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Synthesis and Characterization of Palladium(II)-Phosphole and -Biphosphole Complexes. Regulation of the Homoleptic Coordination Environment of Square-Planar Palladium(II)

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A series of novel square-planar palladium(II)-phosphole complexes was synthesized in good yields by a ligand-substitution reaction of $[\mathrm{Pd(CH_3CN)_4}](\mathrm{BF_4})_2$ with 3,4-dimethyl-1-phenylphosphole (dmpp) and/or 3,3′4,4′-tetramethyl-1,1′-diphenyl-2,2′-biphosphole (bidmpp) in $\mathrm{CH_2Cl_2}$; $[\mathrm{Pd(dmpp)_4}](\mathrm{BF_4})_2$ (**1**), $[\mathrm{Pd(bidmpp)(dmpp)_2}](\mathrm{BF_4})_2$ (**2**), and $[\mathrm{Pd(bidmpp)_2}](\mathrm{BF_4})_2$ (**3**). Those complexes were characterized by ^{1}H and ^{31}P NMR spectroscopies and X-ray crystallography for **3**. The crystal structure of **3** revealed that the configurations of the phosphorus atoms were (*R*, *R*, *S*, *S*), indicating that the structure was a *meso* form with an intramolecular π–π interaction between the phenyl groups. ^{1}H NMR spectroscopy suggested the structures of **1** and **2**: Complex **1** has a water wheel-like C_{4h} structure and complex **2** is C_2 symmetric. In the ^{31}P NMR spectra of those complexes, each resonance showed a smaller downfield shift than that observed for $[\mathrm{Pd(dppe)_2}]\mathrm{Cl_2}$ (dppe = 1,2-bis(diphenylphosphino)ethane), indicating that the palladium-phosphole interaction is governed by mainly a σ-donation, and that there is a small contribution from a π-back bonding interaction.

Phosphole derivatives have been constituting a significant field in heterocyclic chemistry.[1] The intriguing points of phospholes are aromaticity, which is an issue of controversy,[1,2] unique coordination behaviors and their reactivity in both the absence and the presence of metal ions.[1,3] Mathey and co-workers have evolved phosphole chemistry and their synthetic efforts have been devoted to the establishment of preparation, involving the derivation of phospholes and an extension of this fascinating area toward polyphosphole compounds.[4] On the other hand, Mathey, Nelson, and their co-workers have also been establishing the coordination chemistry of phospholes to explore the novel properties of transition metal-phosphole complexes in terms of their structural and spectroscopic aspects.[3] Along this line, it will be possible that transition metal-phosphole complexes will allow us access to a new frontier of organometallic chemistry and catalysis. However, realizing that, we are still behind to understanding the properties and reactivity of those complexes because a limited variety of phosphole complexes have been reported, such as $[\mathrm{Pd(X)_2(dmpp)_2}]$ (X = Cl, Br, I, and pseudo-halides; dmpp = 3,4-dimethyl-1-phenyl phosphole).[5]

In contrast to monophospholes, utilization toward transition metal complexes had not been reported on a bidentate biphosphole ligand, bidmpp (3,3′,4,4′-tetramethyl-1,1′-diphenyl-2,2′-biphosphole), which had originally been synthesized by Mathey and co-workers.[6] Recently, however, Balavoine and co-workers have described the synthesis and charaterization of transition-metal complexes having bidmpp, such as $[\mathrm{NiBr_2(bidmpp)}]$,[7] $[\mathrm{MCl_2(bidmpp)}]$ (M = Pd, Pt),[7] and $[\mathrm{Fe_2(Cp)_2}(\mu\text{-CO})_2(\mu\text{-bidmpp})]$.[8]

We have been interested in transition-metal complexes with P-containing heteroaromatics with respect to an investigation of the metal-ligand interaction, such as π-back bonding.[9] We started our investigation on square-planar complexes with a homoleptic environment in order to consider the coordination behaviors of phospholes. Since the complexes reported so far are electronically neutral with halide ions in coordination spheres, it has been difficult to directly evaluate the properties of coordinated phospholes in light of the metal-ligand interaction. In this paper we describe the synthesis of novel homoleptic Pd(II) complexes with dmpp and bidmpp and their characterization by means of ^{1}H and ^{31}P NMR spectroscopies and X-ray crystallography to consider their structures and palladium-phosphole interactions. Preliminary results have been reported elsewhere.[10]

Experimental

Materials. $[\mathrm{Pd(CH_3CN)_4}](\mathrm{BF_4})_2$ was purchased from Aldrich. All solvents were obtained from Wako Pure Chemical Industries and purified by general procedures. 3,4-Dimethyl-1-phenylphosphole (dmpp)[11] and 2,2′-bi(3,4-dimethy-l-phenylphosphole) (bidmpp)[6a] were synthesized by methods reported by Mathey and co-workers.

Instrumentation. The ^{1}H NMR (400 MHz) and ^{31}P NMR (161.8 MHz) spectra were measured on a JEOL GX-400 spectrometer and the ^{1}H NMR (270 MHz) spectra were obtained on a JEOL EX-270 spectrometer; they were referenced to internal TMS for ^{1}H NMR and external 85% $\mathrm{H_3PO_4}$ aqueous solution for ^{31}P NMR. Infrared spectra were recorded as KBr disks in the range of 4000—400 cm^{-1} on a JASCO IR model 800 infrared spectrophotometer. Elemental analysis were carried out at the Service Center of the

Elemental Analysis of Organic Compounds, Kyushu University.

Synthesis of Complexes. All procedures were performed under a nitrogen atmosphere in a glove bag.

$[Pd(dmpp)_4](BF_4)_2$ (1). To a suspension of 100 mg of $[Pd(CH_3CN)_4](BF_4)_2$ (as 97%, 0.218 mmol) in CH_2Cl_2 (25 mL), was added dmpp (175 mg, 0.928 mmol) with stirring at room temperature to give a pale-yellow solution within a few minutes. The solution was continuously stirred for 30 min, after which the solvent was removed under reduced pressure. The residue was redissolved in a small amount of CH_2Cl_2, and the solution was added dropwise to hexane with stirring, giving a pale-yellow powder. The powder was washed well with hexane to yield 218 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.00$ (s, 6H, CH_3), 5.98 (pseudo-t, 2H, ring-H), 7.47—7.62 (m, 5H, phenyl-H). ^{31}P NMR (161.8 MHz, CD_2Cl_2) $\delta = 23.2$ (s). Calcd for $C_{48}H_{52}P_4PdB_2F_8$: C, 55.82; H, 5.08%. Found: C, 55.95; H, 5.27%.

