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FULL PAPER

Synthesis and characterization of neutral and cationic organopalladium complexes containing an imidazolylphosphine P,N-ligand and their carbonylation reactions

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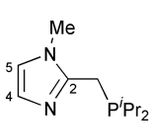
Several new neutral and cationic organopalladium complexes containing a P–N chelating ligand, 2-(diisopropylphosphinomethyl)-1-methylimidazole, have been synthesized and characterized. The neutral complexes [PdPh(I)(P–N)] **1** and [PdMe(I)(P–N)] **2** have been synthesized by oxidative addition of PhI and MeI, respectively to $Pd(dba)_2$ (dba = dibenzylideneacetone) in the presence of the P–N ligand. The cationic complexes $[PdPh(PPh_3)(P–N)]BF_4$ **3** and $[PdMe(PPh_3)(P–N)]BF_4$ **4** were obtained by adding an acetone solution of $AgBF_4/PPh_3$ to the corresponding neutral precursors **1** and **2**, respectively. A cationic allyl complex, $[Pd(\eta^3\text{-}C_3H_5)(P–N)]Br$ **5**, has also been prepared by oxidative addition of 3-bromopropene to $Pd(dba)_2$ in presence of the P–N ligand. Single crystal structure determinations have been carried out for **1**, **4** and **5**. Carbonylation of the metal–carbon bond in these new complexes was also studied. The neutral complexes **1** and **2** react smoothly with CO to give carbonylated products [Pd(C(O)Ph)I(P–N)] **6** and [Pd(C(O)Me)I(P–N)] **7**, respectively. The methyl complex **2** reacted much faster than the phenyl complex **1**. The cationic complexes **3** and **4** are inert and do not give any carbonylated product. However, in the case of the reaction of **3**, evidence has been obtained for the formation of a CO-coordinated complex $[PdPh(PPh_3)(CO)(P–N)]BF_4$ **8** in which the P–N ligand temporarily acts as a monodentate phosphorus-bonded ligand. On the other hand, a cationic complex containing a weakly coordinating acetone molecule, $[PdMe\{(CD_3)_2CO\}(P–N)]BF_4$ **9**, showed an enhanced reactivity toward CO and gave $[Pd\{MeC(O)\}(CO)(P–N)]BF_4$ **10**.

Introduction

The chemistry of P–N and other hybrid ligands continues to attract interest due to their ability to act as hemilabile ligands.[1–5] They also can control the reactivities of metal sites owing to the different steric and electronic properties of the donor groups. This bifunctional character of hybrid ligands has proven to be very useful in homogeneous transition metal catalysis, activation of small molecules and stabilization of reactive transition metal species. Some important organic reactions catalysed by transition metal complexes of P–N ligands are quite impressive in terms of both selectivity and reactivity.[6–12] Recently we reported a new class of hybrid P–N ligands containing an imidazole nitrogen donor.[13] We also reported a very convenient method to modify these imidazolylphosphine P–N ligands by introducing several alkyl, aryl or functional groups in their backbone.[14] This method enables us to prepare a variety of modified P–N ligands with different steric and electronic properties. We are now investigating the catalytic properties of complexes containing these P–N ligands.

It is considered that carbonylation is one of the most important reactions and the key step in many organic transformations such as hydroformylation, alkoxycarbonylation and polyketone production.[15] The mechanism of the carbonylation of metal–carbon bonds has extensively been studied for many systems both experimentally[15] and theoretically.[16] Relatively few works have been carried out on the carbonylation of organopalladium compounds of P–N ligands.[17] Furthermore, most of the carbonylation studies on the P–N systems are confined to only hemilabile ligands. Therefore, we plan to carry out an investigation on the carbonylation reaction of organopalladium complexes containing imidazolylphosphine P–N ligands which are supposed to form stable chelates with palladium. The ultimate aim of this research is the evaluation of these species as potential catalysts in organic synthesis, especially the copolymerization of olefins. In recent years several groups have reported on the Pd^{II}-catalysed copolymerization of carbon monoxide and olefins to yield copolymers which possess very attractive properties.[18] Among the studied systems, catalysts are confined to either bidentate phosphine[19] and imine[20] or monodentate phosphine.[21] Although the soft and hard donor natures of phosphorus and nitrogen are known to bind in a unique way, this system has not been well explored.

We report here the syntheses, characterizations and crystal structures of some neutral and cationic organometallic palladium(II) complexes of P–N ligands of types [PdR(I)(P–N)] and $[PdR(PPh_3)(P–N)]^+$ [where P–N = 2-(diisopropylphosphinomethyl)-1-methylimidazole and R = Ph or Me] and their reactions with CO. We also report a palladium allyl complex and its structure.



Results and discussion

Synthesis and characterization of neutral complexes [PdR(X)(P–N)]

The neutral complexes [PdPh(I)(P–N)] **1** and [PdMe(I)(P–N)] **2** were prepared by oxidative additions of iodobenzene and iodomethane respectively to a palladium(0) complex $Pd(dba)_2$

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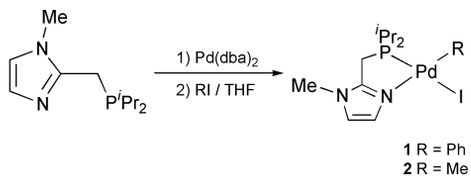
(dba = dibenzylideneacetone) in the presence of the P–N ligand (eqn. 1). The reactions were carried out in THF at refluxing



(1)

1 R = Ph
2 R = Me

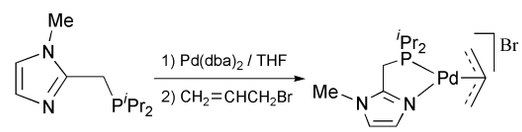
temperature for about 40 min. However, the complexes can also be formed at ambient temperature by stirring the reaction mixture for about 6 h.

