Synthesis and NMR structural studies of allyl(polypyrazolylborate)palladium and platinum complexes

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Abstract

Mono- and binuclear palladium and platinum complexes containing the tetrakis(pyrazolyl)borate ligand were prepared. The solution structure and dynamic properties of these complexes were investigated with NMR techniques. In the mononuclear triphenylphosphine platinum complexes, $PtX(PPh_3)(BPz_4)$, the activation energy for inversion of the boat-like $B(N–N)_2Pt$ ring decreased in the order, $X = I > Cl > Br > \eta^1$-methallyl, as a result of the combined effects exerted by the electronic and steric requirements. Complexes $M(\eta^3$-methallyl$)(BPz_4)$ (M = Pd, Pt) accepted metal ions (Ag^+, $[(\eta^3$-methallyl$)M]^+$) to give the binuclear complexes. 1D and 2D NOE spectra of the complex $[(\eta^3$-methallyl$)Pt(BPz_4)Pt(\eta^3$-methallyl$)]BF_4$ suggested the occurrence of a fast intramolecular interconversion between some conformational isomers arising from the $Pt(N–N)_2B$ ring inversion.

Introduction

Polypyrazolylborate complexes of transition metals continue to attract intensive attention from various chemical points of view [1]. Some rhodium complexes with the borate ligands exhibited an unusual ability to cleave otherwise unreactive carbon–hydrogen bonds of hydrocarbons [2], and others (iron and copper complexes) served as good models for active centers of metal containing oxygenases [3]. From a viewpoint of structural coordination chemistry, the ligands offer unique opportunities to look into detailed dynamic behaviors in solution, particularly by use of NMR spectroscopy [1].

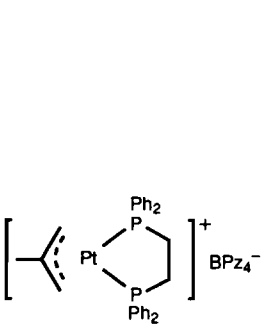
Most of the hitherto synthesized pyrazolylborate complexes of Pd(II) contain the bidentately coordinating tris- and tetrakis(pyrazolyl)borate ligands, and they were shown to exhibit primarily two fluxional movements, one involving the inversion of the boat-like $B(N–N)_2Pd$ ring, and the other the interchange of the free and the coordinated pyrazolyl groups [4, 5]. By contrast, less attention was paid to platinum complexes of polypyrazolylborate with the exception of some complexes having the tridentate coordination mode [6].

We wish to describe here synthesis and fluxional behaviors of some new poly(pyrazolyl)borate complexes of Pt(II) derived from η^3-allylplatinum complexes. For comparison analogous allylic palladium complexes of polypyrazolylborates were also studied.

Results and discussion

Synthesis of complexes

Introduction of the tetrakis(pyrazolyl)borate ligand to platinum complexes was easily done by using η^3-methallylplatinum chloride as the starting material (Scheme 1). The parent η^3-methallyl complex **1a** reacted with 1 equiv. PPh_3 to afford the η^1-methallylplatinum complex **2**. In contrast to the behavior of **1a**, the palladium analog **1b** did not react at all with excess PPh_3. This difference is in accord with the relative ease of η^3-allylpalladium and platinum to rearrange to the η^1-allyl complexes (Pt ≫ Pd) [7]. An attempt to prepare a bis{(η^1-methallyl)platinum} complex bridged by $Ph_2PCH_2CH_2PPh_2$ (dppe) from **1a** and even 1/2 equiv. dppe resulted in the formation of ion pair **3**, whereas treatment of **1a** with 1/2 equiv. $Ph_2PCH_2CH_2$-$CH_2CH_2PPh_2$ gave a satisfactory yield of the bis(η^1-methallyl) complex **4**.



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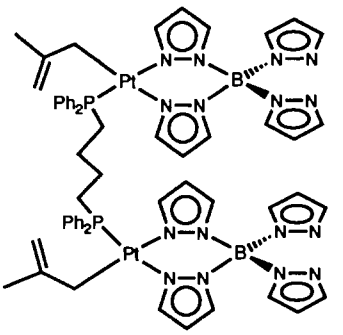

