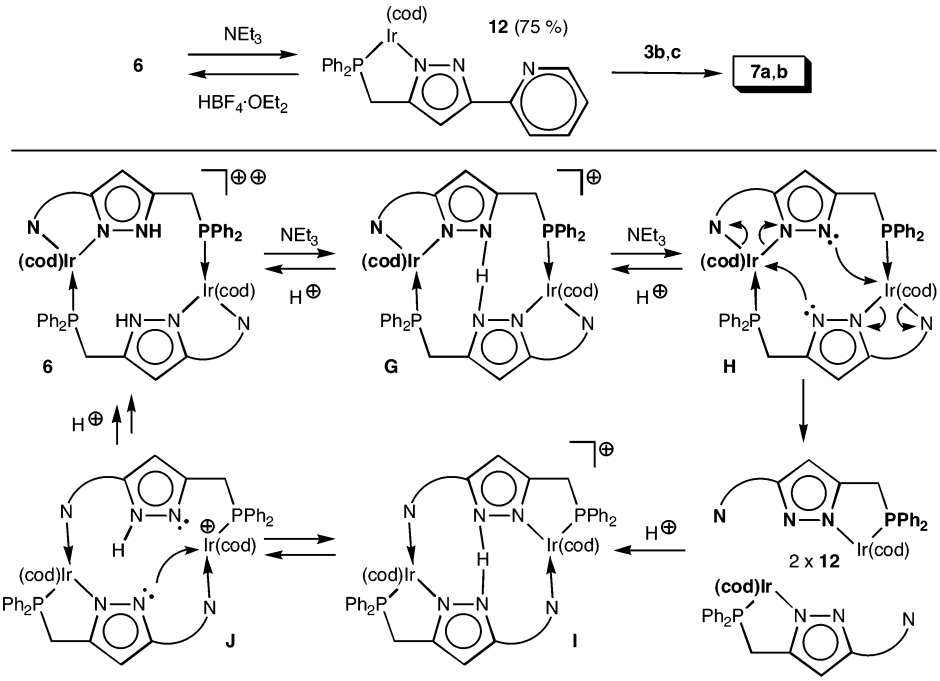
A dynamic feature is noted for the PNNN system (Scheme 6). The 1:1 reaction of **1**-H with **3a** gives **6** as described above,

Scheme 6



but a 2:1 reaction affords the 2:1 adduct **11**, which is converted to the 1:1 adduct **6** upon further addition of 1 equiv of **3a**. Furthermore, treatment of **6** with 2 equiv of **1**-H reverts the reaction to give **11**. Although the Ir/PNNP-H system is dynamic, the selective formation of the dimeric species is ascribed to the

Scheme 7



low solubility of **6** in organic solvents. A 1:1 mixing of **1**-H and **3a** may form a mixture containing **11** and **6**, but precipitation of the dimer **6** finally drives the reaction to the selective formation (precipitation) of the 1:1 adduct **6**. The 2:1 adduct **11** with the unsymmetrical coordination of two PNNN ligands is characterized on the basis of (1) a pair of doublet ^{31}P NMR signals coupled with each other (δ_P −19.6 (d), 8.9 (d) (J_{P-P} = 11.7 Hz)) being very similar to that of **9** with a similar metal coordination structure, (2) two sets of ^{1}H and ^{13}C NMR signals for the PNNN ligands, and (3) a deshielded H_6 signal for the pyridyl moieties (δ_H 8.73, 8.99), indicating no N,N coordination of the Ir(cod) fragment. Although intra- or interligand N−H−N hydrogen-bonding interactions are possible, they cannot be defined by the obtained spectroscopic data alone.

(ii) Reaction 1 Initiated by Deprotonation of 6 and 9. To get information on reaction 1 the 1:1 adducts are treated with NEt_3.

(a) PNNN System Involving Switching of Metal Coordination Site. Reaction of the PNNN complex **6** with NEt_3 gives the neutral red complex **12**, which reverts to **6** upon acidification with HBF_4·OEt_2 (Scheme 7). The pH-dependent interconversion is quantitative. The characterization of **12** is based on (1) the ^{31}P NMR data (δ_P 31.2) comparable to those of P,N-chelated species such as **7**, **8**, and **10** and (2) the diagnostic H_6 signal of the pyridyl part (δ_H 8.50), and its molecular structure has been determined by X-ray crystallography (Figure 1e).

The mechanism of the pH-dependent interconversion summarized in Scheme 7 deserves comment. The deprotonation of **6** should form the monoprotonated, monocationic species **G** and then the neutral species **H**. Although these intermediates cannot be detected, a PNNP intermediate (**13**) corresponding to **G** is observed, as described in the next section (ii(b)). At the stage of **G**−**H**, the change of the charge of the complexes (+1 → 0) causes reorganization of the coordination structure associated with the changes of (i) the coordination number (5 → 4) and (ii) the chelation parts (N,N → P,N), and it is remarkable that the Ir(cod) fragment is mutually shifted from one PNNN ligand to the other PNNN ligand to complete the neutralization process. On the other hand, protonation of **12** should initially form the dimeric adduct **I**, which may be equilibrated with the four-coordinate species **J**, and subsequent switching of the coordination site followed by proton transfer and repetition of similar processes regenerates **6**. Thus, the formation mechanism of the heterodinuclear complexes is in sharp contrast to the anticipated one described in Scheme 2 and involves the supramolecular dimeric intermediates **G**−**J**. The acidity of the N−H protons in the monomeric (**6′**) and dimeric structures (**6**), however, may not be significantly different, and therefore, deprotonation of the labilized N−H protons discussed in the Introduction (Scheme 2) may be hindered by the supramolecular structure. For consideration of the spatial arrangement of the dimeric structure **6**, structural optimization has been performed by means of MM2,[10] and the obtained optimized structure is shown in Figure 3, where the result of the PNNP species **9** showing essentially

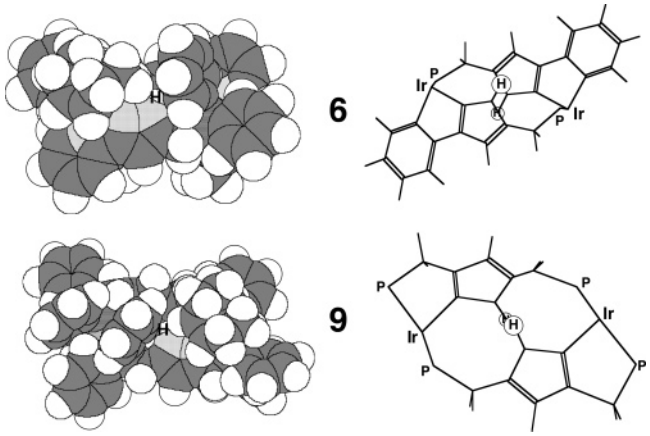
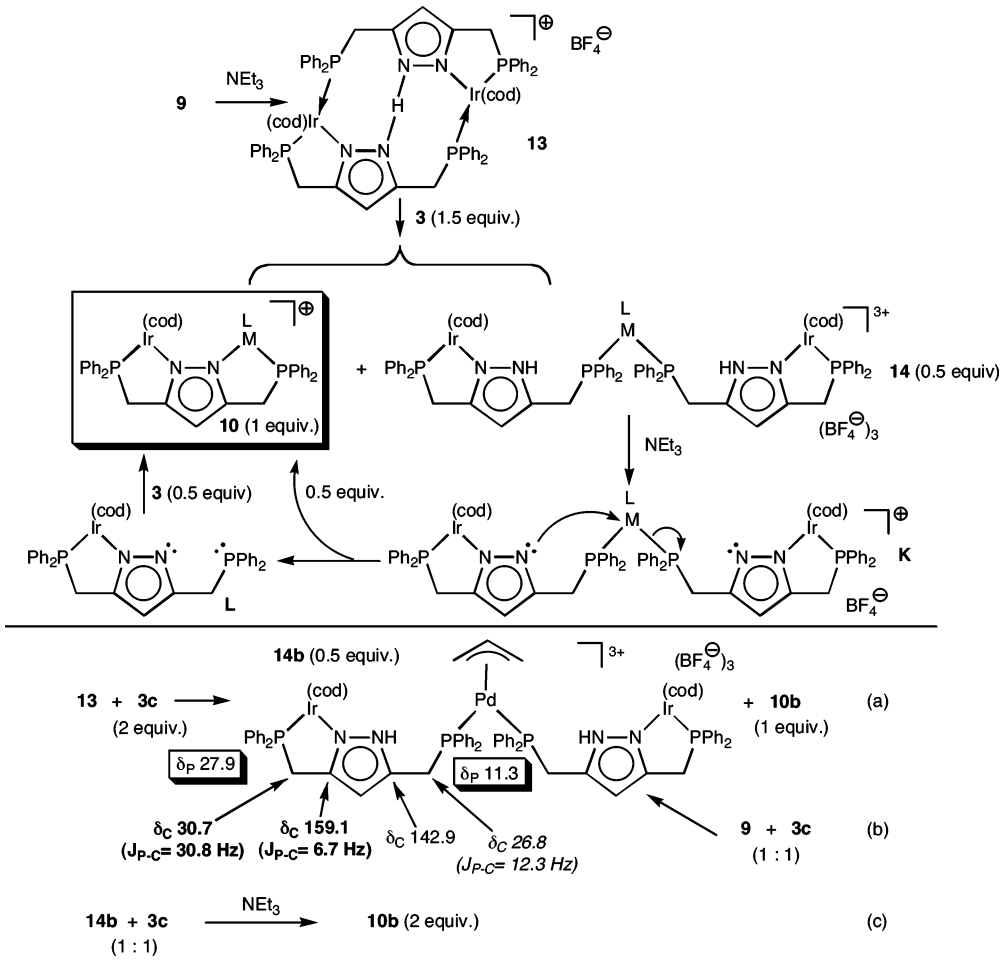


Figure 3. Structures of **6** and **9** obtained by MM2 optimization (with space-filling and wire frame expressions; for the wire frame expressions the Ph and cod groups are omitted for clarity).

the same feature is also included. The most significant feature is that the N−H part is surrounded by the cod and phenyl groups

(10) The MM2 optimization was carried out with the software included in the CS ChemBats3D Pro package (version 5.0).