Both complexes were obtained as yellow powders after filtration of the reaction mixture to remove the trace amount of metallic palladium, concentration of the filtrate to dryness, and repeated washing with diethyl ether. They are quite stable in the solid state but tend to decompose slowly in solution. A small amount of diiodo-complex [PdI_2(P–N)] was also formed in the preparation of **2** under the refluxing condition. The diiodo and the methyl complexes crystallized separately while the acetone solution of the crude products was allowed to crystallize by slow diffusion of diethyl ether; it is possible to separate them manually by using a microscope. The color and the crystal habit of these two complexes are different. The diiodo-complex is orange, whereas the methyl complex is yellow. The formation of the diiodo complex was confirmed from its preliminary X-ray crystallographic study.[22]

The coordination of both P and N donors of the ligand in complex **1** was directly observed from its single crystal structure. In addition, the ^{1}H and ^{31}P NMR spectra are also very useful and informative for determining the structures of the complexes. The coordination was easily confirmed from the observation of the resonances for imidazole H^4 and the backbone methylene (CH_2) protons, respectively. Upon coordination, relatively large downfield shifts of the resonances were observed for these protons compared with those of the free ligand due to their close proximity to the nitrogen and phosphorus donors, respectively: δ 7.72 and 2.90, respectively, for **1** δ 6.86 and 2.59 for the free ligand. The differences indicate that both donor atoms are coordinated. These two resonances for complex **2** were observed at δ 7.62 and 2.86, respectively. The coordination of the P-donor was also confirmed from the ^{31}P chemical shift value. Upon coordination, the peak shifted significantly downfield compared with that of the free ligand: for complexes **1** and **2**, δ 49.34 and 59.46, respectively. These values are significantly different from that of the free ligand which was observed at δ 1.37.[13] Furthermore, the presence of one ^{31}P resonance for each complex indicates the existence of single species in solution although two isomers (*cis* P,I and *trans* P,I) are possible for each complex. The phenyl protons of **1** appeared at δ 6.76–7.36 as a multiplet and the methyl protons of **2** appeared at δ 0.72 as a doublet. The assignment of the molecular structure (*cis* or *trans*) of **2** is possible by virtue of the $^3J_{PH}$ constant for coordinated methyl protons coupling to phosphorus. The methyl group is in the *cis* position to the phosphorus donor as indicated by the small scalar coupling [$^3J_{PH}$ = 2.93 Hz],[23] as expected by the different *trans* influences of the ligand in the coordination sphere of palladium.[24] The available spectroscopic data are not sufficient to establish the geometry of the phenyl coordinated complex **1**. However, the *trans* P,I structure was confirmed from the crystal structure and we suppose this remains intact in solution. The formation of the single isomer (*trans* P,I) for both cases can be rationalized by the effect called *transphobia*.[25] According to this effect, palladium complexes with a phosphine ligand *trans* to an aryl or acyl group are very unstable. However, in some cases both isomers can also be made, for instance an aminophosphine P–N ligand, 2-(diphenylphosphanyl)-*N*,*N*-dimethylaniline, gave a mixture of *trans* P,I and *cis* P,I isomers in 3 : 1 ratio.[26]

Syntheses and characterizations of cationic complexes

The cationic complexes [PdPh(PPh_3)(P–N)]BF_4 **3** and [PdMe(PPh_3)(P–N)]BF_4 **4** were prepared by adding an acetone solution of $AgBF_4$/PPh_3 to the corresponding neutral precursor [PdR(I)(P–N)] in acetone at 0 °C (eqn. 2). Removal of the precipitated silver salt and recrystallization from acetone–diethyl ether afforded pure complexes **3** and **4** as white and faint yellow powders, respectively. A cationic allyl complex, [Pd(η^3-C_3H_5)(P–N)]Br **5**, was also prepared by an oxidative addition of 3-bromopropene to Pd(dba)$_2$ in presence of the P–N ligand (eqn. 3). Recrystallization from acetone and diethyl ether



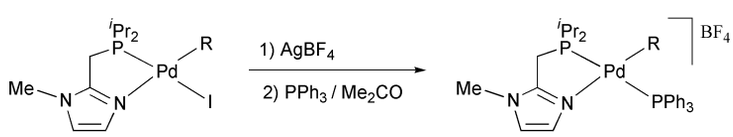
(3)

5

afforded the pure complex as a cream-colored powder. All the cationic complexes are stable in the solid state and can be exposed to air without any apparent decomposition.

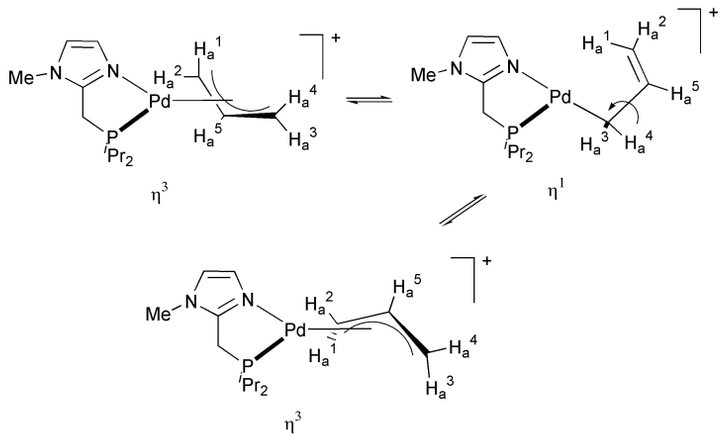
The cationic complexes were characterized by various physicochemical techniques. The ^{31}P NMR spectrum of **3** showed two doublets at δ 23.85 and 49.84 with a coupling constant $^2J_{PP}$ = 368 Hz. This large scale coupling clearly indicates that the two phosphorus donors are *trans* to each other.[27] Similarly, the two phosphorus resonances of **4** were observed at δ 27.53 and 57.54 with a coupling constant $^2J_{PP}$ = 376 Hz, indicating the *trans* configuration. The configuration of **4** can also be deduced from the coupling constant of the methyl protons with phosphorus. The methyl protons of **4** appeared at δ 0.11 as a doublet of doublets with coupling constants $^3J_{PH}$ = 4.40 and 4.39 Hz. These small coupling constants indicate the methyl group of **4** occupies the *cis* position with respect to both phosphorus donors. This structure was also confirmed by X-ray crystallography (see below). On the other hand, both *cis* and *trans* isomers have been reported for a similar type of complex of an aminophosphine P–N ligand.[26]