$[Pd(bidmpp)(dmpp)_2](BF_4)_2$ (2). To a suspension of 110 mg of $[Pd(CH_3CN)_4](BF_4)_2$ (as 91%, 0.225 mmol) in 15 mL of CH_2Cl_2, was added a mixture of dmpp (97 mg, 0.515 mmol) and bidmpp (97 mg, 0.259 mmol) in CH_2Cl_2 with stirring at room temperature to give an orange solution within 5 min. The solution was continuously stirred for 30 min and filtered through a short celite column. The solvent was removed under reduced pressure and the residue was redissolved into a small volume of CH_2Cl_2. The solution was poured into hexane with stirring to give an orange powder, which was washed well with hexane. The yield was 221 mg (95%). ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 1.50$ (d, $J = 2$ Hz, 6H, 3,3′-methyl-H of bidmpp), 1.54 (s, 6H, 3-methyl-H of dmpp), 1.74 (s, 6H, 4-methyl-H of dmpp), 2.28 (s, 6H, 4,4′-methyl-H of bidmpp), 6.29 (d, 36 Hz, 2H, ring-H2 of dmpp), 6.34 (d, 34 Hz, 2H, ring-H of bidmpp), 6.75 (d, $J = 36$ Hz, 2H, ring-H5 of dmpp), 7.23—7.56 (m, 20H, phenyl-H's of dmpp and bidmpp). ^{31}P NMR (161.8 MHz, CD_2Cl_2) $\delta = 21.7$ (d, $J = 320$ Hz, dmpp), 33.9 (d, $J = 320$ Hz, bidmpp). Calcd for $C_{48}H_{50}P_4PdB_2F_8$: C, 55.93; H, 4.89%. Found: C, 55.30; H, 4.74%.

$[Pd(bidmpp)_2](BF_4)_2$ (3).[7,10] To a suspension of 120 mg of $[Pd(CH_3CN)_4](BF_4)_2$ (as 91%, 0.246 mmol) in 12 mL of CH_2Cl_2, was added a solution of bidmpp (200 mg, 0.534 mmol) in CH_2Cl_2 with stirring at room temperature. Within 5 min, the suspension turned to be a reddish-orange solution, which was stirred for 30 min. After filtration through a small celite column, the solution was evaporated to remove the solvent and the residue was redissolved into a small volume of CH_2Cl_2; the solution was then poured into hexane to give a reddish-orange powder. The powder was washed well with hexane to afford 180 mg of **3** (71%). ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 1.76$ (s, 6H, *meso*-3,3′-methyl-H), 1.88 (s, 6H, *rac*-methyl-H), 2.23 (d, $J = 1$ Hz, 6H, *rac*-methyl-H), 2.37 (pseudo-s, 6H, *meso*-4,4′-methyl-H), 7.3 (d, *rac*-ring-H), 7.7 (d, *meso*-ring-H), 7.0—7.8 (m, phenyl-H's for both isomers). ^{31}P NMR (161.8 MHz, CD_2Cl_2) $\delta = 34.5$ (s, *meso*), 37.3 (s, *rac*). Calcd for $C_{48}H_{48}P_4PdB_2F_8$: C, 56.04; H, 4.70%. Found: C, 55.67; H, 4.74%. FAB-MS spectrum; 941.23 ($\{M-BF_4\}^+$). Crystallographic data for **3**: Space group, $R\bar{3}$ (trigonal); $a = 31.21(3)$ Å, $c = 14.41(2)$ Å; $Z = 9$; $R = 0.055$, $R_w = 0.086$ ($R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$) for 2492 reflections with $I > 3\sigma(I)$.

Results and Discussion

Synthesis of Complexes. Three Pd(II) complexes ($[Pd(dmpp)_4](BF_4)_2$ (**1**), $[Pd(bidmpp)(dmpp)_2](BF_4)_2$ (**2**), $[Pd(bidmpp)_2](BF_4)_2$ (**3**)) were synthesized in high yields by ligand substitution reactions between $[Pd(CH_3CN)_4](BF_4)_2$ and the corresponding ligands in CH_2Cl_2. Completion of the synthetic reaction was confirmed by IR spectroscopy to observe the disappearance of $\nu(C{\equiv}N)$ at 2150 cm^{-1}. For synthesizing **2**, a 1 : 2 mixture of bidmpp and dmpp was used to obtain the complex in quantitative yield without the formation of a mixture of **1** and **3**. In order to obtain those complexes, we examined the reaction of ligands with $[PdCl_2(PhCN)_2]$ or after a treatment with $AgBF_4$; however, the attempts ended in vain.

It has been reported that Pd(II)-phosphine complexes can undergo fluoride-induced reductions to generate Pd(0)-phosphine complexes in the presence of BF_4^- in polar solvent, such as DMSO.[12] However, we could obtain the corresponding Pd(II) complexes in high yields, owing to using CH_2Cl_2 as solvent to prevent those undesirable side reactions.