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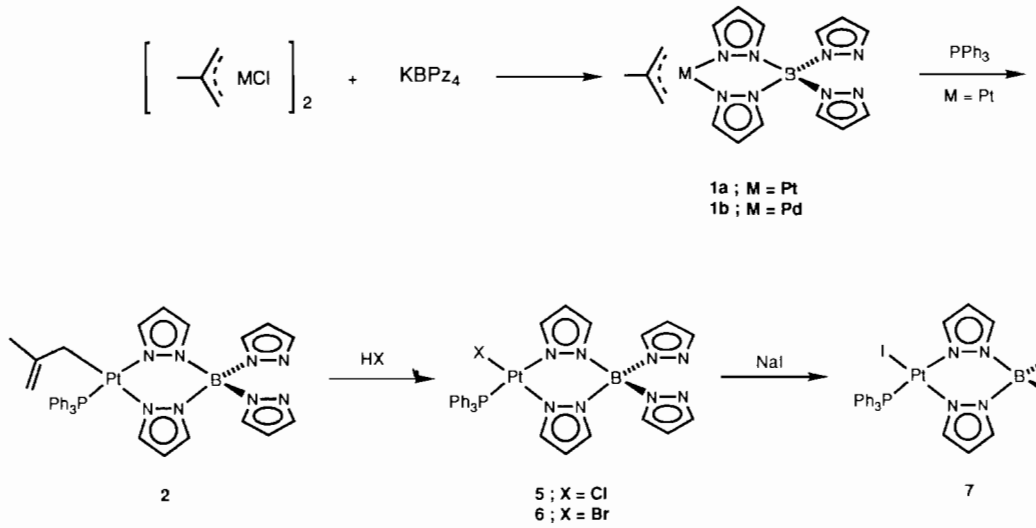
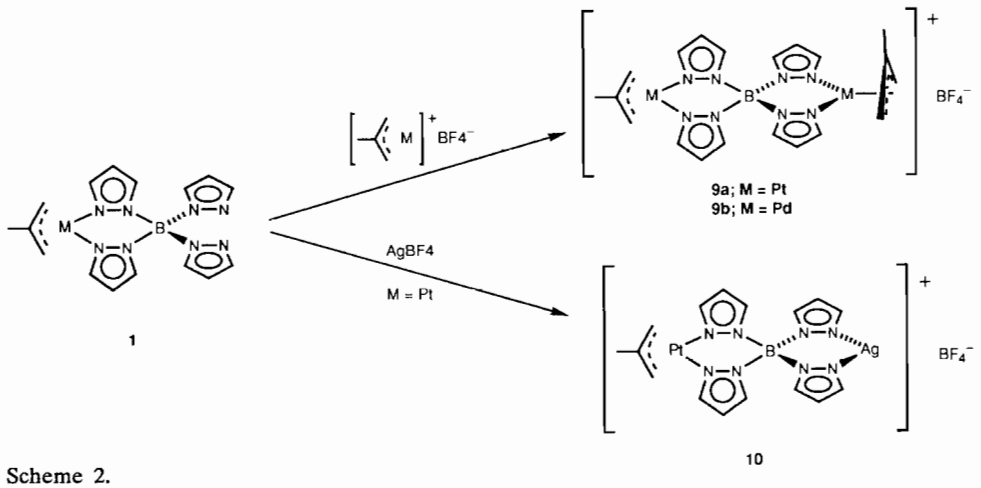
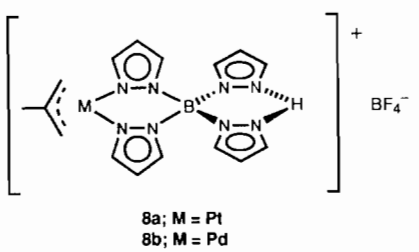


Scheme 1.



Scheme 2.

Treatment of **2** with an equiv. HX (X = Cl, Br) readily afforded the corresponding halo(pyrazolylborate)-platinum complexes **5** and **6** as a result of a facile electrophilic attack of H^+ at the η^1-allyl–platinum bond [7]. The iodide complex **7** could be obtained by treating **5** with sodium iodide. Interestingly, HBF_4 reacted with **1** without cleaving the allyl–metal bond, and instead a 1:1 adduct possibly having the N-protonated structure (**8**) was obtained in good yields. The uncoordinated



pyrazolyl group(s) in **1** interacted with not only a proton but a metal ion, affording bimetallic complexes **9** [8] and **10** (Scheme 2).

^{1}H NMR studies of mononuclear pyrazolylborate complexes

The ^{1}H NMR spectrum of **1a** showed three sets of pyrazolyl ring protons in a ratio 2:1:1 (see Table 1). The assignment of these ring protons was based on the spin coupling patterns, if observable, and NOE results. We attribute each proton resonance of the intensity 1 to the two non-equivalent, uncoordinated rings. This assignment was confirmed by carrying out NOE experiments which indicated the proximity of H^3 (see Table 1) to the *syn* protons of the η^3-methallyl ligand. In the tetrakis(pyrazolyl)borate complexes of η^3-allylplatinum and palladium moieties, there should be two geometrical isomers, i.e. one is **A** and the other