The allyl complex, [Pd(η^3-C_3H_5)(P–N)]Br **5**, is stereochemically non-rigid in $CDCl_3$ solution. In the ^{1}H NMR spectrum, the protons H_a^1, H_a^2 and H_a^5 of the allyl ligand give rise to sharp signals, whereas the protons *trans* to the nitrogen donor, H_a^3 and H_a^4, give a broad signal at δ 3.24 due to the *syn–anti* interchange of these protons through the usual η^3–η^1–η^3 interconversion process (Scheme 1). This interchange is well documented for square–planar allyl complexes with a hard and soft donor ligand.[28] The resonance for H_a^5 was observed at δ 5.48 as a complex multiplet, whereas H_a^1 (*anti* in relation to H_a^5) and H_a^2 (*syn* in relation to H_a^5) were observed as doublets of doublets at δ 4.76 ($^3J_{HH}$ = 7.0 and $^3J_{PH}$ = 6.1) and 3.63



(2)

3 R = Ph
4 R = Me



Scheme 1

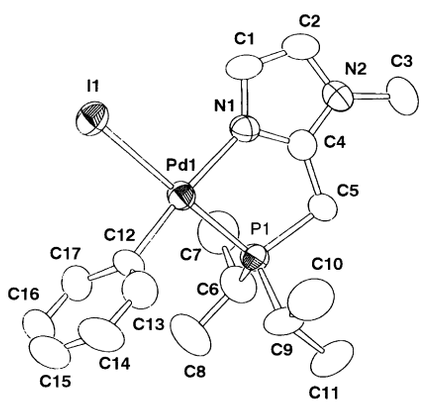


Fig. 1 An ORTEP view of the molecular structure of complex **1**. All hydrogen atoms are omitted for clarity (in all Figures).

($^3J_{HH}$ = 14.1 and $^3J_{PH}$ = 9.1 Hz), respectively. The assignments are based on the magnitudes of the coupling constants.[29]

Crystal structures of complexes 1, 4 and 5

The solid state structures of three complexes **1**, **4**, and **5** were determined by X-ray diffraction methods. An ORTEP[30] view of the molecular structure of **1** is depicted in Fig. 1; selected bond distances and angles are listed in Table 1. The solid state structure consists of an approximately square-planar [PdPh(I)(P–N)] molecule. The P–N ligand coordinates *via* both phosphorus and nitrogen atoms forming a 5-membered chelate ring. The phenyl group occupies the *cis* position with respect to the phosphine donor of the P–N ligand and is roughly orthogonal to the mean coordination plane. The P1–Pd–N1 bite angle is 82.9(2)° and the bond angles around the palladium sum to about 360°. The angle between the coordinated carbon of the phenyl group and the phosphorus atom, P1–Pd–C12 [92.9(2)°], is significantly different from that of 87.7(2)° found in a related complex of an aminophosphine P–N ligand [PdPh(I)(PNMe$_2$)] [where PNMe$_2$ = 2-(diphenylphosphanyl)-*N*,*N*-dimethylaniline].[26] This deviation might be due to the steric repulsion between the bulky isopropyl groups of the phosphorus atom and the coordinated phenyl ligand. The aminophosphine ligand of the latter complex contains phenyl groups at its phosphorus atom. The Pd–I distance [2.6585(7) Å] is consistent with the values observed in [PdPh(I)(PNMe$_2$)] [2.655(1) Å].[25] The Pd–P distance [2.241(2) Å] is slightly longer than that of 2.208(2) Å and the Pd–C_{Ph} distance [2.002(7)] is comparable with the value of 2.029(6) Å found for [PdPh(I)(PNMe$_2$)].[26] However, the Pd–N1 distance [2.123(6) Å] is significantly shorter than that of 2.252(5) Å found for [PdPh(I)(PNMe$_2$)].[26] This shortening might be due to the stronger donor ability of the imidazole nitrogen compared to that of the amine ligands. This value is also considerably shorter compared with those observed for the related complexes, PdPh(I)(PC=NR), of iminophosphine ligands. A mean Pd–N distance of 2.17 Å was observed in PdPh(I)(PC=NR), where PC=NR is *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-methylamine or *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-ethylamine.[26]

Table 1 Selected bond distances (Å) and angles (°) for complex **1**

Pd1–N1	2.123(6)	P1–C6	1.838(9)
Pd1–P1	2.241(2)	P1–C9	1.827(10)
Pd1–I	2.6585(7)	N1–C4	1.334(9)
Pd1–C12	2.002(7)	N2–C4	1.357(9)
P1–C5	1.863(7)	C4–C5	1.46(1)
I1–Pd1–N1	94.3(2)	P1–Pd1–C12	92.9(2)
I1–Pd1–C12	90.3(2)	Pd1–N1–C4	118.5(5)
I1–Pd1–P1	173.65(6)	Pd1–P1–C5	103.7(2)
P1–Pd1–N1	82.9(2)	N1–C4–C5	124.1(6)
N1–Pd1–C12	173.9(3)	C4–C5–P1	108.8(5)

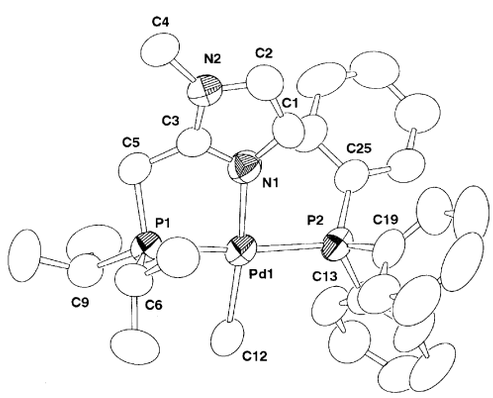


Fig. 2 An ORTEP view of the cation of complex **4**.