Molecular Structure of $[Pd(bidmpp)_2](BF_4)_2$ (3). The X-ray crystallography of **3** has been independently reported by Balavoine and coworkers[7] and us.[10] As for the structure, they have described the bond lengths and angles, but discussed on only a few points. To clarify our standpoints toward descriptions of other complexes, we describe some structural features of **3**. Compound **3** was shown to possess a structure with an inversion center at the Pd(II) ion (Fig. 1); the square-planar Pd(II) ion was surrounded by four phosphorus atoms (Fig. 1(b)). The Pd–P bond lengths were both 2.343(3) Å and the bite angle of bi-dmpp (P(1)–Pd–P(2)) was 84.5(1)°, which were comparable to those found in homoleptic $[Pd(dppe)_2]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) in which the Pd–P bond distances had been 2.342(2) and 2.347(2) Å and the bite angle was 81.65(8)°.[13] The geometry around the phosphorus atoms of bidmpp was distorted tetrahedral having 92.4(6)° for C(1)–P(1)–C(4), 133.1(4)° for Pd–P(1)–C(1), 92.3(6)° for C(13)–P(2)–C(16), and 129.5(4)° for Pd–P(2)–C(16) bond angles. The configuration of the chiral phosphorus atoms of bidmpp in **3** was *S*, *S*, *R*, *R*, for P(1), P(2), P(1)*, P(2)*, respectively; the structure determined by X-ray analysis was a *meso* form. The chirality of the conformation of both chelate rings was λ for the *S*,*S*-bidmpp and δ for the counterpart. For the bidmpp, due to the steric hindrance of the methyl groups on the phosphole rings, two phenyl groups of one bidmpp ligand is fixed to be an *anti* fashion. Therefore, this ligand should be compelled to be chiral. As observed in the crystal structure, the interatomic distance between the two nearest methyl groups (C(6) and C(17)) was 3.87 Å and the dihedral angle between two phosphole rings was 126.6° to avoid any repulsion. In this configuration, the phenyl rings on the same side of Pd coordination plane were co-facial, as shown in Fig. 1(b), and exhibited an intramolecular π–π interaction with 3.41 Å for C(12)$\cdots$C(20)* and 3.65 Å for C(11)$\cdots$C(21)*. This kind of π–π interaction has not been reported so far, even in a similar complex, $[Pd(dppe)_2]^{2+}$ or [Ni(2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)$_2$]$^{2+}$.[13,14]

Pd(II) complexes having phospholes or related compounds reported so far are all electrostatically neutral and contain halide or SCN$^-$ ligands.[5] Complex **3** represents the first homoleptic coordination environment with phospholes.[7] A

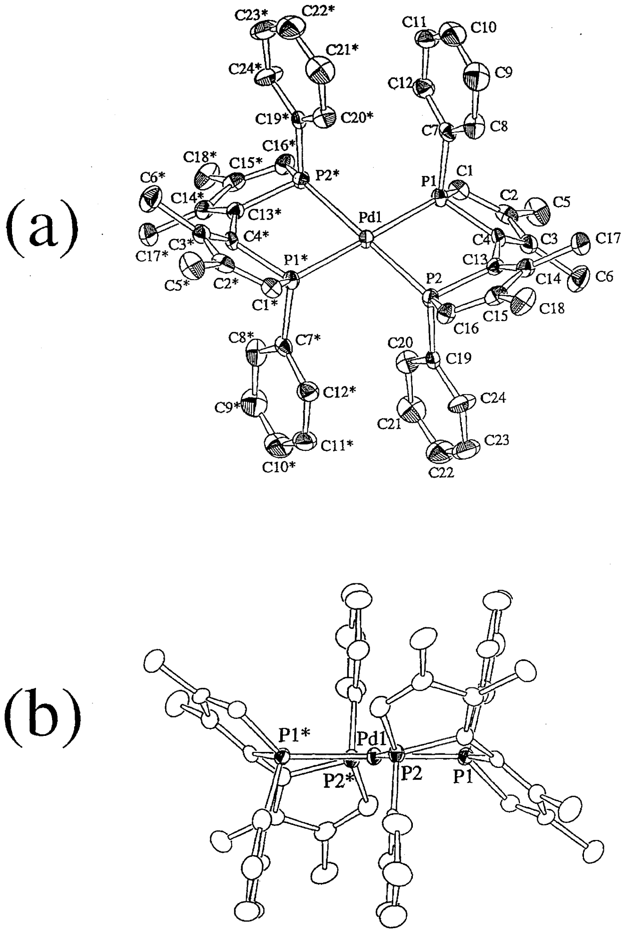

Fig. 1. ORTEP drawings of cation of **3**: (a) Perspective view and (b) side view. Thermal ellipsoids are represented at 30% probability level.

compilation of the Pd–P bond lengths is given in Table 1. As can be seen in Table 1, compound **3** possesses the longest Pd–P bond length, which is ascribed to the stronger trans influence of the phosphorus atom of the phospholes than those of the halides or pseudo-halides.[15] This kind of tendency was observed in comparison with the Pd–P bond lengths for $[Pd(dppe)_2]^{2+}$ (2.342(2) and 2.347(2) Å)[13] with those for $[PdCl_2(dppe)]$ (2.233(2) and 2.226(2) Å).[16] This is also attributable to a steric hidrance among the phenyl substituents of bidmpp.

Concerning the π-electron delocalization on the phosphole ring, as can be seen in the bond length of C4–C13 (1.46(2) Å), which is within the range of the normal C–C single bond lengths, conjugation between the two phosphole rings is unlikely, as indicated for a tetraphosphole compound.[4a)] The inner-ring P–C bond lengths were found to be 1.78(1) Å [P(1)–C(1)], 1.79(1) Å [P(1)–C(4)], 1.79(1) Å [P(2)–C(13)], and 1.78(1) Å [P(2)–C(16)], respectively. These values are comparable to those found in phosphole-complexes reported so far,[5,17)] but shorter than those of tertiary phosphines.[18)]

^{1}H NMR Spectroscopy. The characterization of **1**—**3** was carried out by ^{1}H NMR spectroscopy in $CDCl_3$. All data concerning the ^{1}H NMR spectra including free ligands are summarized in Table 2. As for **1**, a signal due to the ring hydrogens at the 2 and 5 positions was observed at 5.98 ppm as a complicated pseudo-triplet and a singlet assigned to the methyl groups was observed at 2.00 ppm. This result indicates that all four dmpp ligands are equivalent and symmetric in solution. A comparison of the chemical shifts of **1** with those of the free dmpp, as shown in Table 2, indicates that resonances due to the ring hydrogens and the methyl groups are both upfield-shifted.