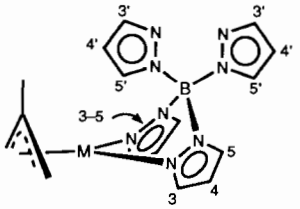
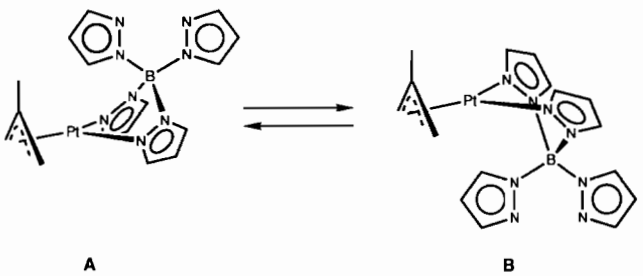


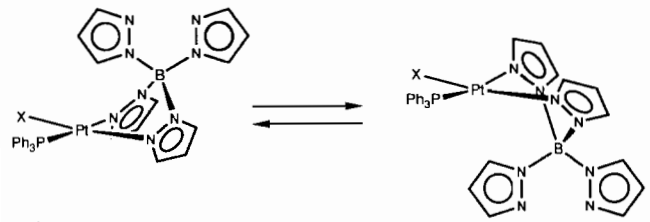
TABLE 1. δ (^{1}H) for mononuclear {tetrakis(pyrazolyl)borate}(η^3-methallyl)metal complexes[a]

Complex	temperature	Coordinated ring			Uncoordinated ring		
		3	4	5	3′	4′	5′
1a	25	7.82[c]	6.35	7.34	7.62, 7.82[c]	6.15, 6.26	6.67, 6.86
1b	25	7.66[b]	6.26[b]	7.02[b]			
	−60	7.62	6.32	7.28	7.64, 7.68	6.17, 6.24	6.63, 6.73
8a	25	7.96	6.50[c]	7.40	7.94, 8.27	6.50[c], 6.61	7.10, 7.13
8b	25	8.02[b]	6.55[b]	7.32[b]			
	−40	7.75	6.45[c]	7.32	7.94, 8.23	6.45[c], 6.62	7.00, 7.05

[a]In $CDCl_3$. [b]Resonances due to the coordinated and uncoordinated ring protons. [c]Overlapped with other resonance.



Scheme 3.



Scheme 4.

B resulting from inversion of the boat-like ring (Scheme 3). Lowering the temperature of the solution containing **1a** down to −90 °C resulted in no spectral change. This may be due to a very fast ring inversion and/or the existence of only one dominant (or almost exclusive) isomer.

In contrast to the spectrum of **1a**, that of the palladium analog **1b** at room temperature showed only one set of pyrazolyl ring proton resonances. However, these separated into the three sets in a ratio 2:1:1 at −60 °C. This spectral feature is most probably associated with fast exchange between the coordinated and uncoordinated pyrazolyl rings via a tridentate tetrakis(pyrazolyl)borate–palladium structure, as already suggested previously for the analogous complex Pd(η^3-CH_2CHCH_2)(BPz_4) [4a], even though the non-equivalent nature of the two uncoordinated rings could not be confirmed in the previous study. An apparently larger activation barrier to the ring exchange in the platinum complex than the palladium complex is in accord with the smaller trend of the Pt(II) atom than the Pd(II) atom to attain the penta-coordination [9].

The two coordinated pyrazolyl groups in the complexes **2** and **5–7** were non-equivalent, as expected. Moreover, the two uncoordinated pyrazolyl groups became non-equivalent at the lower temperatures and equivalent at the higher temperatures owing to the restricted ring inversion (Scheme 4 and Table 2). The barriers to the Pt(N–N)$_2$B ring inversion for these complexes were determined by the variable temperature ^{1}H NMR studies. The results in Table 3 show apparently complicated features. Both electronic and steric effects exerted by the Pt–X (X = halogen, carbon) bonds may play a role in determining these barriers. The large E_a for the chloro complex **5** may be attributable to the strong Pt–N bonds brought about by the high electron-withdrawing ability of the chloride ligand. On the electronic grounds, the Pt–N bonds should become progressively weaker and E_a would become smaller as X in the Pt–X bond is varied from Cl to Br, I, through η^1-methallyl. However, it is conceivable that the large size of the iodide ligand exerts considerable steric constraints about the coordinated pyrazolyl groups, particularly in the transition state of the ring inversion

TABLE 2. δ (^{1}H) for {tetrakis(pyrazolyl)borate}(triphenylphosphine)platinum complexes[a]

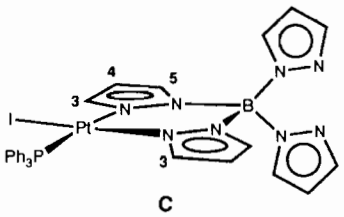
Complex	Coordinated ring (25 °C)			Uncoordinated ring			
	3	4	5	Temperature	3′	4′	5′
2	7.34, 8.02	5.65, 6.03	6.45, 6.96	25	7.70	6.20	6.85
				−90[b]	7.70, 7.80	6.19, 6.30	6.62, 7.17
5	7.5[c], 8.17	5.78, 6.39	7.24, 6.52	40	7.67	6.32	7.10
				−10	7.52, 7.80	6.27, 6.40	6.38, 7.25
6	7.5[c], 8.39	5.80, 6.39	6.55, 7.21	55	7.68	6.32	7.10
				25	7.60, 7.81	6.31, 6.47	6.87, 7.31
7	7.54, 8.49	5.76, 6.33	6.56, 7.13	65	7.70	6.88	6.40
				25	7.62, 7.79	6.26, 6.52	6.77, 7.4[c]

[a]In $CDCl_3$. [b]In CD_2Cl_2. [c]Overlapped with the resonances of PPh_3.