An ORTEP view of the cation of complex **4** is depicted in Fig. 2; selected bond distances and angles are listed in Table 2. The cationic complex **4** possesses a palladium atom with approximately square-planar coordination in which the methyl group is positioned *trans* with respect to the imidazole nitrogen donor. The P1–Pd–N1 bite angle is 81.2(1)°, which is very similar to that observed in complex **1**, and the bond angles around the palladium sum to about 360°. The two phosphorus atoms occupy *trans* positions to each other with the distances 2.288(2) and 2.348(2) Å for Pd–P1 and Pd–P2 respectively. The Pd–P distance for the P1 donor of the chelating P–N ligand is significantly shorter than that for P2 of triphenylphosphine. However, it is considerably longer than that observed in the neutral complex **1**. This elongation is due to the strong *trans* weakening effect in **4** where two phosphorus atoms occupy the *trans*

Table 2 Selected bond distances (Å) and angles (°) for complex **4**

Pd1–N1	2.149(5)	P1–C6	1.830(7)
Pd1–P1	2.288(2)	P1–C9	1.838(7)
Pd1–P2	2.348(2)	N1–C3	1.324(8)
Pd1–C12	2.166(9)	N2–C3	1.338(8)
P1–C5	1.825(7)	C3–C5	1.493(9)
P1–Pd1–N1	81.2(1)	P2–Pd1–C12	92.8(2)
P1–Pd1–C12	91.3(2)	Pd1–N1–C3	117.5(4)
P1–Pd1–P2	174.99(6)	Pd1–P1–C5	102.6(2)
P2–Pd1–N1	94.9(1)	N1–C3–C5	124.1(5)
N1–Pd1–C12	171.5(2)	C3–C5–P1	107.5(4)

Table 3 Selected bond distances (Å) and angles (°) for complex **5**

Pd1–N1	2.072(6)	P1–C6	1.839(9)
Pd1–P1	2.292(2)	P1–C9	1.846(8)
Pd1–C12	2.129(9)	N1–C4	1.344(9)
Pd1–C13	2.102(10)	C4–C5	1.47(1)
Pd1–C14	2.223(10)	C12–C13	1.39(2)
P1–C5	1.862(8)	C13–C14	1.22(2)
P1–Pd1–N1	83.2(2)	N1–Pd1–C14	103.4(3)
P1–Pd1–C12	104.0(3)	Pd1–P1–C5	102.7(2)
P1–Pd1–C13	141.5(5)	Pd1–N1–C4	119.3(5)
P1–Pd1–C14	173.1(3)	P1–C5–C4	108.1(5)
N1–Pd1–C12	172.8(3)	N1–C4–C5	124.8(6)
N1–Pd1–C13	134.4(5)	C12–C13–C14	143(1)

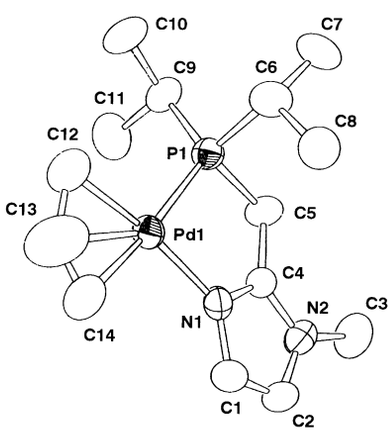


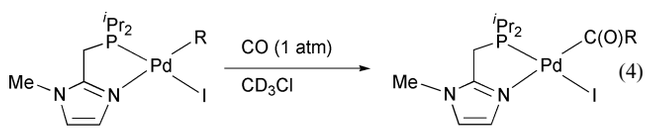
Fig. 3 An ORTEP view of the cation of complex **5**.

positions. The Pd–N1 distance of 2.149(5) Å is also slightly longer than that of **1**. The Pd-C_{Me} distance of 2.166(9) Å is comparatively longer than those observed in organopalladium methyl complexes of other P–N ligands, for instance 2.068(2) and 2.142(8) Å in chloro[1-(dimethylamino)-8-(diphenylphosphino)naphthalene]methylpalladium[17b] and bromo-[*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine]methylpalladium,[23a] respectively.

An ORTEP view of the cation of the allyl complex **5** is depicted in Fig. 3; selected bond distances and angles are listed in Table 3. The complex possesses a palladium atom with approximately square-planar coordination with a bite angle P1–Pd–N1 of 83.2(2)°. The four coordination sites are occupied by the P and N atoms of the ligand and by the η^3-allyl ligand. The coordination plane can be defined by the P,N donor atoms of the imidazolylphosphine and the terminal carbon atoms C12 and C14 of the allyl ligand. The central carbon atom of the allyl ligand, C13, deviates from the coordination plane by 0.26 Å. Similarly, the backbone carbon atom of the P–N ligand, C5, resides 0.36 Å above of this plane on the same side as the central allyl carbon. The distances from the two terminal allyl carbon atoms to palladium are significantly different due to the different *trans* influences of the P and N donors: 2.129(9) and 2.223(10) Å, respectively for C12 (*trans* to N) and C14 (*trans* to P). The Pd–P distance, 2.292(2) Å, is normal but the Pd–N distance, 2.072(6) Å, is considerably shorter than other reported values for aminophosphine complexes; this may be ascribed to the stronger donor ability of the imidazole N-donor compared with the amine N-donor.[26] The C–C bond lengths within the allyl ligand are noteworthy, 1.39(2) Å for C12–C13 and 1.22(2) Å for C13–C14, indicating somewhat more double-bond character between C13 and C14 and this difference might be caused by different donor properties of the P–N ligand.