The ^{1}H NMR spectrum of **2** showed two sets of resonances for dmpp and bidmpp. Peak assignments were performed using ^{1}H-^{1}H COSY and peak integration. As depicted in Fig. 2, we could observe cross peaks due to a long-range

Table 1. Comparison of Bond Lengths of Pd–P Bonds in Pd(II) Complexes with Phospholes and Their Related Compounds

Complex	Pd–P (Å)	Reference
$[Pd(bidmpp)_2](BF_4)_2$ (**3**)	2.343(3)	7, 10
$[PdCl_2(bidmpp)]$	2.2287(9)	7
cis-$[Pd(SCN)_2(1,3,4\text{-}Me_3\text{-phosphole})_2]$	2.277(2)	5b)
cis-$[Pd(SCN)(NCS)(dmpp)_2]$	2.248(2) (*trans* to N) 2.290(2) (*trans* to S)	5c)
$[PdCl_2(L1)]$[a)]	2.210(1), 2.225(1)	b)
$[PdBr_2(L2)_3]$[c)]	2.355(9), 2.303(9) (axial) 2.294(9) (equatorial)	d)
cis-$[PdCl_2(dmpp)_2]$	2.243(3), 2.338(2)	5a)
trans-$[PdBr_2(dmpp)_2]$	2.319(2), 2.313(2)	5d)
trans-$[PdI_2(dmpp)_2]$	2.324(2), 2.312(2)	5d)
$[PdBr_2(L3)]$[e)]	2.238(5), 2.224(8)	5d)
$[PdBr_2(L4)]$[f)]	2.219(3), 2.213(4)	5d)

a) L1 = 2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole). b) F. Mercier, F. Mathey, J. Fisher, J. H. Nelson, *Inorg. Chem.*, **24**, 4141—4149 (1985). c) L2 = 5-ethyl-5*H*-dibenzophosphole. This complex has a trigonal bipyramidal geometry. d) K. M. Chui and H. M. Powell, *J. Chem. Soc., Dalton Trans.*, **1974**, 1879—1889. e) L3 = {$(dmpp)_2[2+2]$}. f) L4 = {$(dmpp)_2$(*exo*-methylene)}.

Table 2. ^{1}H NMR Spectroscopic Data for dmpp, bidmpp, and Complex **1**—**3**$^{a)}$

	Assignments					
	dmpp			bidmpp		
	ring-H	Me	Ph	ring-H	Me	Ph
dmpp	6.47 (d, $J=39$ Hz)	2.10 (d, $J=2$ Hz)	7.21—7.34 (m)			
bidmpp				6.44 (m)	1.81 (s) 2.09 (d, $J=2$ Hz)	7.15—7.30 (m)
1	5.98 (peudo-t)	2.00 (s)	7.47—7.62 (m)			
2	6.29 (d, $J=36$ Hz, 2-H) 6.75 (d, $J=36$ Hz, 5-H)	1.54 (s, 3-Me) 1.74 (s, 4-Me)	7.23—7.56 (m)	6.34 (d, $J=34$ Hz)	1.50 (d, $J=2$ Hz, 3,3′-Me) 2.28 (s, 4,4’-Me)	7.23—7.56 (m)
3				7.3 (d, *rac*)$^{b)}$ 7.7 (d, *meso*)$^{b)}$	1.76 (s, *meso*-3,3′-Me) 2.37 (pseudo-s, *meso*-4,4′-Me) 1.88 (s, *rac*-3,3′-Me) 2.23 (d, $J=1$ Hz, *rac*-4,4′-Me)	7.0—7.8 (m, *meso*) 7.3—7.6 (m, *rac*)

a) Measured in $CDCl_3$. b) Observed only in ^{1}H–^{1}H COSY spectrum.