TABLE 3. Activation energies for $Pt(N{-}N)_2B$ ring inversion

Complex	X	E_a (kJ mol^{-1})
2	$CH_2{=}C(Me)CH_2$	39
5	Cl	91
6	Br	72
7	I	102

(C) where the H^3 lies within the coordination plane and thus near to the *cis* ligands. The PPh_3 ligand may also be pushed by the iodide ligand toward the H^3 on the other side. This effect of destabilizing the transition



C

state can explain E_a for the iodide complex which was considerably larger than expected on an electronic basis.

Structure and ^{1}H NMR spectral studies of binuclear polypyrazolylborate complexes

The uncoordinated pyrazolyl groups in **1** accepted a η^3-methallylmetal cation to give the binuclear complex **9** (Scheme 2). The preliminary X-ray structure determination of **9a** (Fig. 1) showed the existence of the spiro structure. Both of the boat-like $Pt(N{-}N)_2B$ rings bend to the direction of the η^3-methallyl methyl, and thus the cation possesses C_2 symmetry. In contrast to **1a**, the ^{1}H NMR spectrum of **9a** showed two sets of pyrazolyl ring protons in a ratio 1:1. At the same time, both *syn* and *anti* protons of the η^3-methallyl ligand gave two resonances. There may be several possibilities

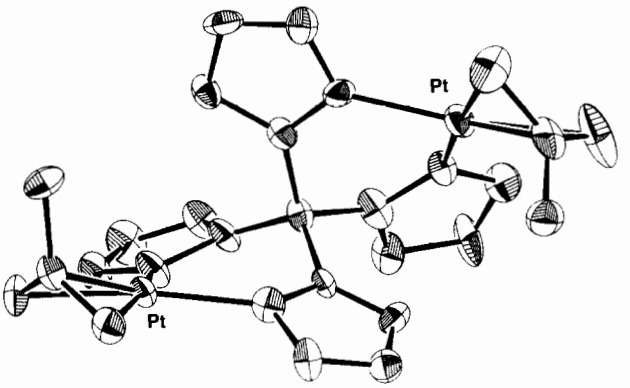
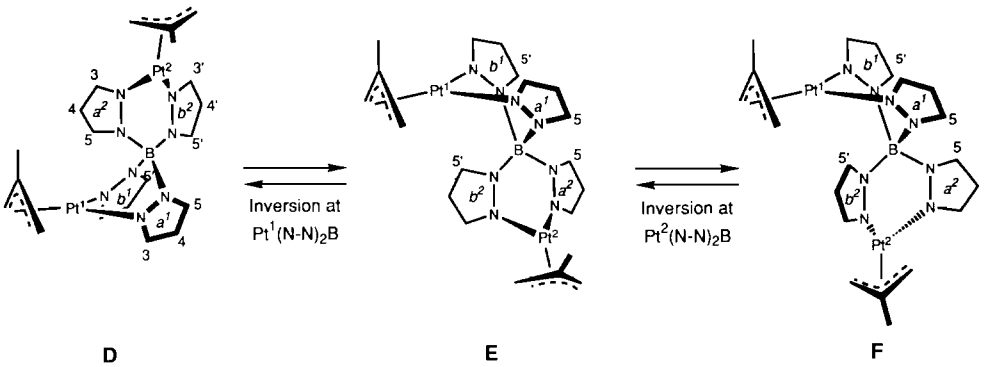


Fig. 1. Molecular structure of **9a**, viewing down nearly the C_2-symmetrical axis. The counteranion BF_4^- was omitted.

concerning the solution structure of **9a**. Both the solid state structure **D** (Scheme 5) and structure **F**, which has resulted from the inversion of both of the $Pt(N{-}N)_2B$ rings in **D**, possess C_2 symmetry. However, structure **E** in which only the $Pt^1(N{-}N)_2B$ ring has inverted (Scheme 5) has no C_2 symmetry, and thus all the four pyrazolyl rings are non-equivalent to each other. It should be pointed out here that the $Pt^2(N{-}N)_2B$ ring inversion in **D** gives rise to the structure (**E′**) which is identical to **E**, and the rapid interconversion between **E** and **E′** leads to coalescence of the a^1 and a^2 ring proton resonances as well as the coalescence of b^1 and b^2 resonances. Similarly to the mononuclear complex **1a**, no spectral change was observed in **9a** at lower temperatures (room temperature to −90 °C). Thus, the ring inversions may be very fast or interlocked to either **D** or **F**, but not to **E**. The palladium complex **9b** exhibited the same spectral features as **9a**.