Reactions of neutral and cationic complexes with CO

The reactions of the neutral and cationic complexes **1**, **2**, **3**, and **4** with CO were followed by ^{1}H and ^{31}P NMR spectroscopies either in $CDCl_3$ or CD_2Cl_2 at ambient temperature and pressure. The insertion of carbonyl in the neutral complex **1** was completed within 4 h to give the corresponding carbonylated product [Pd(C(O)Ph)I(P–N)] **6**, whereas it took only 15 min for complex **2**, giving [Pd(C(O)Me)I(P–N)] **7** (eqn. 4). No decom-



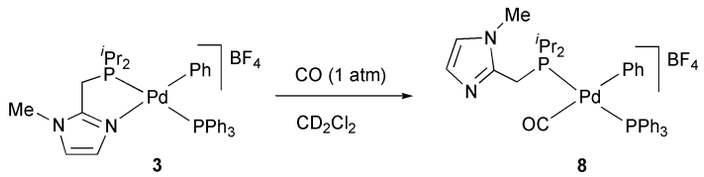
(4)

1 R = Ph
2 R = Me

6 R = Ph
7 R = Me

position was observed during the reactions of both complexes. These two complexes were also isolated in the solid state as yellow powders in almost quantitative yields. Both are air and thermally stable in the solid state. Their formation was confirmed from NMR and IR studies. The ^{1}H NMR spectrum is very informative for the acetyl complex **7**. A characteristic downfield shift of the methyl protons from δ 0.72 to 2.64 was observed, indicating insertion of CO into the Pd–Me bond.[31,32] The ^{31}P signal shifted to upfield from δ 59.46 to 45.57. The magnitude of this shift ($\Delta\delta(^{31}P) = \approx 14$ ppm) is somewhat large for the electron rich isopropylphosphine. Such a difference is usually observed for diphenylphosphino derivatives.[17a,32] The ^{31}P NMR signal for **6** appeared at δ 43.70. The IR spectrum shows a new band at 1627 cm^{-1} for complex **6** and 1654 cm^{-1} for **7** which we assign to the C=O stretching bands of Pd–benzoyl and Pd–acetyl, respectively.

The reactivities of the cationic complexes **3** and **4** toward carbonyl were examined by means of NMR and IR. Carbonyl insertions into Pd–C bonds were not observed under normal conditions even after prolonged reaction time. However, it is evident from the spectroscopic data that after keeping **3** in a CO-bubbled CD_2Cl_2 solution for about a week at −10 °C the imidazole N-donor was replaced by CO to afford the complex $[PdPh(PPh_3)(CO)(P–N)]BF_4$ **8**, where the P–N ligand acts as a P-monodentate (eqn. 5). The ^{1}H NMR spectrum of **8** shows a significant upfield shift of the imidazole-H^4 proton from δ 6.57 to 5.59, indicating the imidazole group of the P–N ligand is free from the coordination site. This upfield shift of H^4 adjacent to the imidazole N-donor is due to a strong shielding effect caused by decoordination of the N-donor. The two ^{31}P resonances, δ 49.30 and 23.78 with J_{PP} = 367.4 Hz, are very similar to those of the original complex **3**. This high coupling indicates that the resultant complex **8** also exists as a P,P *trans* isomer similar to that of the parent complex and probably this arrangement inhibited the CO insertion into the Pd–Ph bond. This fact is in accord with the assumption of *cis* migratory insertion.[33] For carbonyl insertion into the M–C bond it is important to insure a coordination site available at the *cis* position with respect to the coordinated alkyl or aryl group for the incoming CO in a



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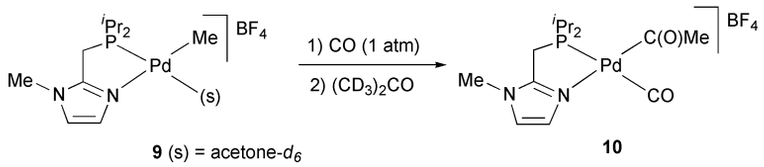

(6)

square-planar geometry. The solution IR spectrum of **8** shows an absorption around 2120 cm^{-1}, which indicates that the CO group is loosely bonded to the palladium atom. Previously, Vrieze and co-workers[17b] found such a high frequency band around 2135 cm^{-1} for CO loosely bonded to palladium. The carbonyl coordinated species **8** is very unstable and easily converted into the parent complex **3**. In contrast the methyl complex **4** does not give any such carbonyl species.

The results obtained in the present study indicate that the reactivity of the organopalladium complexes toward CO insertion highly depends on the nature of the ligands occupying the *cis* position with respect to the alkyl or aryl group and this dependency is well documented for many other systems. The carbonyl insertion into Pd–C bonds was inhibited when the iodo group of **1** and **2** was replaced by a strong ligand, triphenylphosphine. It is well established that cationic organopalladium complexes show enhanced reactivities toward carbonyl insertion when the *cis* position with respect to an alkyl or aryl group is occupied by a weakly coordinating ligand. In order to clarify this, we chose acetone as a ligand for the carbonylation reaction. An acetone coordinated cationic complex $[PdMe\{(CD_3)_2CO\}(P–N)]BF_4$ **9** was prepared in an NMR tube by addition of an equimolar or small excess amount of $AgBF_4$ to an acetone-d_6 solution of **2**. In this experiment **2** (methyl) was used because the progress of the carbonylation reaction was expected to easily be monitored by observing the development of the new resonance for the acetyl protons. About 25% conversion of **9** into its acetyl derivative $[Pd\{MeC(O)\}(CO)(P–N)]BF_4$ **10** was observed after 3 min bubbling of CO at ambient pressure and temperature followed by vigorous shaking (eqn. 6). The ^1H NMR spectrum showed a new resonance at δ 2.22 upon bubbling CO into the solution of **9** which was assigned to acetyl protons. The ^{31}P NMR spectrum showed two resonances at δ 67.67 and 57.14 with an intensity ratio of about 4 : 1. The first resonance is assignable to the original complex **9** and that at δ 57.14 to the acetyl derivative **10**. However, we failed in monitoring the complete conversion because of the instability of complex **10** and rapid precipitation of palladium black.