Scheme 8



to hinder approach of a base. A similar feature is noted for **9**. Thus, it is concluded that the N−H proton embedded in the ligand pocket is so kinetically stabilized as to be sluggish with respect to deprotonation.

The driving force for the present unique interconversion can be explained in terms of the favored coordination number and chelate set, which depend on the charge of the Ir center. The electron-rich neutral species **12** should prefer the softer P,N chelate to form a four-coordinate structure peculiar to 16e species of d^8 metals, whereas the cationic hard species **6** prefers a five-coordinate structure with the hard N,N chelate. At the stage of **H** and **I**, where the two coordination modes are exchangeable, the Ir center chooses the coordination site (NN vs PN), which fits the properties of the Ir center (cationic hard Ir(I)/N,N-chelate/5-coordinate vs neutral soft Ir(0)/P,N-chelate/4-coordinate). These coordination features are characteristic of Ir, and therefore, similar reactions of the Rh and Pd species do not result in the selective formation of the 1:1 adducts corresponding to **6** but afford mixtures of products.

A related metal migration process was reported for μ-pyrazolato complexes, $L_2Ir(\mu\text{-pz})_2IrL'_2$, by Oro.[11] The mechanism proposed (σ-1,2-metallotropic shift) involves a shift of the metal center via a π-coordinated μ-η^1:η^2-intermediate and is totally different from our system.

Thus in reaction 1 of the PNNN system, deprotonation of **6** with NEt_3 causes the interligand metal migration to furnish the P,N-chelated neutral mononuclear species **12**, which further reacts with the second metal reagent to give the **7**-type products (Scheme 7).

(b) PNNP System. The PNNP complex **9** is also susceptible to deprotonation, but a different type of product is obtained, owing to the different properties of the bridging ligands PNNP (**1**) and PNNN (**2**) (Scheme 8). The deprotonation does not afford a neutral product like **12** but is terminated at the stage of the monodeprotonated, monocationic species **13**, even in the presence of an excess amount of NEt_3. ^1H and ^{31}P NMR spectra of an isolated sample of **13** are shown in Figure 2b. The ^{31}P NMR spectrum (a pair of doublets coupled with each other; δ_P −19.3 (d), 6.9 (d) (J_{P-P} = 29.4 Hz)), which is very similar to that of **9**, indicates a dimeric structure, which is also supported by the ESI-MS data (*m*/*z* 1527.1 ([(PNNP-H)(PNNP)-$Ir_2(cod)_2]^+$). The most characteristic feature is the sharp singlet ^1H NMR signal at low field (δ_H 13.38) assignable to N−H, and its intensity (1H) as well as a single set of ^1H NMR signals for the PNNP parts is in accord with the symmetrical structure, in which the two noncoordinating N atoms are bridged by the proton.

Accordingly, the mechanisms of the subsequent steps are different from those of the PNNN system described above, and a proposed mechanism is also included in Scheme 8. To verify the proposed mechanism, the intermediate **13** is subjected to reactions with **3b** (Rh) and **3c** (Pd). Although both reactions afford the heterodinuclear complexes **10** in the presence of NEt_3 (Scheme 5), intermediates can be characterized spectroscopically for the Ir−Pd system **14b** as described below.

(11) Yuan, Y.; Jiménez, M. V.; Sola, E.; Lahoz, F. J.; Oro, L. A. *J. Am. Chem. Soc.* **2002**, *124*, 752. Tejel, C.; Villoro, C. C.; Ciriano, M. A.; López, J. A.; Eguizábal, E.; Lahoz, F. J.; Bakhmutov, V. I.; Oro, L. A. *Organometallics* **1996**, *15*, 2967.

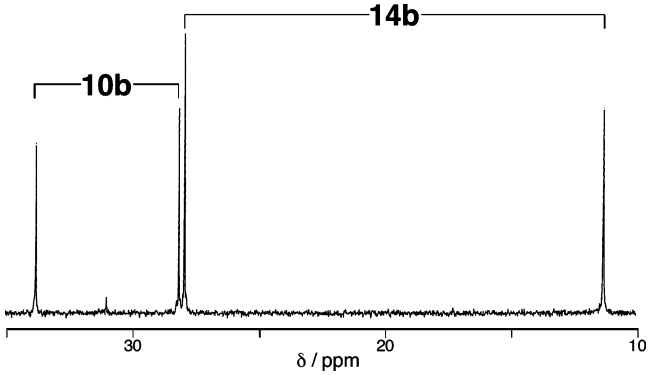


Figure 4. ^{31}P NMR spectrum for a 1:2 reaction mixture of **13** and **3c** (observed at 81 MHz in $CDCl_3$).

A 1:2 reaction between **13** and **3c** gives a mixture of the heterodinuclear complex **10b** and a trinuclear species **14b** (Scheme 8a), as can be seen from the ^{31}P NMR chart (Figure 4). The trinuclear complex **14b** can be alternatively prepared in a selective manner by a 1:1 reaction between **9** and **3c** (Scheme 8b), and ^{1}H and ^{31}P NMR spectra of **14b** obtained from the reaction of Scheme 8b are shown in Figure 2c. The intensities of the allyl and cod signals and a single set of the PNNP signals reveal a 1:2 incorporation of the Pd and Ir fragments and a symmetrical structure as well. The signals for the allyl ligand are located at δ_H 5.6, 4.05, and 3.27, being typical for η^3 coordination. The ^{13}C NMR data for the PNNP ligand of **14b** are comparable to those of **12**, and comparison with the reference compounds in Chart 1 suggests a μ-κ^1:κ^2-bridging coordination mode for the PNNN ligand. In accord with this mode, the ^{31}P NMR signal at 27.9 ppm is assigned to the phosphorus atom in the P,N chelate and the other signal to the κ^1-coordinating phosphorus atom. The lack of P−P coupling supports coordination of the phosphorus atoms to different metal centers. The composition of the trinuclear structure is supported by the ESI-MS data (*m*/*z* 1849.8 ({[(PNNP-H)$_2$Ir$_2$(cod)$_2$Pd(allyl)](BF$_4$)$_2$}$^+$)).

Then reaction of the Pd−Ir adduct **14b** with NEt_3 has been examined. An equimolar amount of **3c** is added to **14b** so that the stoichiometry becomes comparable to reaction 1 (Ir:Pd = 1:1), because **14b** is a 2 (Ir):1 (Pd) adduct (Scheme 8c). Figure 5a shows a ^{31}P NMR spectrum for a 1:1 mixture of **14b** and **3c**. When 0.6 equiv of NEt_3 is added to the mixture, a part of **14b** is converted into **10b** (Figure 5b) and further addition of NEt_3 causes quantitative conversion of **14b** into **10b** (Figure 5c).

On the basis of the above-mentioned results, a plausible mechanism for reaction 1 of the PNNP system is proposed, as summarized in Scheme 8. The first event occurring in this system is reaction of the dinuclear 1:1 adduct **9** with NEt_3, which causes monodeprotonation of **9** to give the monocationic intermediate **13**. The resultant **13** then interacts with the second metal reagent **3** to give a mixture of the heterodinuclear product **10** and the trinuclear 1:2 adduct **14**, and the latter species **14** is deprotonated by NEt_3 present in excess in the reaction mixture to give the monocationic species **K**, which separates into **10** and the neutral mononuclear species **L**. **L** is converted to **10** upon interaction with **3** in the reaction mixture to accomplish the selective transformation.

(iii) Reaction 2 Involving a Second Metal Reagent−Base Addition Sequence. (a) PNNN System. Comparison of the structures of the intermediate **6** and the product **8** suggests that reaction 2 can be apparently explained in terms of a simple combination of dissociation, coordination, and deprotonation

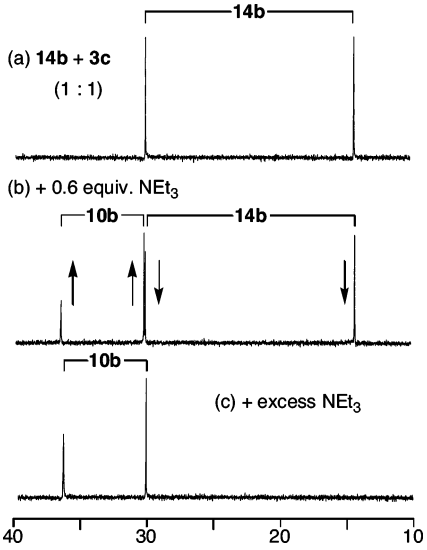
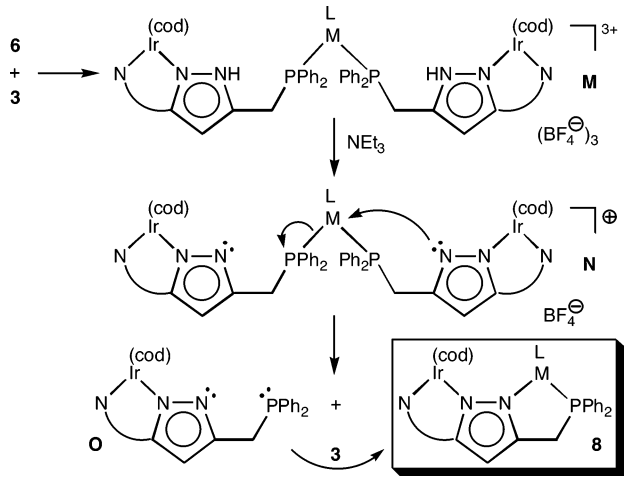


Figure 5. Reaction of **14b** and **3c** in the presence of NEt_3 monitored by ^{31}P NMR (at 81 MHz in CD_2Cl_2): (a) a mixture of **14b** and **3c** (before addition of NEt_3); (b) after addition of 0.6 equiv of NEt_3; (c) after further addition of an excess amount of NEt_3.