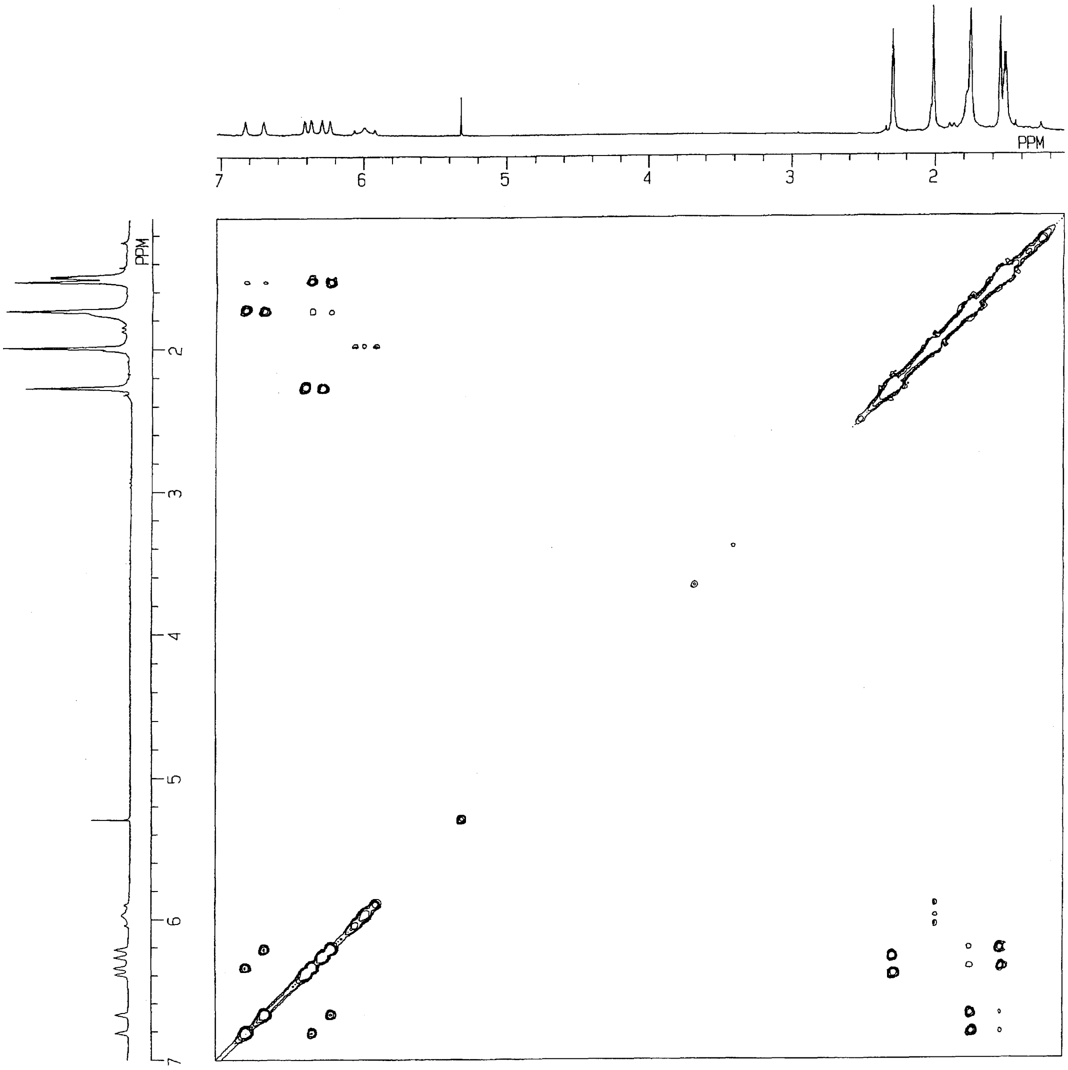

Fig. 2. ^{1}H–^{1}H COSY spectrum of **2** in CD_2Cl_2.

coupling between the methyl groups and the ring hydrogens for both dmpp and bidmpp. As for the dmpp moiety, we could assign resonances at 6.29 (2-H, d, J(P–H) = 36 Hz) and 6.75 ppm (5-H, d, J(P–H) = 36 Hz) to the dmpp ring hydrogens coupled with the methyl groups observed at 1.54 (3-Me) and 1.74 ppm (4-Me), respectively. The resonance due to 2-H were upfield shifted, and that of 5-H was downfield shifted, compared to that of the free dmpp. For the bidmpp moiety, a doublet at 6.34 ppm (J(P–H) = 34 Hz) was assigned to the 5,5′-H of phosphole rings, which was coupled with a singlet of the 4,4′-methyl groups at 2.28 ppm via a long-range coupling; also, a doublet at 1.50 ppm was ascribed to the

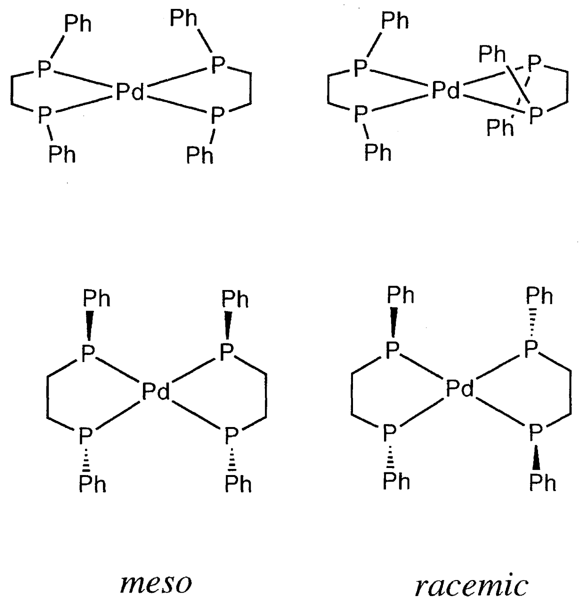

Fig. 3. Possible isomers for **3**.

3,3′-methyl groups. These data suggest that this compound **2** has a symmetric configuration for each ligand. Based on the argument on the configuration of bidmpp described above, there should be two enantiomers for **2**, i.e., (*R*,*R*)-**2** and (*S*,*S*)-**2** in accordance with the chirality of the bidmpp ligand.

In the ^{1}H NMR spectrum of **3** measured in $CDCl_3$, two sets of peaks were observed. Four resonances assigned to the methyl groups of the bidmpp ligand were observed at 1.76, 1.88, 2.23, and 2.37 ppm. This suggests that two isomers exist in the solution. The results of an elemental analysis and FAB-MS spectroscopy indicate that the contents of the sample should have the same molecular formula. As described above, compound **3** isolated was determined to be the *meso* form by X-ray crystallography; however, it is reasonable to consider the existence of *racemic* configurations, such as the chiralities of (*R*, *R*, *R*, *R*) or (*S*, *S*, *S*, *S*) at four phosphorus atoms. Therefore, the two components observed in the ^{1}H NMR spectrum are assigned to the *meso* form and the *racemic* form, structures which are depicted in Fig. 3. Based on the assignments made by Balavoine and coworkers,[7] the peaks at 1.76 and 2.37 ppm were assigned to the methyl groups of the *meso*-**3** and resonances at 1.88 and 2.23 ppm to those of the *rac*-**3**. Balavoine and coworkers pointed out that only the *meso* form was obtained in their synthetic procedure; however, we could obtain a mixture of the *meso* and *rac* forms. This discrepancy could be due to a different work-up; we used hexane as a poor solvent to obtain a powder sample of **3** from CH_2Cl_2, while they obtained crystals of **3** from a CH_2Cl_2 solution.

On the other hand, we could observe cross peaks due to a long-range coupling between the methyl groups and the ring hydrogens. We could assign the peak at 2.23 ppm (d, $J = 1$ Hz) to the 4,4′-methyl groups of the *rac*-**3**; a pseudo-singlet peak at 2.37 ppm was assigned to the 4,4′-methyl groups of the *meso*-**3**. Two other singlets for the methyl groups, which gave no cross peaks, were assigned to 1.88 ppm for the 3,3′-methyl groups of the *rac*-**3** and 1.76 ppm for the 3,3′-methyl groups of the *meso*-**3**, respectively. Although no clear peaks for 5-H and 5′-H were recognized in 1D ^{1}H NMR spectrum, in the COSY spectrum of **3** (Fig. 4) we could observe two doublets due to the 5,5′-H ring hydrogens of bidmpp at 7.3 and 7.7 ppm. The former was ascribed to that of the *rac*-**3** and the latter to the *meso*-**3**, respectively. Interestingly, both resonances were downfield-shifted relative to that of the free bidmpp in contrast to the upfield shifts observed in compounds **1** and **2**.