Conclusion

The present study demonstrates that the imidazolylphosphine P–N ligand is effective to stabilize organopalladium complexes both in the solid and solution states. The solid state structures of neutral and cationic complexes show the significant shortening of Pd–N distances compared with other reported distances for aminophosphine complexes. The neutral organopalladium complexes are reactive toward carbonyl insertion reactions, whereas the reactivities of cationic complexes depend upon the nature of the ligands occupying the *cis* position with respect to the alkyl or aryl group. A rapid insertion of CO into the Pd–C bond was observed for a cationic complex while this *cis* position was occupied by a weakly coordinating solvent molecule.

Experimental

Methods

All reactions were run in oven-dried glassware under an atmosphere of N_2 gas. Anhydrous solvents used in reactions either were purchased in anhydrous form or distilled prior to use (THF from sodium–benzophenone). The ligand 2-(diisopropylphosphinomethyl)-1-methylimidazole[13] and $Pd(dba)_2$[34] were prepared according to published procedures. All chemicals were reagent grade used as received.

Instruments

All NMR spectra were recorded with a JEOL JMTC 400 MHz spectrometer and are reported in δ units. ^1H spectra were referenced to TMS, ^{13}C to the $CDCl_3$ peak at δ 77.0 and ^{31}P spectra 85% H_3PO_4 as external standard. Elemental analyses were performed by the Faculty of Pharmaceutical Science, Kanazawa University. X-Ray measurements were made on a Rigaku AFC7R diffractometer or Rigaku Raxis IV imaging plate area detector.

Preparations

[PdPh(I)(P–N)] 1. To a stirred solution of $Pd(dba)_2$ (1 mmol, 0.57 g) in THF (70 ml), a THF (20 ml) solution of the P–N ligand (1 mmol, 0.21 g) was added dropwise. After stirring for 10 min a fourfold excess of PhI (4 mmol, 448 μl) was added and the reaction mixture refluxed for 40 min. The resultant solution was then filtered in order to remove the trace amount of palladium black. The solvent was removed from the filtrate by evaporation and the residue washed several times with Et_2O until the washings were colorless. Recrystallization of the residual solid from chloroform–diethyl ether gave the complex as a yellow powder (0.40 g, 78%). Calc. for $C_{17}H_{26}IN_2PPd$: C, 39.06; H, 5.01; N, 5.36%. Found: C, 38.62; H, 4.73; N, 4.98%. ^1H NMR ($CDCl_3$): δ 0.96–1.23 (m, 12H, CH_3 of *i*Pr), 2.22 (m, 2H, CH of *i*Pr), 2.90 (d, 2H, $^2J_{PH}$ = 9.53 Hz, PCH_2), 3.67 (s, 3H, NCH_3), 6.84 (d, 1H, H^5), 7.72 (d, 1H, H^4) and 6.76–7.36 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.12 (s, CH_3 of *i*Pr), 17.50 (s, CH_3 of *i*Pr), 20.30 (d, *α*-CH, $^1J_{CP}$ = 22.6), 23.64 (d, CH of *i*Pr, $^1J_{CP}$ = 23.1 Hz), 35.13 (s, NMe), 122.10 (s, C^5), 129.61 (s, C^4) and 122.44–138.53 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 49.34 (s).

[PdMe(I)(P–N)] 2. This complex was prepared by the same procedure as described for **1** by using 0.57 g of $Pd(dba)_2$ (1 mmol), 0.21 g of the P–N ligand (1 mmol) and 250 μl of MeI (4 mmol). The complex was obtained as yellow crystals after recrystallizing from chloroform–diethyl ether. Under the reflux condition some diiodo complex was obtained. However, stirring the reaction mixture for about 6 h at ambient temperature affored **2** in moderate yield (0.34 g, 74%). Calc. for $C_{12}H_{24}IN_2PPd$: C, 31.29; H, 5.25; N, 6.08%. Found: C, 30.84; H, 4.91; N, 6.13%. ^1H NMR ($CDCl_3$) δ 0.72 (d, 3H, $^3J_{PH}$ = 2.93, $PdCH_3$), 1.12–1.32 (m, 12H, CH_3 of *i*Pr), 2.30 (m, 2H, CH of *i*Pr), 2.86 (d, 2H, $^2J_{PH}$ = 9.51 Hz, PCH_2), 3.68 (s, 3H, NCH_3), 6.80 (d, 1H,

H^5) and 7.62 (d, 1H, H^4). ^{13}C NMR ($CDCl_3$) δ −16.95 (PdMe), 17.52 (s, CH_3 of *i*Pr), 18.30 (s, CH_3 of *i*Pr), 20.62 (d, *α*-CH, $^1J_{CP}$ = 21.1), 24.10 (d, CH of *i*Pr, $^1J_{CP}$ = 24.0 Hz), 34.90 (s, NMe), 121.80 (s, C^5) and 129.70 (s, C^4). ^{31}P NMR ($CDCl_3$): δ 59.46 (s).

[PdPh(PPh$_3$)(P–N)]BF$_4$ 3. To an acetone solution (10 ml) of the neutral complex **1** (0.5 mmol, 0.26 g), a solution containing PPh_3 (0.5 mmol, 0.13 g) and $AgBF_4$ (0.5 mmol, 0.10 g) in acetone (5 ml) was added slowly at 0 °C, resulting in immediate silver iodide precipitation. After stirring the mixture for 40 min the precipitate was removed by filtration and the solution was concentrated to approximately 4–5 ml. Diethyl ether was cautiously layered on the surface. The colorless crystals formed were separated by filtration and dried *in vacuo* (0.32 g, 88%). Calc. for $PdC_{35}H_{41}BF_4N_2P_2Pd$: C, 56.44; H, 5.55; N, 3.76%. Found: C, 55.97; H, 5.55; N, 3.69%. ^1H NMR ($CDCl_3$): δ 0.97–1.31 (m, 12H, CH_3 of *i*Pr), 2.33 (m, 2H, CH of *i*Pr), 3.42 (d, 2H, $^2J_{PH}$ = 8.78 Hz, PCH_2), 3.82 (s, 3H, NCH_3), 5.53 (d, 1H, H^5), 6.57 (d, 1H, H^4) and 6.64–7.44 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.09 (s, CH_3 of *i*Pr), 17.54 (s, CH_3 of *i*Pr), 19.50 (d, *α*-CH, $^1J_{CP}$ = 21.7), 23.49 (d, CH of *i*Pr, $^1J_{CP}$ = 22.3 Hz), 35.48 (s, NMe), 122.35 (s, C^5), 129.52 (s, C^4) and 123.07–136.84 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 23.85 and 49.84 (d, $^2J_{PP}$ = 368 Hz).