Each structure shown in Scheme 5 and the mirror image of each constitute a pair of enantiomers. They may interconvert to each other via the intramolecular switching of the coordination of one pyrazolyl groups from Pt^1 to Pt^2 and the other from Pt^2 to Pt^1 or via

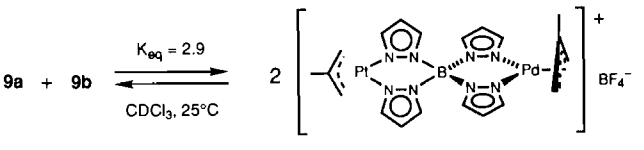


D E F

Scheme 5.

a totally intermolecular ligand exchange. Rotation of the η^3-methallyl ligand by 180° about the Pt–methallyl bond, the occurrence of which, if any, would be via a η^1-methallyl intermediate [10, 11], can also in principle bring about the racemization. The observation of two sets of each proton resonances shown above indicates that the rate of the racemization, if any, is slow on the NMR time scale. However, the intermolecular pyrazolyl ligand exchange must indeed be occuring with the much smaller rate, since mixing two types of binuclear complexes (**9a** and **9b**) in $CDCl_3$ led to gradual increase of the resonances due to the mixed binuclear complex **9c** (Scheme 6).

The NOESY spectrum of **9a** is shown in Fig. 2. Most of the cross peaks in Fig. 2 are associated with the pairs of nearby protons belonging to the same ligand framework. Other than these, two cross peaks between the *syn* protons of the η^3-methallyl ligand and H^3 or $H^{3'}$ were observed as expected from the close distance between them (see before for **1a**). Interestingly, the methyl protons of the η^3-methallyl ligand gave a cross peak with one of the 5-position protons (H^5 or $H^{5'}$). It seems unlikely that one η^3-methallyl group and two pyrazolyl groups that share one platinum atom in coordination bring about a sufficiently close Me–H^5 distance for the observed NOE result. On the other hand, there may indeed be a short distance between the η^3-methallyl methyl on Pt^1 and a^2 ring on Pt^2 (or methyl on Pt^2 and a^1 ring on Pt^1) in **D**, or between the η^3-methallyl methyl on Pt^2 and a^1 ring on Pt^1 in **E**. Thus, a possibility that **F** is the dominant structure in solution can be ruled out.



9c

Scheme 6.

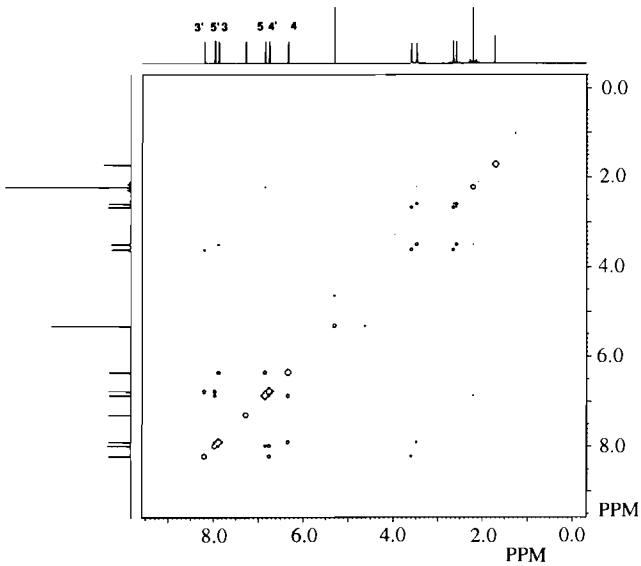


Fig. 2. 600 MHz NOESY spectrum of **9a**. Mixing time was 5 s with 90° excitation and mixing pulses used.

Surprisingly, the NOESY spectrum also exhibited a cross peak associated with a pair of protons each of which belongs to non-equivalent pyrazolyl rings (H^5/$H^{5'}$). Enhancement of the $H^{5'}$ (2%) resonance was also confirmed by selective irradiation at H^5 in the 1D NOE difference spectrum. In the structure of either **D** or **F** in Scheme 5, these two protons are not close to each other. The appearance of this cross peak is attributable to the geometrical isomer **E** in which these two protons are close to each other (H^5 in a^2 and $H^{5'}$ in b^1) and exchange energies. Selective irradiation at H^5 in the 1D NOE difference spectrum also resulted in a small enhancement (<1%) of the intensity of $H^{3'}$. At the moment we cannot explain this result. In conclusion, we propose that in solution the complex **9a** undergoes the fast intramolecular interconversion mainly between **D** and **E** and the slower intermolecular ligand exchange.