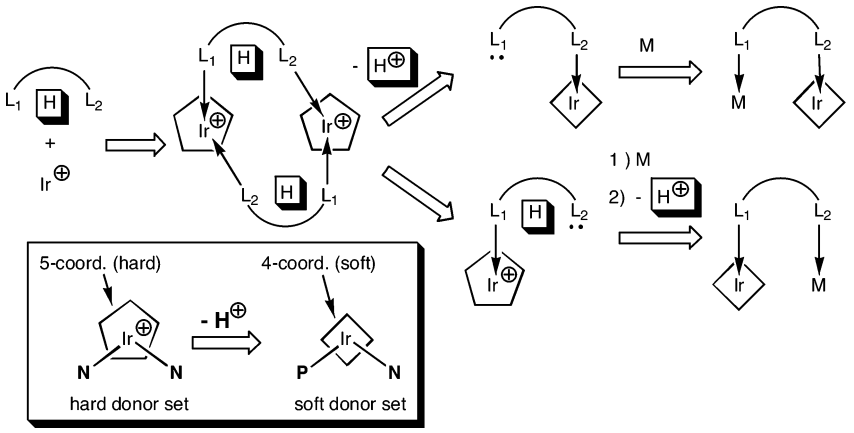
Scheme 9



processes, and a plausible mechanism is summarized in Scheme 9. Dissociation of the dimeric species **6** into the monomeric N,N-coordinated intermediate [(PNNN-H)Ir(cod)]$^+$ followed by coordination of the free P atom to **3** gives the trinuclear intermediate **M** analogous to **14**. Subsequent deprotonation (**N**) and chelation afford the cationic heterodinuclear product **8** and the neutral N,N-chelated mononuclear species **O**, which is also converted to **8** via coordination of **3** to the free P,N site. ESI-MS signals for **M** (M(L) = Pd(allyl)) support the proposed mechanism, while attempted reaction between **6** and **3** results in a mixture of products and no intermediate can be characterized by other spectroscopic methods, including NMR.

(b) PNNP System. The reaction of **9** with **3c** gives the trinuclear adduct **14b** as described above (Scheme 8b), and subsequent steps should be analogous to those described in Scheme 8 to lead to **10** in a selective manner. In contrast to the Pd system, the reaction of **8** with the Rh reagent **3b** gives a mixture of products and, accordingly, subsequent treatment with NEt_3 also results in a mixture, being consistent with the results of the preparative reaction (Scheme 5). The difference can be attributed to the instability of **14a** (M(L) = Rh(cod)) compared to **14b** (M(L) = Pd(allyl)). In the presence of NEt_3 (reaction 1), as soon as **14a** is formed, immediate deprotonation leads to **K**

Scheme 10



etc. eventually to give **10a** in a selective manner. However, in reaction 2, where the reaction mixture is stirred for a while before addition of NEt_3, the intermediate **14a** gradually degrades to mono- and dinuclear species, which lead to the mixture of products.

Molecular Structures of PNNN and PNNP Complexes. The cationic dinuclear PNNN complexes **5c**, **7a**, **7b**, and **8b** and the mononuclear neutral complex **12** have been characterized by X-ray crystallography. Their ORTEP views are shown in Figure 1, and their selected structural parameters are compared in Table 1.

No metal−metal interaction is present, judging from the intermetallic distances (>4.2 Å). All metal centers adopt square-planar coordination geometries, as usually observed for four-coordinate d^8-metal complexes with 16 valence electrons, and coordination of the allyl ligand to the N,N-chelated metal is virtually symmetrical, in contrast to that of the P,N-chelated metal, owing to the trans effect of the phosphorus atom. The most significant difference noted is the ∠M−N1−N2−M′ dihedral angle, which apparently results from the steric repulsion between the ML and M′L′ moieties. An envelope-type conformation is observed for the five-membered P,N chelate, but the N,N counterpart is much less folded. In the five-membered P,N chelate, the most bulky fragment (M(cod) > PPh_2 > Pd(allyl)) is folded up from the plane defined by the other four vertices to form an envelope conformation. It is notable that, in the case of **7b** with the two bulky M(cod) fragments, the two fragments are folded up and down as can be seen from the ∠M−N1−N2−C13 and ∠M′−N2−N1−C11 dihedral angles. The cod ligands on the two different metal centers are close enough to distort the backbone, suggesting the possibility of interaction between the two ligands on the different metal centers. Such a ligand arrangement would lead to a new mode of dimetallic activation and interaction of two different substrates on the two metal centers.

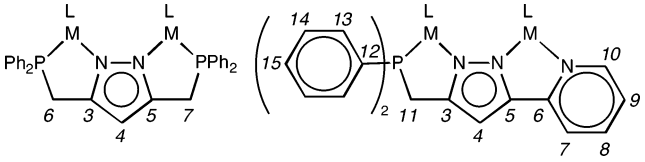
Conclusions. In this article we present a novel synthetic method for a series of homo- and heterodinuclear complexes with the dinucleating PNNN and PNNP ligands. It is remarkable that, in the case of the PNNN system, a simple change of the experimental procedure (addition order of the reagents) brings about formation of pairs of heterodinuclear complexes with the switched metal arrangements and the method can be applied to the synthesis of the heterodinuclear PNNP complexes. The present unique transformations are realized by a combination of the following unique features (Scheme 10; the squares and the pentagons stand for four- and five-coordinate structures, respectively). The key intermediates are **6** and **9**, having the supramolecular dimeric structures, which prevent spontaneous deprotonation, leading to the formation of homodinuclear byproducts as noted in Scheme 2. The dimeric structures result from the coordination properties of the cationic Ir centers, which prefer five-coordinate structures. It is also noteworthy that the coordination properties of the Ir center can be switched by the protonation−deprotonation process. Deprotonation changes the cationic Lewis acidic hard Ir center into the neutral soft one and, as a result, (1) the coordination number decreases from 5 to 4 and (2) the Ir center is transferred from the hard N,N site to the soft P,N site. Thus, it is concluded that the present unique transformations are based on the peculiar coordination properties of Ir.

In the following paper, the reactivity of the obtained complexes will be discussed and, in combination with the present results, a library of homo- and heterodinuclear PNNP and PNNN complexes has been established.

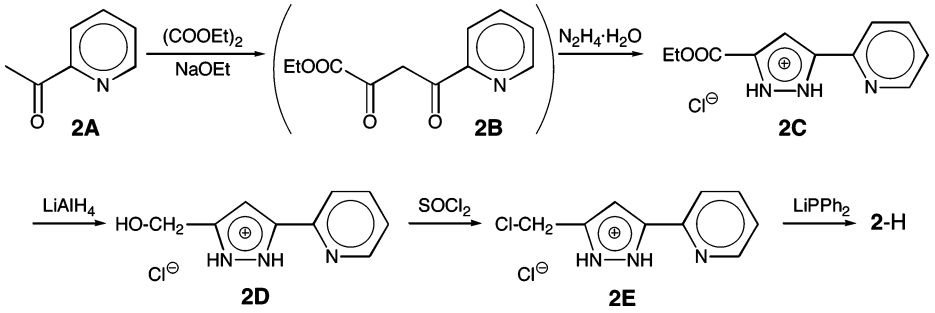
Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. THF and ether (Na−K alloy), CH_2Cl_2 (P_2O_5), and EtOH ($Mg(OEt)_2$) were treated with appropriate drying agents, distilled, and stored under argon. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (^1H, 200 MHz; ^{31}P, 81 MHz) and JEOL EX-400 spectrometers (^1H (VT, 2D), 400 MHz; ^{13}C, 100 MHz). Chemical shifts (downfield from TMS (^1H and ^{13}C) and H_3PO_4 (^{31}P)) and coupling constants are reported in ppm and in Hz, respectively. Ph, py, and pz stand for the phenyl, pyridyl, and pyrazolyl parts, respectively, and the numbering schemes for the PNNP and PNNN ligands are shown in Chart 2. Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR spectra were obtained on a FT/IR 5300 spectrometer. ESI-MS and FD-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer and a JEOL JMS-700 mass spectrometer, respectively.[13] The metal reagents **3a**,[14a] **3b**,[14a] and **3c** [14b] were prepared according to the published procedures. Other chemicals were purchased and used as received. Chromatography was performed on silica gel.