[PdMe(PPh$_3$)(P–N)]BF$_4$ 4. This complex was prepared by the same procedure as described for **3** by using 0.23 g of **2** (0.5 mmol), 0.10 g of $AgBF_4$ (0.5 mmol) and 0.13 g of PPh_3 (0.5 mmol). The complex was obtained as faint yellow crystals (85%). Calc. for $C_{30}H_{39}BF_4N_2P_2Pd$: C, 52.77; H, 5.76; N, 4.10%. Found: C, 52.28; H, 5.84; N, 4.13%. ^1H NMR ($CDCl_3$): δ 0.11 (dd, 3H, $^3J_{PH}$ = 4.40, $PdCH_3$), 1.19–1.32 (m, 12H, CH_3 of *i*Pr), 2.49 (m, 2H, CH of *i*Pr), 3.43 (d, 2H, $^2J_{PH}$ = 10.24 Hz, PCH_2), 3.80 (s, 3H, NCH_3), 5.56 (d, 1H, H^5), 6.53 (d, 1H, H^4) and 7.44–7.57 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ −8.16 (PdMe), 17.70 (s, CH_3 of *i*Pr), 17.37 (s, CH_3 of *i*Pr), 19.80 (d, *α*-CH, $^1J_{CP}$ = 21.5), 23.64 (d, CH of *i*Pr, $^1J_{CP}$ = 24.0 Hz), 35.44 (s, NMe), 122.12 (s, C^5), 126.80 (s, C^4) and 128.88–134.73 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 27.53 and 57.54 (d, $^2J_{PP}$ = 376 Hz).

[Pd(η^3-C$_3$H$_5$)(P–N)]Br 5. The same procedure was used as for the preparation of complex **1** by using 0.57 g of $Pd(dba)_2$ (1 mmol) and 345 μl of BrC_3H_5 (4 mmol). The complex was obtained as a cream-colored powder after recrystallizing from $CHCl_3$-Et_2O (0.32 g, 73%). Calc. for $C_{14}H_{26}BrN_2PPd$: C, 38.25; H, 5.96; N, 6.37%. Found: C, 37.88; H, 5.81; N, 6.18%. ^1H NMR ($CDCl_3$): δ 1.18–1.26 (m, 12H, CH_3 of *i*Pr), 2.51 (m, 2H, CH of *i*Pr), 3.24 (br, 2H, allyl H^3 and H^4), 3.63 (m, 1H, $^3J_{HH}$ = 14.1, $^3J_{PH}$ = 9.1, allyl H^2), 3.93 (d, 2H, $^2J_{PH}$ = 10.24, PCH_2), 4.07 (s, 3H, NCH_3), 4.76 (m, 1H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 6.1 Hz, allyl H^1), 5.48 (m, 1H, allyl H^5), 6.93 (d, 1H, H^5) and 6.99 (d, 1H, H^4). ^{13}C NMR ($CDCl_3$): δ 18.54 (s, CH_3 of *i*Pr), 18.88 (s, CH_3 of *i*Pr), 21.28 (d, *α*-CH, $^1J_{CP}$ = 24.0), 24.72 (d, CH of *i*Pr, $^1J_{CP}$ = 23.1 Hz), 36.54 (s, NMe), 46.92 (allyl C *cis* to P), 76.34 (allyl C *trans* to P), 118.83 (CH_2CHCH_2), 123.04 (s, C^5) and 129.75 (s, C^4). ^{31}P NMR ($CDCl_3$): δ 65.92 (s).

[Pd(C(O)Ph)I(P–N)] 6. The neutral complex **1** (0.3 mmol, 0.15 g) was dissolved in chloroform (5 ml) and CO gas bubbled into the solution for 5 min at room temperature. The solution was then vigorously shaken and left for about 4 h. After completion of the reaction diethyl ether was layered cautiously on the surface of the solution. The yellow crystals were separated by filtration, washed with diethyl ether and dried *in vacuo* (0.16 g, 96%). Calc. for $C_{19}H_{26}IN_2OPPd$: C, 39.25; H, 4.76; N, 5.09%. Found: C, 38.83; H, 4.55; N, 5.03%. ^1H NMR ($CDCl_3$): δ 1.09–1.15 (m, 12H, CH_3 of *i*Pr), 2.20 (m, 2H, CH of *i*Pr), 2.84 (d, $^2J_{PH}$ = 9.27 Hz, 2H, PCH_2), 3.64 (s, 3H, NCH_3), 6.84 (d, 1H, H_5), 7.70 (d, 1H, H^4) and 6.76–7.36 (m, 5H, PdC(O)Ph). ^{31}P NMR ($CDCl_3$): δ 43.70 (s). IR (KBr): ν(C=O) 1627 cm^{-1}

[Pd(C(O)Me)I(P–N)] 7. This complex was prepared by the same procedure as described for **6** by using **2** but in this case the reaction was completed within 15 min. The complex was obtained as a yellow powder (93%). Calc. for $C_{13}H_{24}IN_2OPPd$: C, 31.95; H, 4.95; N, 5.73%. Found: C, 31.54; H, 4.91; N, 6.13%. ^1H NMR ($CDCl_3$): δ 1.19–1.33 (m, 12H, CH_3 of *i*Pr), 2.23 (m, 2H, CH of *i*Pr), 2.64 (s, 3H, $PdC(O)CH_3$), 2.86 (d, $^2J_{PH}$ = 9.50 Hz, 2H, PCH_2), 3.68 (s, 3H, NCH_3), 6.83 (d, 1H, H^5) and 7.34 (d, 1H, H^4). ^{13}C NMR ($CDCl_3$): δ 17.53 (s, CH_3 of *i*Pr), 18.14 (s, CH_3 of *i*Pr), 19.54 (d, *α*-CH, $^1J_{CP}$ = 20.7), 24.08 (d, CH of *i*Pr, $^1J_{CP}$ = 20.6 Hz), 34.63 (s, NMe), 46.97 (s, CH_3CO), 122.19 (s, C^5), 128.56 (s, C^4) and 147.14 (s, CO). ^{31}P NMR ($CDCl_3$): δ 45.57 (s). IR (KBr): ν(C=O) 1654 cm^{-1}.