Experimental

Most of the commercially available reagents were used without further purification. Silver tetrafluoroborate in n-pentane (purity 90%) was purchased from WAKO Pure Chem. Ind., Ltd. and used after drying under vacuum. Potassium tetrakis(pyrazolyl)borate was prepared by the method of Trofimenko [12]. ^{1}H NMR spectra were obtained on JEOL JMN-PS-100, GSX-270, GSX-400, and Bruker AM600 spectrometers. The chemical shifts were referenced to tetramethylsilane.

Preparation of ***1a, b***

η^3-Methallylplatinum chloride (0.28 g; 0.49 mmol) was treated with potassium tetrakis(pyrazolyl)borate (0.42 g; 1.3 mmol) in CH_2Cl_2 (10 ml). After stirring for 20 min, potassium chloride was filtered off and the filtrate was evaporated under reduced pressure. Recrystallization of residual solids from benzene/n-hexane gave white crystals of **1a** (79%), m.p. 166–170 °C. *Anal.* Calc. for $C_{16}H_{19}N_8BPt$: C, 36.31; H, 3.62; N, 21.17. Found: C, 36.56; H, 3.71; N, 20.91%. ^{1}H NMR ($CDCl_3$) data of the η^3-methallyl group: δ 1.85 (s, $J_{Pt}=75$ Hz, 3H), 2.34 (s, $J_{Pt}=75$ Hz, 2H) 3.24 (s, $J_{Pt}=28$ Hz, 2H). **1b** was prepared similarly (77%): m.p. 168–170 °C. *Anal.* Calc. for $C_{16}H_{19}N_8BPd$: C, 43.62; H, 4.35; N, 25.43. Found: C, 43.94; H, 4.36; N, 25.31%. ^{1}H NMR ($CDCl_3$) data of the η^3-methallyl group: δ 1.78 (s, 3H), 2.79 (s, 2H), 3.55 (s, 2H).

Preparation of ***2***

1a (0.21 g; 0.40 mmol) and triphenylphosphine (0.105 g; 0.40 mmol) were dissolved in benzene (5 ml). Addition of n-hexane gave white microcrystals of **2** (86%), m.p. 164–165 °C. *Anal.* Calc. for $C_{34}H_{34}N_8PBPt$: C, 51.59; H, 4.33; N, 14.16. Found: C, 51.67; H, 4.14; N, 14.13%. ^{1}H NMR ($CDCl_3$) data of the η^1-methallyl group: δ 1.17 (s, 3H), 1.86 (s, $J_{Pt}=76$ Hz, 2H), 4.28 (s, 1H), 4.69 (s, 1H). IR: ν (C=C) 1620 cm^{-1}.

Preparation of ***4***

To a solution of **1a** (0.40 g; 0.76 mmol) in CH_2Cl_2 (5 ml) kept at −7 °C, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (0.16 g; 0.38 mmol) in CH_2Cl_2 (5 ml) was added dropwise and the mixture stirred for 10 min. Addition of n-hexane gave white microcrystals of **4** (93%), m.p. 140–143 °C. *Anal.* Calc. for $C_{60}H_{66}N_{16}P_2B_2Pt_2$: C, 48.53; H, 4.48; N, 15.09. Found: C, 48.61; H, 4.40; N, 15.02%. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 6H), 1.9–2.5 (br, 8H), 4.35 (s, 2H), 4.61 (s, 2H), 5.80 (s, 2H, H^4), 6.33 (s, 2H, H^4), 6.64 (s, 2H, H^5), 7.10 (s, 2H, H^5), 7.50 (s, 2H, H^3), 7.79 (s, 4H, $H^{3'}$), 8.04 (s, 2H, H^3). The other resonances due to the pyrazolyl groups and the phenyl groups were too broad to be assigned. IR: ν (C=C) 1630 cm^{-1}.

Reaction of ***1a*** *with* $Ph_2PCH_2CH_2PPh_2$

1a (12 mg; 11.2 μmol) and 1,2-bis(diphenylphosphino)ethane (4.5 mg; 11.2 μmol) were dissolved in $CDCl_3$ in an NMR tube. ^{1}H NMR spectrum was examined to show the resonances at δ 1.95 (s, $J_{Pt}=56$ Hz, 3H), 2.30 and 2.45 (m, PCH_2), 2.75 (d, $J_{Pt}=44$ Hz, $J_{PH}=8.8$Hz, 2H), 4.40 (s, $J_{Pt}=30$ Hz, 2H), and those at δ 6.0 (s, 4H), 7.4 (s, 4H), and 7.5 (s, 4H), which are very close to those of [Pt(η^3-methallyl)($Ph_2PCH_2CH_2PPh_2$)]PF_6 [13] and $KBPz_4$, respectively.