Chart 2



Scheme 11



Preparation of PNNP-H (1-H). PPh_3 (3.1 g, 12 mmol) was dissolved in dry THF (25 mL). Finely cut lithium (0.18 g, 26 mmol) was added, and the red solution was stirred for 4 h at ambient temperature. To the resultant solution cooled to −75 °C was added 3,5-bis(chloromethyl)pyrazole (0.60 g, 3.0 mmol) in one portion. The mixture was stirred for 10 min at −75 °C and for 2 h at 0 °C. After addition of deoxygenated water (25 mL), the products were extracted with ether (20 mL × 4). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated to 7 mL under reduced pressure. The mixture was separated by silica gel column chromatography with ether−hexane (1:1) and then with ether as eluent. PNNP-H (**1**-H) was obtained as a sticky white solid from the second fraction after removal of the volatiles under reduced pressure. **1**-H (1.39 g, 2.34 mmol, 78% yield): δ_H ($CDCl_3$) 3.32 (s, 4H, H6,7), 5.71 (s, 1H, H4), 7.27−7.40 (m, 20H, Ph); δ_P ($CDCl_3$) −22.07 (s); δ_C ($CDCl_3$) 26.9 (dt, J_{C-H} = 130, J_{C-P} = 15, C6,7), 104.8 (dd, J_{C-H} = 178, J_{C-P} = 6, C4), 128.4−132.8 (Ph), 137.9 (d, J_{C-P} = 15, Ph), 144.44 (s, C3,5); IR (KBr) 3195, 3069, 1953, 1562, 1432, 1096, 1024, 740, 694 cm^{-1}; FD-MS *m*/*z* 464 (M^+).[15]

Preparation of PNNN-H (2-H). The reaction sequence for **2**-H is summarized in Scheme 11.[16]

(i) Preparation of 2C. Sodium (2.5 g, 0.11 mol) was dissolved in dry ethanol (150 mL) at room temperature under argon. (*Caution!* Because hydrogen is released from the reaction, sodium cut in small pieces should be added carefully so that that the reaction does not become vigorous.) To the resultant NaOEt solution was added diethyl oxalate (14.0 mL, 0.10 mol) followed by 2-acetylpyridine (**2A**; 11.5 mL, 0.10 mol). After the solution was stirred for 18 h, the volatiles were evaporated, and the resultant dark-colored paste was dissolved in water (100 mL). The aqueous solution was neutralized with acetic acid and extracted with diethyl ether (100 mL; four times). The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated to yield **2B** (20.19 g, 0.097 mol; crude yield: 97%) as a brownish white solid. **2B** was used as obtained without further purification.

The crude solid sample of **2B** (20.19 g, 0.097 mol) was dissolved in dehydrated ethanol, and then $NH_2NH_2 \cdot H_2O$ (4.26 mL, 1 equiv) was added dropwise to the solution. After the mixture was refluxed for 3 h, the volatiles were removed under reduced pressure. The resultant brownish paste was dissolved in ether (100 mL), and the organic phase was washed with water (40 mL × 2). The combined aqueous phases were extracted again with ether (100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to leave a sticky white solid. The solid was dissolved in ethanol (50 mL), and concentrated HCl (4 mL) was added to form a HCl salt. Slow addition of ether gave the hydrochloride salt of 3-(ethoxycarbonyl)-5-(pyridin-2-yl)pyrazole (**2C**). A second crop was recovered from the filtrate by concentration and cooling of the filtrate. Combined yield of **2C**: 71% (22.0 g, 0.071 mol; with 1 mol of EtOH solvate). **2C**: δ_H (DMSO-d_6) 1.32 (3H, t, J = 6.8, CH_3), 4.34 (4H, q, J = 7.2, CH_2), 7.77−7.86 (2H, m, pz + py-H_5), 8.39 (2H, m, py), 8.73 (1H, d, J = 5.2, py-H_6); IR (KBr) 3106 (ν_{CH}; py), 2974, 2859 (ν_{CH}), 1725 cm^{-1} ($\nu_{C=O}$); ESI-MS *m*/*z* 218.2 (M − Cl). Anal. Calcd for $C_{11}H_{14}N_3O_2Cl$: C, 48.62; H, 5.19; N, 15.47; O, 17.67; Cl, 12.88. Found: C, 48.23; H, 5.20; N, 15.48; O, 17.67; Cl, 13.04.

(ii) Preparation of 2D. An 11.14 g portion (44 mmol) of **2C** was dissolved in H_2O (30 mL). The pH was adjusted to 8 by addition of saturated aqueous Na_2HPO_4 solution. The aqueous phase was extracted with ether (three times). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to leave a slightly brown solid, which was dissolved in dry ether (300 mL). The ethereal solution was slowly added to $LiAlH_4$ (5 g) suspended in 50 mL of dry ether, and the mixture was refluxed for 10 h. The flask was immersed in an ice−water bath, and the reaction mixture was hydrolyzed with water carefully. The volatiles were removed under reduced pressure, and the obtained white cake was suspended in methanol (350 mL). CO_2 gas was bubbled through the solution for 10 min, and the mixture was refluxed for 8 h. Filtration and evaporation under reduced pressure gave a white solid. Water in this residue was removed by azeotropic distillation with ethanol (three times). The resultant solid was dissolved in EtOH, and concentrated aqueous HCl (5 mL) was added. Addition of ether caused precipitation of **2D**, which was purified by crystallization from MeOH−ether. **2D** (8.22 g, 39 mmol, 89% yield): δ_H (DMSO-d_6) 4.57 (2H, s, CH_2OH), 7.27 (1H, s, pz), 7.82 (1H, t, J = 5.9, py-H_4), 8.39 (1H, d, J = 8.4, py-H_3), 8.48 (1H, t, J = 7.6, py-H_5), 8.70 (1H, d, J = 5.2, py-H_6); IR (KBr) 3292, 3129, 3003, 2768, 1608 cm^{-1}; ESI-MS: *m*/*z* 176.1 (M − Cl).

(iii) Preparation of 2E. 2D (6.02 g, 28.6 mmol) was dissolved in $SOCl_2$ (50 mL) and refluxed for 30 min. The excess $SOCl_2$ was removed under reduced pressure, the residue was dissolved in ethanol, and the solution was filtered. The product **2E** (5.95 g, 26.0 mmol, 91% yield) was obtained as a brownish solid by slow addition of ether. **2E**: δ_H (DMSO-d_6) 4.89 (2H, s, CH_2Cl), 7.40 (1H, s, pz), 7.79 (1H, t, J = 6.6, py-H_4), 8.35 (1H, d, J = 7.6, py-H_3), 8.43 (1H, t, J = 7.6, py-H_5), 8.71 (1H, d, J = 5.6, py-H_6); IR (KBr) 3122, 3067, 2953, 1631, 1616, 785 cm^{-1}.

(iv) Preparation of 2-H. To a dry THF solution of PPh_3 (2.82 g) was added lithium wire (186 mg) cut in small pieces. Stirring the mixture for 3 h at ambient temperature gave $LiPPh_2$ as a dark red solution. The mixture was cooled with a dry ice−MeOH bath, and **2E** (1.31 g, 5.7 mmol) was added in one portion. After the mixture was stirred for 10 min at the same temperature, the mixture was further stirred for 2 h at 0 °C and then for 30 min at room temperature. Addition of deoxygenated water was followed by extraction with deoxygenated ether (three times). The ether extract was dried over $MgSO_4$, filtered, and concentrated to 10 mL. Products were separated by silica gel column chromatography under argon using dry and deoxygenated solvents. Elution with Et_2O−

(12) The unsymmetrical coordination of the Pd_2(allyl) moiety in **5c** is an artifact due to the disorder of the allyl ligand (supine vs prone).

(13) For cationic complexes, M^+ stands for the molecular weight of the cationic part.

(14) (a) Reference 4a. (b) White, D. A. *Inorg. Synth.* **1972**, *13*, 61.

(15) Despite several attempts an analytically pure sample could not be obtained.

(16) The wrong structure of **2B** in the Supporting Information of ref 5d has been corrected.

hexane (1:1) was followed by elution with ether. From the second ether eluent, **2**-H (1.33 g, 3.9 mmol, 68% yield) was isolated as a white solid after removal of the volatiles under reduced pressure. **2**-H: δ_H ($CDCl_3$) 3.47 (2H, s, H12), 6.43 (1H, s, H4), 7.11 (1H,m, H9), 7.33−7.35 (6H, m, Ph), 7.46−7.50 (4H, m, Ph), 7.52 (1H, d, J = 7.8, H7), 7.61 (1H, dt, J = 8.0 and 1.6, H8), 8.54 (1H, d, J = 4.8, H10), 11.01 (1H, bs, N−H); δ_C ($CDCl_3$) 27.7 (dd, J_{C-H} = 132, J_{P-H} = 15, C11), 104.0 (dd, J_{C-H} = 174, J_{P-H} = 6, C4), 120.0 (d, J_{C-H} = 163, C7), 122.6 (d, J_{C-H} = 164, C9), 128.4 (dd, J_{C-H} = 162, J_{C-P} = 7, C14), 128.78 (d, J_{C-H} = 160, C15), 132.7 (dd, J_{C-H} = 162, J_{C-P} = 21, C13), 136.8 (d, J_{C-H} = 163, C8), 138.2 (d, J_{C-P} = 15, C12), 144.6 (s), 147.8 (s), 149.2 (s, C3/5/6), 149.3 (d, J_{C-H} = 177, C10); FD-MS *m/z* 343 (M^+). Anal. Calcd for $C_{21}H_{18}N_3P$: C, 73.44; H, 5.38; N, 12.24. Found: C, 73.01; H, 5.51; N, 11.67.