CO insertion reactions of neutral and cationic complexes

Each organopalladium complex (**1**, **2**, **3** and **4**) was dissolved in an appropriate solvent (0.60 ml), and CO gas (1 atm) bubbled into the solution for 5 min at room temperature. The solution was then vigorously shaken and subjected to NMR observation at various intervals. The CO insertions into the M–C bonds occurred smoothly for **1** and **2** and afforded complexes **6** and **7** respectively. On the other hand, **3** and **4** are quite stable to CO insertion. However, a CO-coordinated complex **8** was formed at a specific reaction condition [CO (1 atm) bubbling for 10 min and storing the mixture at −10 °C for 7 d]. [PdPh(PPh$_3$)(CO)(P–N)]BF$_4$ **8**. ^1H NMR (CD_2Cl_2): δ 0.96–1.29 (m, 12H, CH_3 of *i*Pr), 2.32 (m, 2H, CH of *i*Pr), 3.22 (d, 2H, $^2J_{PH}$ = 10.08 Hz, PCH_2), 3.75 (s, 3H, NCH_3), 5.31 (d, 1H, H^5), 5.59 (d, 1H, H^4) and 6.65–7.44 (m, 20H, Ph). ^{31}P NMR (CD_2Cl_2): δ 23.78 and 49.30 (d, $^2J_{PP}$ = 367 Hz). IR (CD_2Cl_2): ν(C=O) 2120 cm^{-1}.

Generation of [PdMe{(CD$_3$)$_2$CO}(P–N)]BF$_4$ 9 in an NMR tube and its reaction with CO to give [Pd{MeC(O)}(CO)(P–N)]BF$_4$ 10

To a solution containing complex **2** in acetone-d_6 (0.4 ml) was added a solution of an equimolar amount of $AgBF_4$ in acetone-d_6 (0.3 ml) at 0 °C in an NMR tube. AgI was formed immediately. The NMR tube was vigorously shaken and kept until the upper layer became clear and subjected to NMR observation. After generating complex **9** in an NMR tube, CO was bubbled at 0 °C for 3 min and NMR again observed revealing two sets of signals which corresponded to **10** and unchanged **9**. [PdMe{(CD$_3$)$_2$CO}(P–N)]BF$_4$ **9**. ^1H NMR (acetone-d_6): δ 0.23 (d, $^3J_{PH}$ = 3.9 Hz, 3H, $PdCH_3$), 1.22–1.36 (m, 12H, CH_3 of *i*Pr), 2.48 (m, 2H, CH of *i*Pr), 3.51 (d, 2H, PCH_2), 3.81 (s, 3H, NCH_3), 6.77 (d, 1H, H^5) and 7.23 (d, 1H, H^4). ^{31}P NMR (acetone-d_6): δ 67.26 (s). [Pd{MeC(O)}(CO)(P–N)]BF$_4$ **10**. ^1H NMR (acetone-d_6): δ 2.27 (s, 3H, $PdC(O)CH_3$), 3.47 (d, 2H, PCH_2), 3.78 (s, 3H, NCH_3), 6.73 (d, 1H, H^5) and 7.21 (d, 1H, H^4). ^{31}P NMR (acetone-d_6): δ 57.14 (s). The resonances for the protons of the isopropyl group were overlapped with those of the respective protons of **9**.

X-Ray crystallographic studies

All crystallographic data for complexes are listed in Table 4. Crystals of **1** were grown by slow evaporation of its chloroform solution, those of **4** and **5** by slow diffusion of diethyl ether into their acetone solutions. All measurements of **1** and **5** were performed on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å). The measurement of complex **4** was carried out by a Rigaku RAXIS-IV imaging plate area detector using graphite monochromated Mo-Kα radiation (λ = 0.71070 Å). The structure of **1** was solved by Patterson methods[35] whereas, those of **4** and **5** were

Table 4 Crystallographic data for complexes **1**, **4** and **5**

	1	**4**	**5**
Formula	$C_{17}H_{26}IN_2PPd$	$C_{30}H_{39}BF_4N_2P_2Pd$	$C_{14}H_{26}BrN_2PPd$
M	522.68	682.80	439.65
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pna2_1$ (no. 33)	$P2_1/c$ (no. 14)	$Pbca$ (no. 61)
a/Å	17.516(1)	11.6414(5)	13.358(4)
b/Å	14.429(1)	8.2299(3)	25.953(6)
c/Å	7.988(1)	33.904(1)	10.350(3)
β/°	—	94.264(1)	
U/Å^3	2018.8(3)	3239.3(2)	3588(1)
Z	4	4	8
μ(Mo-Kα)/cm^{-1}	25.28	7.17	33.49
T/°C	23.0	23.0	23.0
No. of reflections (total)	2667	5100	4619
(unique)	2663	4997	4619
R_{int}	—	0.045	—
R, R_w	0.027, 0.081	0.063, 0.097	0.048, 0.076

solved by SHELXS 86[36] and expanded using Fourier techniques.[37] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **1** and **4** were included in the structure factor calculation but not refined. All calculations were performed using TEXSAN.[38]

CCDC reference numbers 154050–154052.

See http://www.rsc.org/suppdata/dt/b0/b009599k/ for crystallographic data in CIF or other electronic format.

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