The results obtained from ^{1}H NMR spectroscopy for **1**–**3** are confusing in terms of the behavior of the ring hydrogen resonances; those of dmpp shifted toward the upper field for **1** and those of bidmpp did so toward the lower field for **3** and showed a complicated behavior for **2**, compared with those free ligands. This tendency can be rationalized in terms of the following concepts. The upfield shift is due to shielding by a π-electron cloud of the phenyl group or a phosphole diene moiety of the adjacent dmpp and a downfield shift due to a reduction of the electron density of the phosphorus atom by σ-donation. In the structure of *mer*-$[RuCl_2(CO)(dmpp)_3]$,[19] however, the interatomic distances were not mentioned, apparently because the phenyl group of dmpp was directed to shield the adjacent phosphole ring. Two phosphole rings were also coplanar, having a 3.56 Å separation. This observation gives strong support to argue for structures of **1** and **2**. Therefore, we propose that structures of **1** and **2** are as shown in Figs. 5 and 6, respectively. As for complex **1**, all of the ring hydrogens could be shielded by the phenyl rings of the adjacent phospholes, and all of the dmpp are chemically equivalent; the complex should have a water wheel-like structure with C_{4h} symmetry, as shown in Fig. 5. In compound **2**, two ring hydrogens of bidmpp could be shielded by two phenyl groups of two dmpp ligands; the complex should possess C_2 symmetry, as shown in Fig. 6. The upfield shift of 2-H and the downfield shift of 5-H could be due to shielding and deshielding by the adjacent coplanar dmpp rings, respectively.

Variable-temperature ^{1}H NMR measurements were conducted for **3** to consider *meso*–*rac* conversion in solutions. We observed the generation of *rac*-**3**, even in the case where crystals of the *meso*-**3** were dissolved into CD_2Cl_2. In CD_2Cl_2, no change of the peak intensity in the methyl region was observed over the range of −80 to 20 °C. However, in DMSO-d_6, we observed the change of the peak intensity in the region within the range of 30—90 °C, as shown in Fig. 7; above 90 °C, the complex decomposed, presumably due to fluoride-mediated redox reactions, as mentioned above.[12] According to the assignments mentioned above, the *meso* form is converted to the *rac* form. During the measurement, we could not observe any coalescence of the methyl peaks, implying that the conversion is one-way and that the direction is from the *meso* form to the *rac* form. This is because the *rac* form is less sterically hindered than the *meso* form in terms of flexibility of the phenyl groups of the bidmpp in solutions, as can be seen in Fig. 3. The rationale for this conversion is given based on the X-ray structure of **3**;

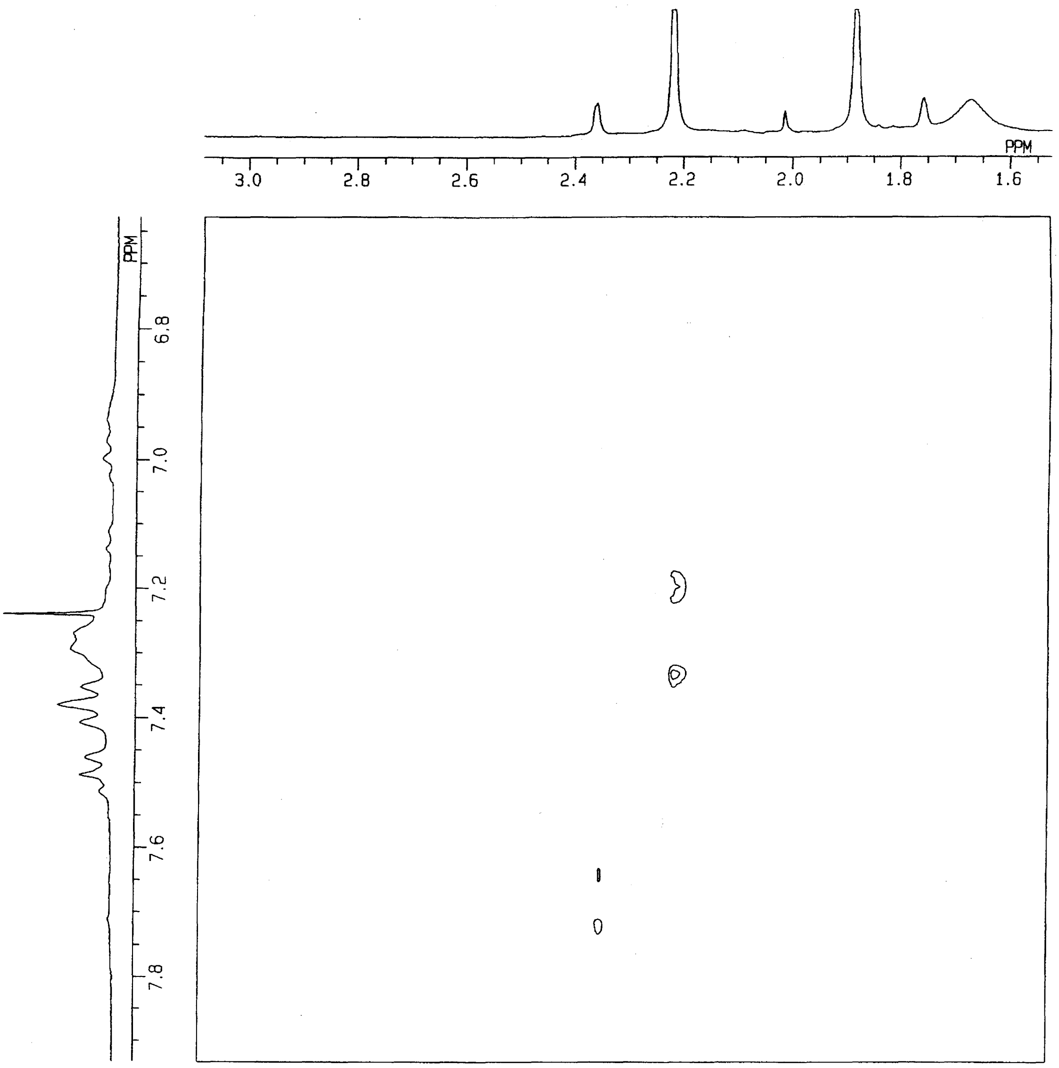

Fig. 4. Part of ^{1}H–^{1}H COSY spectrum of **3** showing cross section between phosphole ring hydrogens and methyl groups.