[(cod)Ir(PNNN)Ir(cod)]BF_4 (5a). To **2**-H (180 mg, 0.52 mmol) dissolved in CH_2Cl_2 (20 mL) was added **3a** (520 mg, 1.04 mmol). After 2 min Et_3N (74 μL, 0.52 mmol) was added and the solution was stirred for 30 min. Evaporation of the solvent gave a dark red solid, which was dissolved in methanol and the resultant solution was filtered through a Celite pad to give an orange solution. The methanol solution was concentrated to 7 mL at 60 °C. Cooling to −12 °C gave **5a** (332 mg, 0.32 mmol, 62% yield). **5a**: δ_H ($CDCl_3$) 1.43−2.64 (16H, m, cod), 2.97 (1H, br, cod), 3.29 (1H, br, cod), 3.92−3.99 (2H, m, cod), 4.26−4.41 (2H, m, H11), 4.69−4.82 (3H, m, cod), 5.34 (1H, br, cod), 7.15 (1H, s, H4), 7.38−7.63 (11H, m, py + Ph), 7.84 (1H, d, J = 5.9, H10), 8.01−8.11 (2H, m, H7,8); δ_P ($CDCl_3$) 34.9 (s); δ_C ($CDCl_3$) 26.1, 28.5, 29.8, 31.6 (cod), 33.9 (td, J_{C-H} = 134, J_{C-P} = 58, C11), 35.0, 38.3 (cod), 61.4 (d, J_{C-H} = 157, cod), 64.2 (d, J_{C-H} = 160, cod), 66.3, 67.4, 67.7 (cod), 75.4 (d, J_{C-H} = 154, cod), 85.6 (d, J_{C-H} = 159, cod), 94.8 (d, J_{C-H} = 154, cod), 101.7 (dd, J_{C-H} = 180, J_{C-P} = 9, C4), 121.5 (d, J_{C-H} = 165, C7), 124.5 (d, J_{C-H} = 168, C9), 129.2−135.2 (Ph), 141.0 (d, J_{C-H} = 172, C8), 147.5 (d, J_{C-H} = 181, C10), 153.1, 156.3, 158.3 (s, C3/5/6); IR (KBr) 2916, 2882, 2833, 1611, 1454, 1083 cm^{-1}; ESI-MS[13] *m/z* 942.5 (M^+), 832.5 (M^+ − cod). Anal. Calcd for $C_{37}H_{31}Ir_2BF_4$: C, 43.15; H, 4.01; N, 4.08. Found: C, 42.98; H, 4.07; N, 3.96.

[(cod)Rh(PNNN)Rh(cod)]BF_4 (5b). 5b (bright orange solid; 62% yield) was prepared as described for **5a**. **5b**: δ_H ($CDCl_3$) 1.6−2.9 (16H, m, cod), 3.4−5.9 (8H, br, cod), 3.99 (2H, d, J = 8.4, H11), 6.84 (1H, s, H4), 7.28 (1H, t, J = 6.0, H9), 7.50−7.30 (10H, m, Ph), 7.68 (1H, d, J = 5.2, H10), 7.75 (1H, d, J = 7.6, H7), 7.92 (1H, t, J = 7.6, H8); δ_P ($CDCl_3$) 37.2 (d, J_{P-Rh} = 154.6); δ_C (CD_2Cl_2) 31.0 (td, J_{C-H} = 133, J_{C-P} = 27, C11), 47.7 (s, cod), 78.9 (dd, J_{C-H} = 162, J_{C-P} = 12, (cod)Rh(P)), 101.0 (dd, J_{C-H} = 176, J_{C-P} = 9, C4), 120.8 (d, J_{C-H} = 163, C7), 123.4 (d, J_{C-H} = 171, C9), 129.1−131.4 (Ph), 140.02 (d, J_{C-H} = 171, C8), 147.3 (d, J_{C-H} = 188, C10), 152.9, 153.1, 156.2 (s, C3/5/6); IR (KBr) 2932, 2878, 2831, 1608, 1450, 1083 cm^{-1}; ESI-MS:[13] *m/z* 764.2 (M^+), 654.3 (M^+ − cod). Anal. Calcd for $C_{38}H_{35}OBF_4Rh_2$ (**5b**·MeOH): C, 51.66; H, 5.13; N, 4.76. Found: C, 51.20; H, 4.92; N, 4.83.

[(allyl)Pd(PNNN)Pd(allyl)]BF_4 (5c). Et_3N (35 μL, 0.25 mmol) was added to a mixture of **2**-H (87 mg, 0.25 mmol) and **3c** (173 mg, 0.50 mmol) dissolved in 10 mL of CH_2Cl_2. The solution was stirred for 30 min, and the volatiles were removed in vacuo. The residue was washed twice with cold methanol and ether, extracted with CH_2Cl_2, and filtered through a Celite pad to give a colorless solution. Concentration of the solution under reduced pressure to 3 mL and slow addition of ether gave **5c** (a mixture of diastereomers; 156 mg, 0.22 mmol, 86% yield) as a colorless solid. **5c**: δ_H (CD_2Cl_2) 2.76 (1H, t, J = 14.8, allyl), 3.15 (1H, d, J = 12.7, allyl), 3.33 (0.6H, d, J = 12.1, allyl), 3.46 (0.4H, d, J = 12.3, allyl), 3.72−4.15 (6H, m, H11 + allyl), 4.89 (0.6H, t, J = 5.2, allyl), 5.09 (0.4H, t, J = 5.5, allyl), 5.65−5.88 (2H, m, allyl), 6.78 and 6.77 (1H, s, H4), 7.31 (1H, t, J = 6.7, H9), 7.45−7.78 (11H, m, H7 + Ph), 8.03 (1H, t, J = 6.5 Hz, H8), 8.53 (1H, d, J = 5.1, H10); δ_P (DMSO-d_6) 36.7 (s); δ_P (CD_2Cl_2) 33.2 (s), 32.7 (s) (5:6; two diastereomers); δ_C (could not be analyzed owing to the presence of two isomers). IR (KBr) 3062, 1603, 1453, 1052 cm^{-1}; ESI-MS: [13] *m/z* 638.1 (M^+), 611.9 (M^+ − allyl + OH), 597.2 (M^+ − allyl), 571.8 (M^+ − 2allyl + OH), 556.2 (M^+ − 2allyl). Anal. Calcd for $C_{27}H_{27}N_3PPd_2BF_4$: C, 44.53; H, 3.77; N, 5.56. Found: C, 44.78; H, 3.76; N, 5.80.

[Ir(PNNN-H)(cod)]$_2$(BF_4)$_2$ (6). Slow addition of **3a** (170 mg, 0.34 mmol) to **2**-H (130 mg, 0.38 mmol) dissolved in 20 mL of CH_2Cl_2 gave a yellow solution, out of which a white solid precipitated. After 1 h the volatiles were removed under reduced pressure. The resultant residue was washed with THF (twice) and ether (once) and dried in vacuo to give **6** as a white solid (241 mg, 0.17 mmol, 96% yield). *6*: δ_H (CD_2Cl_2) 1.8−2.0 (4H, br, cod), 2.4−2.6 (2H, br, cod), 2.6−2.8 (2H, br, cod), 3.2−3.4 (3H, m, 3H, H11 + cod), 3.7−3.8 (1H, m, cod), 5.10 (1H, s, H4), 6.88 (2H, br, cod), 7.29−7.55 (8H, m, Ph + H7,9), 7.7−7.8 (4H, m, Ph), 7.88 (1H, t, J = 7.6 Hz, H8), 7.98 (1H, d, J = 5.1 Hz, H10); δ_P (DMSO-d_6) −5.5; δ_P (solid) 0.59; IR (KBr) 2962 (m), 1261 (m), 1084 (s), 1028 cm^{-1} (s); ESI-MS:[13] *m/z* 644.6 (M^+/2), 942.5 (M^+ − PNNN − 2H), 1285.0 (M^+ − H), 1373.0 (M^+ + BF_4). Anal. Calcd for $C_{59}H_{32}N_6P_2Cl_2Ir_2B_2F_8$ (**6**·CH_2Cl_2): C, 45.83; H, 4.04; N, 5.44. Found: C, 45.43; H, 4.22; N, 5.60.

[(cod)Ir(PNNN)Rh(cod)]BF_4 (7a). To **6** (157 mg, 0.11 mmol) suspended in CH_2Cl_2 (20 mL) was added NEt_3 (34 μL, 0.24 mmol, 1.1 equiv), and the resultant mixture was stirred for 1 h. The suspension turned into an orange solution, which was slowly added to a CH_2Cl_2 solution of **3b** (96 mg, 0.24 mmol, 1.1 equiv). The mixture turned dark red, and after 15 min, the solution was washed with deoxygenated water (20 mL) two times to remove $HNEt_3$·BF_4. The organic layer was dried over $MgSO_4$, filtered through a Celite pad, and concentrated to 3 mL under reduced pressure. Slow addition of ether led to the precipitation of **7a** as a bright orange solid (171 mg, 0.18 mmol, 83% yield). **7a**: δ_H (CD_2Cl_2) 1.35−3.2 (16H, br, cod), 3.30−5.7 (10H, br, cod + H11), 6.80 (1H, s, H4), 7.33 (1H, t, J = 6, H9), 7.40−7.80 (12H, m, py + Ph), 7.96 (1H, t, J = 7.8, H8); δ_P (CD_2Cl_2) 38.1 (s); δ_C (CD_2Cl_2) 26.0 (t, J_{C-H} = 132, cod), 28.8 (t, J_{C-H} = 136, cod), 31.3 (td, J_{C-H} = 131, J_{C-P} = 33, C11), 32.7 (t, J_{C-H} = 133 Hz, cod), 34.8 (t, J_{C-H} = 133 Hz, cod), 38.1 (t, J_{C-H} = 132, cod), 64.0 (d, J_{C-H} = 153, cod), 65.6 (d, J_{C-H} = 160, cod), 79.0 (d, J_{C-H} = 153, cod), 83.08 (d, J_{C-H} = 144, cod), 85.2 (d, J_{C-H} = 148, cod), 94.9 (d, J_{C-H} = 153, cod), 101.1 (dd, J_{C-P} = 9, J_{C-H} = 177, C4), 121.3 (d, J_{C-H} = 166, C7), 123.7 (d, J_{C-H} = 170, C9), 129.0−134.9 (Ph), 140.1 (d, J_{C-H} = 165, C8), 147.4 (d, J_{C-H} = 183, C10), 152.6 (s, C5/6), 156.0 (d, J_{C-P} = 6, C3), 156.3 (s, C5/6); IR (KBr) 2916 (m), 2879 (m), 2831 (m), 1608 (m), 1449 (m), 1060 (s) cm^{-1}; ESI-MS[13] *m/z* 854.3 (M^+ − cod). Anal. Calcd for $C_{37}H_{41}N_3BF_4PRhIr$: C, 47.24; H, 4.39; N, 4.46. Found: C, 47.05; H, 4.63; N, 4.01.