Preparation of ***5*** *and* ***6***

To a suspension of **2** (0.663 g; 0.849 mmol) in acetone (5 ml), 2.98 g of hydrochloric acid diluted with acetone to 1.04% (0.850 mmol) were added. After stirring for 75 min, the solvent was evaporated under reduced pressure. Recrystallization from CH_2Cl_2/n-hexane gave microcrystals of $\mathbf{5}\cdot\frac{1}{2}CH_2Cl_2$ (72%), m.p. 240–242 °C. *Anal.* Calc. for $C_{30.5}H_{28}N_8PBCl_2Pt$: C, 44.98; H, 3.47; N, 13.76. Found: C, 45.42; H, 3.63; N, 13.59%. The presence of CH_2Cl_2 of crystallization was confirmed by ^{1}H NMR spectra. Similarly, reaction of **2** and hydrobromic acid (0.251 mol l^{-1} in methanol) followed by recrystallization from CH_2Cl_2/n-hexane gave white crystals of $\mathbf{6}\cdot\frac{1}{2}CH_2Cl_2$ (86%), m.p. 148–154 °C (dec.). *Anal.* Calc. for $C_{30.5}H_{28}N_8PBClBrPt$: C, 42.66; H, 3.29; N, 13.05. Found: C, 43.19; H, 3.71; N, 13.10%. The presence of CH_2Cl_2 of crystallization was confirmed by ^{1}H NMR spectra.

Preparation of ***7***

To a solution of **5** (0.209 g; 0.257 mmol) in CH_2Cl_2 (5 ml) was added sodium iodide (0.775 g; 5.17 mmol) in acetone (5 ml). A yellow precipitate of sodium iodide formed, and a further volume of acetone was added until the mixture became clear. The mixture was stirred for 2 days and evaporated under reduced pressure. Extraction with CH_2Cl_2 followed by concentration and addition of n-hexane gave pale yellow crystals of $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ (81%), m.p. 229–231 °C (dec.). *Anal.* Calc. for $C_{30.5}H_{28}N_8PBClIPt$: C, 40.44; H, 3.12; N, 12.37. Found: C, 40.59; H, 3.08; N, 12.36%. The presence of CH_2Cl_2 of crystallization was confirmed by ^{1}H NMR spectra.

Preparation of ***8***

To a solution of **1a** (0.053 g; 0.10 mmol) in CH_2Cl_2 (5 ml) was added dropwise 1.45 ml of aqueous HBF_4 diluted with methanol to 0.069 mol l^{-1} (0.10 mmol). The solvents were evaporated. The residues were recrystallized from methanol/diethyl ether to give pale green solid (62%) of **8a**, m.p. 164–166 °C. *Anal.* Calc. for $C_{16}H_{20}N_8B_2F_4Pt$: C, 31.14; H, 3.27; N, 18.16. Found. C, 31.40; H, 3.22; N, 17.97%. ^{1}H NMR ($CDCl_3$) of the

η^3-methallyl group: δ 1.96 (s, $J_{Pt}=81$ Hz, 3H), 2.49 (s, $J_{Pt}=74$ Hz, 2H), 3.50 (s, 2H). **8b** was prepared similarly (71%): m.p. 161 °C. *Anal.* Calc. for $C_{16}H_{20}N_8B_2F_4Pd$: C, 36.37; H, 3.82; N, 21.21. Found: C, 36.37; H, 3.69; N, 20.92%. ^{1}H NMR ($CDCl_3$) of the η^3-methallyl group: δ 1.90 (s, 3H), 3.05 (s, 2H), 3.87 (s, 2H). The resonance of the proton bound to nitrogen(s) of pyrazolyl group(s) could not be observed.

Preparation of 9a, b

To a solution of *1a* (0.93 g; 1.76 mmol) and η^3-methallylplatinum chloride (0.50 g; 0.88 mmol) in CH_2Cl_2 (10 ml), silver tetrafluoroborate (0.17 g; 0.87 mmol) in acetone (5 ml) was added. The solvent was removed. Extraction with CH_2Cl_2 followed by filtration and addition of n-hexane gave colorless crystals of **9a** (42%), m.p. 265–267 °C. *Anal.* Calc. for $C_{20}H_{26}N_8B_2F_4Pt_2$: C, 27.73; H, 3.03; N, 12.94. Found: C, 27.52; H, 3.04; N, 12.64%. ^{1}H NMR ($CDCl_3$); δ 2.22 (s, $J_{Pt}=79$ Hz, 6H), 2.58 (s, $J_{Pt}=76$ Hz, 2H), 2.66 (s, $J_{Pt}=72$ Hz, 2H), 3.48 (s, $J_{Pt}=28$ Hz, 2H), 3.60 (s, $J_{Pt}=28$ Hz, 2H), 6.34 (t, 2H, H^4 of Pz, see Scheme 6), 6.76 (t, 2H, $H^{4'}$), 6.86 (d, 2H, H^5), 7.88 (2H, H^3), 7.99 (d, 2H, $H^{5'}$), 8.19 (2H, $H^{3'}$). Mixing of dimeric η^3-methallylplatinum chloride (0.17 g; 0.30 mmol) and potassium tetrakis(pyrazolyl)borate (0.095 g; 0.30 mmol) in CH_2Cl_2 (5 ml) followed by filtration and addition of silver tetrafluoroborate (0.085 g; 0.39 mmol) in acetone (5 ml) gave the same product (77%).