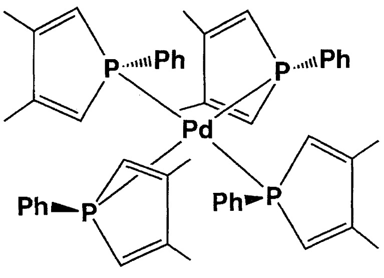

Fig. 5. Proposed structure of **1**.

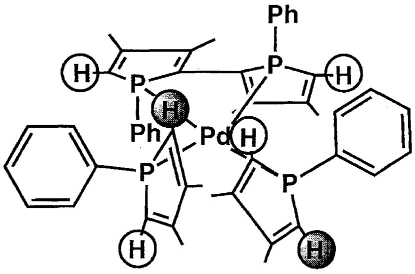

Fig. 6. Proposed structure of **2**. Circled hydrogens showed upfield shifts and shaded ones showed downfield shifts in the ^{1}H NMR spectrum.

as mentioned above, the Pd–P bonds are lengthened by a *trans* influence of the phospholes. The energy barrier for the conversion of 1-substituted phospholes has been estimated to be roughly 16 kcal mol^{-1}, and such low energy barriers have been ascribed to stabilization of the planar transition state relative to the pyramidal ground state due to cyclic (3p-2p)π delocalization.[20] Therefore, the inversion of the phosphorus center could be much easier than the dissociation of one phosphole moiety. Thus, it is reasonable to elucidate the conversion of the *meso* form to the *rac* form via a rate-limiting dissociation process to form a free phosphole group. The reason why no conversion is observed from the *meso*-**3** to the *rac*-**3** at lower temperatures in CD_2Cl_2 would be due to the destabilization of the transition state, which should be polar, such as a three-coordinate intermediate.

^{31}P NMR Spectroscopy. ^{31}P NMR spectra of dmpp, bidmpp, the complexes **1**—**3** were measured in CD_2Cl_2 at room temperatures. Those data are listed in Table 3.

For **1**, a singlet peak was observed at 23.2 ppm, and this observation indicated that four dmpp bound to the Pd center

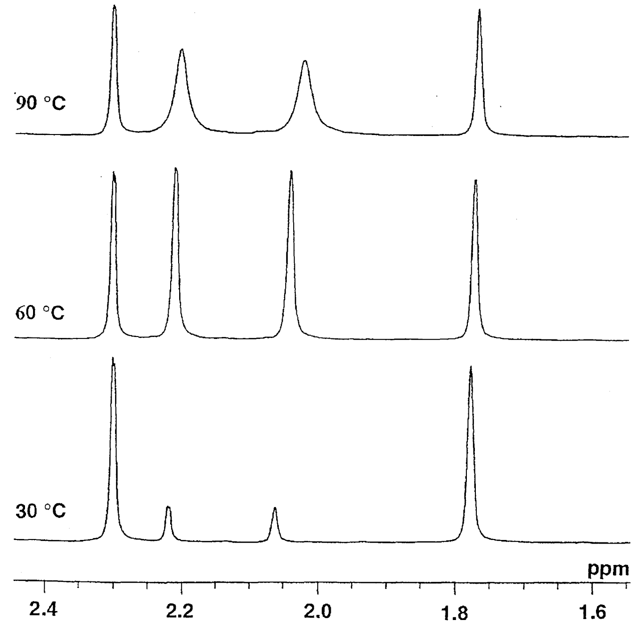

Fig. 7. Variable-temperature ^{1}H NMR spectra of **3** in DMSO-d_6.

Table 3. ^{31}P NMR Data and Coordination Shifts[a)]

Compound	δ (ppm)	$\Delta\delta$ (ppm)[b)]
dmpp	0.7 (t, $J = 37$ Hz)	
bidmpp	17.6 (s)	
dppe[c)]	-11.6	
1	23.2 (s)	22.5
2	21.7 (dmpp)	21.0
	33.9 (bidmpp)	16.3
	(ABq, $J = 320$ Hz)	
rac-**3**	37.3 (s)	19.7
meso-**3**	34.5 (s)	16.9
[Pd(dppe)$_2$]Cl$_2$[c)]	56.5	68.1

a) Measured in CD_2Cl_2 and chemical shifts relative to 85% H_3PO_4 aqueous solution as external reference. b) Coordination shift: $\Delta\delta = \delta$ (complex) $- \delta$ (free ligand). c) In $CDCl_3$. From Ref. 21.

were all equivalent, in agreement with the result of a ^{1}H NMR measurement. Regarding **2**, the spectrum showed a pseudo-AB quartet at 21.7 and 33.9 ppm having J_{AB} = 320 Hz; we assigned the former to dmpp phosphorus nuclei and the latter to those of bidmpp, respectively. As for **3**, two singlets were observed at 34.5 and 37.3 ppm. Integration of those peak intensities was compared with those of the methyl groups in the ^{1}H NMR spectrum to reveal that the signal at 34.5 ppm was assignable to the phosphorus atoms of the *meso*-**3** and that at 37.3 ppm to those of the *rac*-**3**.

Compared with the ^{31}P chemical shifts of free ligands, those of **1**—**3** were downfield shifted, indicating that the electron density on the phosphorus atoms was reduced by a σ-donation of lone pairs. This suggests that the main factor of the Pd–P interactions is σ-bonding in the palladium-phosphole complexes. However, the coordination shifts observed for bidmpp in **2** and **3** were considerably smaller than those of other Pd(II)-tertiary phosphine complexes, such as [Pd(dppe)$_2$]$^{2+}$ ($\Delta\delta$ = 68.1 ppm),[21)] as listed in Table 3. This suggests that the phosphorus atoms of phospholes undergo a stronger π-back bonding interaction than that suggested for tertiary phosphines; otherwise, phospholes are poorer electron donors than tertiary phosphines. We prefer the former assumption rather than the latter, because the Pd–P bond lengths in **3** are comparable to those found for [Pd(dppe)$_2$]Cl$_2$. In addition, the longer bond distance could be attributable to a poorer electron density at the Pd center compared to the other complexes listed in Table 1, because of a lack of appropriate electron donors, such as halides in **3**, which causes poorer π-back bonding interaction.