[(cod)Ir(PNNN)Pd(allyl)]BF_4 (7b). (i) From 6. 7b was obtained in 89% yield as described for **7a**. **(ii) From 12.** To a mixture of **12** (56 mg, 0.087 mmol) and NEt_3 (5 μL) dissolved in CH_2Cl_2 (5 mL) was slowly added a CH_2Cl_2 solution (5 mL) of **3c** (30 mg, 0.088 mmol) and Et_3N (5 μL). The solution was stirred for 15 min and concentrated to 4 mL under reduced pressure, and addition of diethyl ether gave **7b** as a beige solid (74 mg, 0.084 mmol, 97% yield). **7**b: δ_H (CD_2Cl_2) 1.73−2.50 (8H, m, cod), 3.24 (2H, t, J = 10.7, allyl), 3.38 (1H, s, cod), 3.92−4.01 (3H, m, H11 + cod), 4.11 (1H, d, J = 5.9, allyl), 4.58 (1H, d, J = 5.1, allyl), 5.22 (2H, s, cod), 5.81 (1H, m, allyl), 6.83 (1H, s, H4), 7.38 (1H, t, J = 6.1, H9), 7.45−7.70 (10H, m, Ph), 7.77 (1H, d, J = 8.0, H7), 7.99 (1H, t, J = 7.8, H8), 8.53 (1H, d, J = 4.9, H10); δ_P (CD_2Cl_2) 37.70 (s); δ_C (CD_2Cl_2) 28.7 (t, J_{C-H} = 127, cod), 30.4 (td, J_{C-H} = 134, J_{C-P} = 32.2, C11), 31.4 (t, J_{C-H} = 125, cod), 31.6 (t, J_{C-H} = 128, cod), 34.9 (t, J_{C-H} = 124, cod), 60.5 (t, J_{C-H} = 159, allyl), 62.7 (d, J_{C-H} = 161, cod), 63.0 (d, J_{C-H} = 154, cod), 63.0 (t, J_{C-H} = 157, allyl),

89.8 (dd, $J_{C-H} = 149$, $J_{C-P} = 12$, cod), 93.2 (dd, $J_{C-H} = 155$, $J_{C-P} = 10$, cod), 101.7 (dd, $J_{C-H} = 177$, $J_{C-P} = 10$, C4), 115.3 (d, $J_{C-H} = 163$, allyl), 121.5 (d, $J_{C-H} = 168$, C7), 124.3 (d, $J_{C-H} = 168$, C9), 129.2 (d, $J_{C-H} = 163$, Ph), 129.3−133.8 (Ph), 140.2 (d, $J_{C-H} = 164$, C8), 152.3 (s, C5/6), 152.9 (d, $J_{C-H} = 183$, C10), 155.9 (d, $J_{C-P} = 7$, C3), 156.53 (s, C5/6); IR (KBr) 2915, 2880, 2834, 1606, 1449, 1054 cm^{-1}; ESI-MS[13] *m/z* 790.3 (M^+), 746.4 (M^+ − allyl). Anal. Calcd for $C_{32.5}H_{35}N_3BF_4PClPdIr$ (**7b**·$0.5CH_2Cl_2$): C, 42.45; H, 3.83; N, 4.57. Found: C, 42.05; H, 3.86; N, 4.57.

[(cod)Rh(PNNN)Ir(cod)]BF_4 (8a). Addition of NEt_3 (68 μL, 0.49 mmol) to a mixture of **6** (327 mg, 0.22 mmol) and **3b** (200 mg, 0.49 mmol) dissolved in CH_2Cl_2 (20 mL) caused a color change to red. After 20 min the solution was washed twice with deoxygenated water, and the CH_2Cl_2 layer was dried over $MgSO_4$. Filtration through a Celite pad, concentration to 5 mL under reduced pressure, and slow addition of diethyl ether gave **8a** as a bright red precipitate (368 mg, 0.39 mmol, 87% yield). **8a**: δ_H (CD_2Cl_2) 1.5−2.6 (16H, m, cod), 3.7−5.3 (8H, br, cod), 4.03 (2H, d, $J = 8.0$, H11), 6.71 (1H, s, H4), 7.3−7.6 (11H, m, Ph + H9), 7.74 (1H, d, $J = 7.0$, H7), 7.87 (1H, d, $J = 5.3$, H10), 8.01 (1H, t, $J = 7.8$, H8); δ_P (CD_2Cl_2) 38.8 (d, $J_{P-Rh} = 155$ Hz); δ_C (CD_2Cl_2) 31.2 (td, $J_{C-H} = 134$, $J_{C-P} = 28$, C11), 27−32 (m, cod), 79.0 (dd, $J_{C-H} = 159$, $J_{C-Rh} = 12$, C16), 101.7 (dd, $J_{C-H} = 178$, $J_{C-P} = 10$, C4), 121.0 (d, $J_{C-H} = 167$, C7), 124.2 (d, $J_{C-H} = 169$, C9), 129.2−131.5 (Ph), 141.0 (d, $J_{C-H} = 166$, C8), 147.5 (d, $J_{C-H} = 178$, C10), 153.5, 153.7, 158.3 (s, C3/5/6); IR (KBr) 2915, 2878, 2830, 1611, 1453, 1083 cm^{-1}; ESI-MS[13] *m/z* 854.2 (M^+), 744.4 (M^+ − allyl). Anal. Calcd for $C_{37}H_{41}N_3BF_4PRhIr$: C, 47.24; H, 4.39; N, 4.46. Found: C, 46.85; H, 4.36; N, 4.31.

[(allyl)Pd(PNNN)Ir(cod)]BF_4 (8b). 8b (red powder; 82% yield) was prepared as described for **5a**. **8b**: δ_H (CD_2Cl_2) 1.71 (2H, br, cod), 1.92 (2H, br, cod), 2.28 (4H, br, cod), 2.68 (1H, br, allyl), 3.70−4.20 (8H, m, H11 + cod + allyl), 5.24 (1H, t, $J = 6.8$, allyl), 5.69 (1H, m, allyl), 6.76 (1H, s, H4), 7.37 (1H, td, $J_{C-H} = 6.6$ and 1.2, H9), 7.40−7.7 (10H, m, Ph), 7.76 (1H, d, $J = 7.6$, H7), 7.89 (1H, d, $J = 5.6$, H10), 8.00 (1H, td, $J_{C-H} = 8.0$ and 1.2, H8); δ_P (CD_2Cl_2) 34.0; δ_C {^{1}H}[17] (CD_2Cl_2) 30.3 (br, cod), 30.4 (d, $J_{C-P} = 22$), 32.2 (br, cod), 51.0 (d, $J_{C-P} = 5$, allyl), 65.0 (br, cod), 84.1 (d, $J_{C-P} = 31$, allyl), 102.7 (d, $J_{C-P} = 8$, C4), 118.6 (d, $J_{C-P} = 3$, allyl), 120.7 (s, C7), 124.3 (s, C9), 129.1−132.7 (Ph), 141.2 (s, C8), 147.2 (s, C10), 153.7 (d, $J_{C-P} = 5$, C3), 155.0, 158.5 (s, C5/6); IR (KBr) 1608, 1464, 1084, 1053 cm^{-1}; ESI-MS[13] *m/z* 790.3 (M^+), 748.4 (M^+ − allyl). Anal. Calcd for $C_{32}H_{34}N_3PIrPdBF_4$: C, 43.82; H, 3.90; N, 4.88. Found: C, 43.75; H, 3.81; N, 4.79.

[Ir(PNNP-H)(cod)]$_2$(BF_4)$_2$ (9). Slow addition of **3a** (500 mg, 1.00 mmol) to **1**-H (592 mg, 1.12 mmol) dissolved in 5 mL of CH_2Cl_2 caused precipitation of a white solid. After 30 min the volatiles were removed under reduced pressure. The resultant residue was washed with THF and ether and dried in vacuo to give **9** as a white solid (835 mg, 0.49 mmol, 98% yield). **9**: δ_H (DMSO-d_6) 1.0−4.6 (32H, m, H6,7 + cod), 5.1 (2H, s, H4), 5.7−8.3 (40H, m, Ph), 11.60 (2H, s, N−H); δ_P (DMSO-d_6) 4.4 (d, $J_{PP} = 42$), −16.1 (d, $J_{PP} = 42$); δ_C (DMSO-d_6) 27.2 (td, $J_{C-H} = 131$, $J_{C-P} = 21$, C6), 30.1 (d, $J_{C-H} = 132$, cod), 32.3 (td, $J_{C-H} = 128$, $J_{C-P} = 27$, C7), 67.1 (overlapped, cod), 101.5 (dd, $J_{C-H} = 183$, $J_{C-P} = 9$, C4), 128.6−138.3 (Ph), 142.1 (s, C3), 156.8 (d, $J_{C-P} = 9$, C5); IR (KBr) 3053 (m), 2944 (m), 1560 (m), 1434 (s), 1084 (s), 1032 (s) cm^{-1}; ESI-MS[13] *m/z* 765.4 (M^+/2), 1529.1 (M^+ − H), 1615.0 (M^+ − H + BF_4). Anal. Calcd for $C_{74}H_{76}N_4P_4Ir_2B_2F_8$: C, 52.18; H, 4.49; N, 3.29. Found: C, 51.81; H, 4.72; N, 3.11.