In a similar way to the former procedure **9b** was obtained in 89% yield, m.p. 253–255 °C. *Anal.* Calc. for $C_{20}H_{26}N_8B_2F_4Pd_2$: C, 34.87; H, 3.80; N, 16.27. Found: C, 34.46; H, 3.68; N, 16.12%. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 6H), 3.06 (s, 2H), 3.12 (s, 2H), 3.82 (s, 2H), 3.87 (s, 2H), 6.37 (2H, H^4), 6.63 (2H, $H^{4'}$), 6.80 (2H, H^5), 7.70 (2H, H^3), 7.73 (2H, $H^{5'}$), 7.92 (2H, $H^{3'}$).

Preparation of 10

1a (0.10 g; 0.19 mmol) and silver tetrafluoroborate (0.037 g; 0.19 mmol) were stirred in acetone (5 ml). The resulting white precipitates of **10** were filtered and dried *in vacuo* (88% yield), m.p. 178–180 °C. *Anal.* Calc. for $C_{16}H_{19}N_8B_2AgPt$: C, 26.55; H, 2.65; N, 15.48. Found: C, 25.71: H, 2.61; N, 14.83%. ^{1}H NMR (DMSO-d_6): δ 1.86 (s, $J_{Pt}=67$ Hz, 3H), 2.41 (s, 2H), 6.20 (br, 1H), 6.30 (br, 1H), 6.47 (br, 2H), 6.61 (br, 1H), 6.75 (br, 1H), 7.14 (br, 2H), 7.53 (br, 1H), 7.77 (br, 1H), 8.08 (br, 2H).

Variable temperature ^{1}H NMR studies of 2 and 5–7

Coalescence temperatures for each uncoordinated pyrazolyl ring proton of complex **2** were determined by the use of NMR spectrometers with different resonance frequencies. For the Arrhenius plot, least-square relationships between the following rate constants (s^{-1}, calculated by the reported method [14]) and the coalescence temperatures were used. 107 (263 K for $H^{3'}$), 71.1 (252 K for $H^{3'}$), 200 (274 K for $H^{4'}$), 133 (266 K for $H^{4'}$), 746 (290 K for $H^{5'}$), 498 (283 K for $H^{5'}$); $r=0.978$. For the complexes **5–7**, the same procedures were performed. The rate constants and the coalescence temperatures for the chloride complex **5**: 320 (313 K for $H^{3'}$), 213 (311 K for $H^{3'}$), 80.0 (301 K for $H^{4'}$), 53.3 (297 K for $H^{4'}$), 560 (316 K for $H^{5'}$), 373 (313 K for $H^{5'}$); $r=0.991$. For the bromide complex **6**. 280 (318 K for $H^{3'}$), 187 (315 K for $H^{3'}$), 126 (310 K for $H^{3'}$); $r=0.981$. For the iodide complex **7**. 227 (336 K for $H^{3'}$), 151 (332 K for $H^{3'}$), 347 (338 K for $H^{4'}$), 57.8 (323 K for $H^{4'}$); $r=0.991$.

Intermolecular ligand exchange reaction of 9

The binuclear platinum complex **9a** (2.0 mg; 2.3 μmol) and the palladium complex **9b** (1.6 mg; 2.3 μmol) were dissolved in $CDCl_3$ in an NMR tube and allowed to stand for 48 h. Resonances of the mixed binuclear complex **9c** appeared as follows. η^3-methallyl groups: δ 2.12 (s, 3H), 2.16 (s, 3H), 2.56 (s, 1H), 2.61 (s, 1H), 3.09 (s, 1H), 3.19 (s, 1H), 3.46 (s, 1H), 3.52 (s, 1H), 3.84 (s, 1H), 3.97 (s, 1H); pyrazolyl groups: δ 6.28 (t, 1H), 6.44 (s, 1H), 6.68 (s, 1H), 6.71 (s, 1H), 6.97 (s, 1H), 7.71 (s, 1H), 7.81 (s, 1H), 8.01 (s, 1H), 8.12 (s, 1H), **9a**, **9b** and **9c** were observed in a ratio of 1.4:1:2 ($K_{eq}=2.9$).

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