It has been controversial whether the phospholes have aromaticity or not; this issue has been investigated from viewpoints of both experimental and theoretical approaches. According to the results reported by Quin and co-workers,[2a—c)] the aromaticity of phosphole rings could be regulated by substituents on the phosphorus atom. The bulkier substituents exert a steric hindrance to flatten the phosphorus pyramid, which lowers the ionization energy, thus suggesting the delocalization of π-electrons of phospholes. In the case of the phenyl substituent, the aromaticity was reported to be as small as that of the non-substituted (1*H*) phosphole.[2c)] However, once coordination of the phospholes to metal takes place, such arguments could be invalid due to a reorganization of the phosphorus orbitals and stabilization in terms of enthalpy by metal-phosphorus bond formation.

In conclusion, a weak π-back bonding interaction occurs from the Pd center to empty 3d orbitals of phosphorus atoms of phospholes, if any, those electron density localize at the phosphorus and does not seem to delocalize onto the phosphole ring. Metal-bound polyphosphole compounds, such as bidmpp, have no inter-ring π-conjugation, and phosphorus atoms will be isolated from diene conjugation systems, as observed in non-coordinating tetraphosphole.[4a)] The symmetry around metal center can be regulated by different coordination orientations of the monodentate and bidentate phosphole ligands in P$_4$-homoleptic environments.

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References

1) F. Mathey, *Chem. Rev.*, **88**, 429 (1988).

2) a) G. Keglevich, Z. Böcskei, G. M. Keserü, K. Újszászy, and L. D. Quin, *J. Am. Chem. Soc.*, **119**, 5095 (1997); b) L. D. Quin, G. Keglevich, A. S. Ionkin, R. Kalgutkar, and G. Szalontai, *J. Org. Chem.*, **61**, 7801 (1996); c) L. Nyulaszi, G. Keglevich, and L. D. Quin, *J. Org. Chem.*, **61**, 7808 (1996); d) D. B. Chesnut and L.D. Quin, *J. Am. Chem. Soc.*, **116**, 9638 (1993); e) P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Am. Chem. Soc.*, **92**, 5779 (1970); f) W. P. Ozbirn, R. A. Jacobson, and J. C. Clardy, *J. Chem.*

Soc., Chem. Commun., **1971**, 1062.

3) a) F. Mathey, *Coord. Chem. Rev.*, **137**, 1 (1994); b) F. Mathey, J. Fischer, and J. H. Nelson, *Struct. Bonding* (*Berlin*), **55**, 153 (1983); c) W. L. Wilson, J. A. Rahn, N. W. Alcock, J. Fischer, J. H. Frederick, and J. H. Nelson, *Inorg. Chem.*, **33**, 109 (1994).

4) a) E. Deschamp, L. Ricard, and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **33**, 1158 (1994); b) F. Laporte, F. Mercier, L. Ricard, and F. Mathey, *J. Am. Chem. Soc.*, **116**, 3306 (1994); c) E. Deschamp, L. Ricard, and F. Mathey, *J. Chem. Soc., Chem. Commun.*, **1995**, 1561.

5) a) J. J. MacDougall, J. H. Nelson, F. Mathey, and J. J. Mayerle, *Inorg. Chem.*, **19**, 709 (1980); b) J. J. MacDougall, E. M. Holt, P. de Meester, N. W. Alcock, F. Mathey, and J. H. Nelson, *Inorg. Chem.*, **19**, 1439 (1980); c) J. H. Nelson, J. M. MacDougall, N. W. Alcock, and F. Mathey, *Inorg. Chem.*, **21**, 1200 (1982); d) W. L. Wilson, J. Fischer, R. E. Wasylishen, K. Eichele, V. J. Catalano, J. H. Frederick, and J. H. Nelson, *Inorg. Chem.*, **35**, 1486 (1996).

6) a) E. Deschamp and F. Mathey, *Bull. Soc. Chim. Fr.*, **129**, 486 (1992); b) O. Tissot, M. Gouygou, J.-C. Daran, and G. G. A. Balavoine, *Chem. Commun.*, **1996**, 2287.

7) M. Gouygou, O. Tissot, J.-C. Daran, and G. G. A. Balavoine, *Organometallics*, **16**, 1008 (1997).

8) A. Dupuis, M. Gouygou, J.-C. Daran, and G. G. A. Balavoine, *Bull. Soc. Chim. Fr.*, **134**, 357 (1997).

9) a) M. Shiotsuka, Y. Matsuda, *Chem. Lett.*, **1994**, 351; b) M. Shiotsuka, T. Tanamachi, and Y. Matsuda, *Chem. Lett.*, **1995**, 531.

10) T. Kojima, K. Saeki, K. Ono, M. Ohba, and Y. Matsuda, *Chem. Commun.*, **1997**, 1679. Note: The same compound has been reported by Balavoine and co-workers in Ref. 7.

11) A. Breque, F. Mathey, and P. Savignac, *Synthesis*, **1981**, 983.

12) M. R. Mason and J. G. Vercade, *Organometallics*, **11**, 2122 (1992).

13) L. Engelhardt, J. M. Patrick, C. L. Raston, P. Twiss, and A. H. White, *Aust. J. Chem.*, **37**, 2193 (1984).

14) L. Solujic, E. B. Milosavljevic, J. H. Nelson, and J. Fischer, *Inorg. Chem.*, **33**, 5654 (1994).

15) a) M. M. Gofman and V. I. Nefedov, *Inorg. Chim. Acta*, **28**, 1 (1978); b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed, Wiley, New York (1988), pp. 1299—1300.

16) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **15**, 2432 (1976).

17) S. Attar, W. H. Bearden, N. W. Alcock, E. C. Alyea, and J. H. Nelson, *Inorg. Chem.*, **29**, 425 (1990).

18) A. Guy Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, **1989**, S1-S83.

19) L. M. Wilkes, J. H. Nelson, L. B. McCulsker, K. Seff, and F. Mathey, *Inorg. Chem.*, **22**, 2476 (1983).

20) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971).

21) C. H. Lindsey, L. S. Benner, and A. L. Balch, *Inorg. Chem.*, **19**, 3503 (1980).