[(cod)Ir(PNNP)Rh(cod)]BF_4 (10a). NEt_3 (107 μL, 1.1 equiv) was added to **9** (584 mg, 0.34 mmol) suspended in CH_2Cl_2 (20 mL), and the resultant mixture was stirred for 12 h to give an orange solution. Upon slow addition of **3b** (278 mg, 0.686 mmol) the color changed to dark red. After 15 min the solution was washed two times with deoxygenated water (15 mL), and the CH_2Cl_2 layer was dried over $MgSO_4$. The solution was filtered through a Celite pad and concentrated to 3 mL under reduced pressure. Slow addition of hexane led to the precipitation of **10a** as an orange solid (675 mg, 0.635 mmol, 93% yield). **10a**: δ_H ($CDCl_3$) 1.3−3.2 (18H, br, cod), 3.6−4.3 (4H, m, H6,7), 4.3−4.7 (4H, br, cod), 6.27 (2H, bt, $J = 6.6$, cod), 6.37 (1H, s, H4), 7.3−7.8 (20H, m, Ph); δ_P ($CDCl_3$) 31.9 (s), 35.0 (d, $J_{Rh-P} = 154$ Hz); δ_C (CD_2Cl_2) 25.7 (td, $J_{C-H} = 125$, $J_{C-Rh} = 3$, cod), 25.8 (td, $J_{C-H} = 138$, $J_{C-Rh} = 3$, cod), 28.5 (t, $J_{C-H} = 121$, cod), 30.6 (td, $J_{C-H} = 138$, $J_{C-P} = 27$, C6/7-Rh), 30.5 (td, $J_{C-H} = 133$, $J_{C-P} = 33$, C6/7-Ir), 32.3 (m, cod), 34.0 (t, $J_{C-H} = 131$, cod), 37.0 (m, cod), 38.3 (m, cod), 61.7 (d, $J_{C-H} = 149$, (cod)Ir), 61.8 (d, $J_{C-H} = 149$, (cod)Ir), 75.3 (dd, $J_{C-H} = 150$, $J_{C-Rh} = 12$, (cod)Rh), 77.4 (dd, $J_{C-H} = 155$, $J_{C-Rh} = 12$, (cod)-Rh), 86.6 (dd, $J_{C-H} = 158$, $J_{C-P} = 17$, (cod)Ir), 94.6 (dd, $J_{C-H} = 158$, $J_{C-P} = 8$, (cod)Ir), 100.9 (ddd, $J_{C-H} = 151$, $J_{C-Rh,C-P} = 14$ and 7, (cod)Rh), 101.9 (dt, $J_{C-H} = 182$, $J_{C-P} = 10$, C4), 105.8 (dt, $J_{C-H} = 158$, $J_{C-P,C-Rh} = 7$, (cod)Rh), 128−135 (Ph), 153.7 (dd, $J_{C-P,C-Rh} = 8$ and 3, C3), 156.2 (d, $J_{C-P} = 6$, C5); IR (KBr) 2920, 1434, 1084 cm^{-1}; ESI-MS[13] *m/z* 975.3 (M^+), 865.6 (M^+ − cod). Anal. Calcd for $C_{45}H_{49}N_2BF_4P_2RhIr$: C, 50.90; H, 4.65; N, 2.63. Found: C, 51.08; H, 4.75; N, 2.58.

[(cod)Ir(PNNP)Pd(allyl)]BF_4 (10b). 10b (yellow solid; 90% yield) was prepared as described for **10a**. **10b**: δ_H (CD_2Cl_2) 1.4−3.9 (9H, m, cod + allyl), 2.96 (1H, br, cod), 3.7−3.9 (3H, m, H6,7 or cod or allyl), 3.9−4.1 (3H, m, H6,7 or cod or allyl), 4.14 (1H, br, cod), 4.94 (1H, br, cod), 5.31−5.34 (2H, m, allyl), 5.7−5.8 (1H, m, allyl), 6.36 (1H, s, H4), 7.4−7.8 (20H, m, Ph); δ_P (CD_2Cl_2) 28.1 (s), 33.7 (s); δ_C (CD_2Cl_2) 27.3 (t, $J_{C-H} = 125$, cod), 29.7 (t, $J_{C-H} = 122$, cod), 30.2 (td, $J_{C-H} = 134$, $J_{C-P} = 32$, C7−Ir), 31.0 (td, $J_{C-H} = 135$, $J_{C-P} = 27$, C6−Rh), 32.7 (t, $J_{C-H} = 129$, cod), 36.3 (t, $J_{C-H} = 122$, cod), 51.6 (td, $J_{C-H} = 152$, $J_{C-P} = 4$, allyl), 60.4 (d, $J_{C-H} = 151$, cod), 61.4 (d, $J_{C-H} = 155$, cod), 81.2 (td, $J_{C-H} = 159$, $J_{C-P} = 29$, allyl), 87.9 (dd, $J_{C-H} = 149$, $J_{C-P} = 16$, cod), 93.7 (dd, $J_{C-H} = 154$, $J_{C-P} = 10$, cod), 102.1 (dt, $J_{C-H} = 177$, $J_{C-P} = 9$, C4), 118.5 (dd, $J_{C-H} = 160$, $J_{C-P} = 6$, allyl), 129. 1−134.6 (Ph), 154.8 (d, $J_{C-P} = 6$, C3/5), 156.1 (d, $J_{C-P} = 7$, C3/5); IR (KBr) 3052, 2914, 2877, 2830, 1434, 1058 cm^{-1}; ESI-MS[13] *m/z* 911.2 (M^+), 869.4 (M^+ − allyl). Anal. Calcd for $C_{40}H_{42}N_2BF_4P_2PdIr$: C, 48.13; H, 4.24; N, 2.80. Found: C, 48.26; H, 4.42; N, 2.80.

[Ir(PNNN-H)$_2$(cod)]BF_4 (11). **2**-H (49 mg, 0.014 mmol) and **3a** (30 mg, 0.006 mmol, 0.42 equiv) were dissolved in CH_2Cl_2 (3 mL). After the mixture was stirred for 10 min, ether was added to precipitate the product. Removal of the solvent by a cannula and washing twice with diethyl ether gave **11** as a white solid (65 mg, 0.006 mmol, 100% yield). **11**: δ_H (CD_2Cl_2) 1.4−1.8 (6H, br, cod), 2.10 (2H, br, cod), 3.40 (2H, br, cod), 3.85 (4H, br, cod + H11), 4.3−4.6 (2H, m, H11), 6.65 (1H, s, H4), 6.8−7.9 (27H, m, aromatic), 8.73 (1H, d, $J = 3.8$, H10), 8.99 (1H, d, $J = 4.4$, H10); δ_H (−80 °C) 12.93 (1H, bs, NH), 16.41 (1H, bs, NH); δ_P (CD_2Cl_2) −19.6 (d, $J_{P-P} = 12$, P in the P,N chelate), 8.9 (d, $J_{P-P} = 12$, κ^1(P)); δ_C {^{1}H}[17] (CD_2Cl_2) 30.8 (t, $J_{C-H} = 129$ cod), 32.1 (d, $J_{C-P} = 26$, C11), 32.2 (d, $J_{C-P} = 25$, C11), 32.9 (t, $J_{C-H} = 131$, cod), 63.4 (br. d, $J_{C-H} = 150$, cod), 64.5 (dd, $J_{C-H} = 160$, $J_{C-P} = 7$, cod**),** 101.9 (dd, $J_{C-H} = 177$, $J_{C-P} = 12$, C4), 104.3 (dd, $J_{C-H} = 179$, $J_{C-P} = 7$, C4), 120.4 (d, $J_{C-H} = 163$, C7), 120.8 (d, $J_{C-H} = 163$, C7), 123.8 (d, $J_{C-H} = 164$, C9), 124.2 (d, $J_{C-H} = 163$, C9), 127.6−133.4 (Ph), 137.4 (d, $J_{C-H} = 164$, C8), 137.8 (d, $J_{C-H} = 163$, C8), 142.7, 146.1, 146.2, 147.1, 147.3 (s, C3,5,6), 149.8 (d, $J_{C-H} = 179$, C10), 156.4 (d, $J_{C-P} = 13$, C3); IR (KBr) 2962, 1625, 1261, 1083 (BF_4) cm^{-1}; ESI-MS[13] *m/z* 877.5 (M^+ − cod), 644.4 (M^+ − PNNN-H). Anal. Calcd for $C_{50}H_{48}N_6BF_4P_2Ir$: C, 55.92; H, 4.51; N, 7.83. Found: C, 56.33; H, 4.87; N, 7.20.

(cod)Ir(PNNN) (12). A mixture of **6** (303 mg, 0.21 mmol) and NEt_3 (57 μL, 0.41 mmol) dissolved in 10 mL of CH_2Cl_2 was stirred

(17) J_{C-H} coupling constants could not be determined, owing to the low solubility in organic solvents or instability.

for 30 min. The volatiles were removed under reduced pressure, and the resultant residue was dissolved in hot MeOH (30 mL). Filtration through a Celite pad and concentration to 10 mL under reduced pressure followed by slow cooling to −30 °C gave a red powder. The supernatant was removed by a cannula and the red powder washed once with cold MeOH and twice with cold ether to give **12** as a red solid (164 mg, 0.25 mmol, 62% yield). From the combined organic phases a second crop of **12** (34 mg, 0.05 mmol) was obtained: overall yield 198 mg, 0.31 mmol, 75%). **12**: δ_H (CD_2Cl_2) 2.10 (4H, br, cod), 2.28 (4H, br, cod), 3.33 (2H, br, cod), 3.59 (2H, d, J = 10.4, H11), 5.79 (2H, br, cod), 6.73 (1H, s, H4), 7.07 (1H, dd, J = 7.4 and 1.4, H9), 7.42−7.73 (11H, m, Ph + py), 8.00 (1H, d, J = 8.0, H7), 8.50 (1H, d, J = 4.7, H10); δ_H (DMSO-d_6) 1.6−2.0 (8H, br, cod), 3.62 (2H, d, J = 10.2, H11), 3.87 (4H, br, cod), 6.65 (1H, s, H4), 7.11 (1H, t, J = 6.1, H9), 7.4−7.6 (10H, br, Ph), 7.67 (1H, td, J = 7.4 and 1.4, H8), 7.85 (1H, d, J = 8.0, H7), 8.43 (1H, d, J = 4.1, H10); δ_P (CD_2Cl_2) 31.21; δ_C (CD_2Cl_2) 29.4 (t, J_{C-H} = 126, cod), 32.3 (td, J_{C-H} = 131, J_{C-P} = 33, C11), 33.4 (t, J_{C-H} = 125.6, cod), 58.2 (d, J_{C-H} = 150, cod), 94.3 (dd, J_{C-H} = 155, J_{C-P} = 11, cod), 99.8 (dd, J_{C-H} = 176, J_{C-P} = 10, C4), 119.4 (d, J_{C-H} = 161, C7), 121.0 (d, J_{C-H} = 158, C9), 128.7−132.9 (Ph), 135.7 (d, J_{C-H} = 160, C8), 148.8 (d, J_{C-H} = 164, C10), 154.1, 154.6, 155.2 (s, C3/5/6); IR (KBr) 2910, 2876, 2828, 1610, 1591, 1452, 1433, 1083 cm^{-1}; ESI-MS m/z 642.5 (M^+ + H). Anal. Calcd for $C_{30}H_{33}N_3OPIr$ (**12**·MeCN): C, 53.39; H, 4.93; N, 6.23. Found: C, 53.13; H, 4.59; N, 6.19.

{[Ir(PNNP)(COD)]$_2$H}BF$_4$ (13). To **9** (190 mg, 0.11 mmol) suspended in CH_2Cl_2 (20 mL) was added NEt_3 (34 μL, 1.1 equiv), and the mixture was stirred for 12 h. The solution was washed twice with H_2O and then dried over $MgSO_4$. Filtration and removal of the volatiles under reduced pressure gave **13** as a white solid (93 mg, 0.058 mmol, 53% yield). **13**: δ_H (CD_2Cl_2) 1.5−2.3 (16H, br, cod), 2.99 (4H, br, cod), 3.1−4.0 (8H, m, H6), 4.4 (4H, br, cod), 5.61 (2H, s, H4), 6.6−7.5 (40H, m, Ph), 13.28 (1H, s, N−H); δ_P (CD_2Cl_2) 6.9 (d, J_{P-P} = 29), −19.3 (d, J_{P-P} = 29); ^{13}C NMR data could not be obtained due to the low solubility in organic solvents; IR (KBr) 3053, 1561, 1434, 1084, 694 cm^{-1}; ESI-MS[13] m/z 765.4 ((M^+ + H)/2), 1063.4 (M^+ − PNNP−H), 1527.1 (M^+). Anal. Calcd for $C_{74.75}H_{76.5}N_4BF_4P_4Cl_{1.5}Ir_2$ (**13**·0.75CH_2Cl_2): C, 53.46; H, 4.59; N, 3.33. Found: C, 53.28; H, 4.97; N, 3.38.

[(allyl)Pd{(PNNP-H)Ir(cod)}$_2$](BF$_4$)$_3$ (14b). To **9** (20 mg, 0.012 mmol) suspended in CH_2Cl_2 (5 mL) was added **3c** (4.0 mg, 0.012 mmol), and the suspension was stirred until a red solution was obtained. Then the volatiles were removed under reduced pressure, and the resultant red solid was washed twice with ether to give **14b** (21 mg, 0.011 mmol, 90% yield). **14b**: δ_H (CD_2Cl_2) 2.0−2.4 (16H, br, cod), 3.27 (2H, m, allyl), 3.44 (4H, br, cod), 3.59 (2H, d, J_{C-P} = 10.2, H6 or H7), 3.73 (2H, t, J = 3.92, H6 or H7), 4.05 (2H, d, J = 5.1, allyl), 5.25 (4H, br, cod), 5.6−5.7 (3H, m, H4 + allyl), 7.1−7.6 (40H, m, Ph), 11.42 (2H, s, N−H); δ_P (CD_2Cl_2) 12.2 (s), 27.9 (s); δ_C (CD_2Cl_2) 26.8 (td, J_{C-H} = 136, J_{C-P} = 19, C7−Pd), 29.7 (t, J_{C-H} = 127, cod), 30.7 (td, J_{C-H} = 134, J_{C-P} = 31, C6−Ir), 32.6 (t, J_{C-H} = 127, cod), 62.2 (dd, J_{C-H} = 157, J_{C-P} = 8, cod), 74.7 (tt, J_{C-H} = 151, J_{C-P} = 13, allyl), 93.4 (dd, J_{C-H} = 155, J_{C-P} = 12, cod), 105 (d, J_{C-H} = 181, C4), 122.9 (dd, J_{C-H} = 132, J_{C-P} = 7, allyl), 122.9−133.0 (Ph), 142.92 (s), 159.1 (d, J_{C-P} = 7, C3/5); IR (KBr) 2920, 1561, 1435, 1083 (s), 694 cm^{-1}; ESI-MS[13] m/z 1849.8 (M^+), 1617.0 ({[(PNNP-H)Ir(cod)$_2$](BF$_4$)}$^+$), 911.3 [(PNNP)Ir(cod)Pd(allyl)]$^+$), 765.5 [(cod)Ir(PNNP)Ir(cod)]$^+$). Anal. Calcd for $C_{79}H_{85}N_4B_3F_{12}P_4Cl_2Ir_2$ (**14b**·CH_2Cl_2): C, 45.02; H, 4.07; N, 2.73. Found: C, 45.34; H, 4.11; N, 2.73.

X-ray Crystallography. Single crystals of **5c**, **7a**·2CH_2Cl_2, **7b**·0.5CH_2Cl_2, **8b**, and **12** were obtained by recrystallization from CH_2Cl_2−ether. Diffraction measurements, except for **5c**, were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.710 69 Å) at −60 °C. Indexing was performed from three oscillation images, which were exposed for 3 min. The crystal-to-detector distance was 110 mm ($2\theta_{max}$ = 55°). In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[18] The data collection of **5c** was made on a Rigaku AFC7R automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at room temperature. The unit cell was determined and refined by a least-squares method using 20 independent reflections ($2\theta \approx 20°$). Data were collected with $\omega-2\theta$ scan techniques. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. Absorption correction was made with the Ψ-scan technique. Data collections were performed with a VENTURIS FX 5133 computer. The crystallographic data for **5c** and **7a** are summarized in Table 2. The crystallographic data and CIF files for the other compounds, which appeared in ref 5d and therefore are not included in the Supporting Information, are available from the CSD (**7b**, CCDC 243414; **8b**, CCDC 243413; **12**, CCDC 243415).

Table 2. Crystallographic Data for 5c and 7a

	5c	7a
solvate		2CH_2Cl_2
formula	$C_{27}H_{27}N_3BF_4PPd_2$	$C_{39}H_{45}N_3BF_4PCl_4RhIr$
formula wt	724.11	1110.52
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.638(4)	12.795(3)
b/Å	11.351(3)	13.033(4)
c/Å	12.251(4)	14.044(5)
α/deg	97.89(2)	99.43(1)
β/deg	110.574(8)	103.25(2)
γ/deg	91.28(2)	91.89(2)
V/Å^3	1367.9(8)	2242(1)
Z	2	2
d_{calcd}/g cm^{-3}	1.758	1.644
μ/mm^{-1}	1.423	3.660
no. of diffractions collected	10 296	15 787
no. of variables	361	469
R1 for data with $I > 2\sigma(I)$	0.0658 (for 3082 data)	0.0907 (for 7162 data)
wR2	0.1746 (for all 5648 data)	0.2660 (for all 9062 data)

The structural analysis was performed on an IRIS O2 computer using the teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan.[19] Neutral scattering factors were obtained from the standard source.[20]

The structures were solved by a combination of direct methods (SHELXS-86)[21] and Fourier synthesis (DIRDIF94).[22] Least-squares refinements were carried out using SHELXL-97 [21] (refined on F^2) linked to teXsan. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms were refined using riding models, and other hydrogen atoms were fixed at the calculated positions. For **5c**, one of the two allyl groups was found to be disordered and refined with two components (C4−C5:C4A−C5A = 0.53:0.47). Hydrogen atoms attached to the disordered parts

(18) Higashi, T. Program for Absorption Correction; Rigaku Corp., Tokyo, Japan, 1995.

(19) teXsan; Crystal Structure Analysis Package, version 1.11; Rigaku Corp., Tokyo, Japan, 2000.

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were not included in the refinement. For **7a**, the two CH_2Cl_2 molecules were refined isotropically, and hydrogen atoms attached to CH_2Cl_2 were not included in the refinement. One of the two CH_2Cl_2 molecules, being found to be disordered, was refined by taking into account two components (Cl3−C52−Cl4:ClA−C52A−Cl4A = 0.60:0.40).

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Supporting Information Available: Tables and figures giving crystallographic results (12 pages); data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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