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Synthesis and reactions of heterodinuclear organopalladium complex having an unsymmetrical PN ligand

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This paper is dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Novel heterodinuclear organopalladium complexes having an unsymmetrical PN ligand ($Et_2NC_2H_4PPh_2$-κ^2N,P)RPd–ML_n ($ML_n = Co(CO)_4$; R = Me (**2a**), Ph (**2b**), $ML_n = MoCp(CO)_3$; R = Ph (**3b**)) are synthesized by metathetical reactions of PdRX($Et_2NC_2H_4PPh_2$-κ^2N,P) (X = I, NO_3) with $Na^+[ML_n]^-$. Reversible dissociation of the Pd–N bond in **3b** is revealed by variable temperature NMR studies. Reactions of **2a** and **2b** with CO yield corresponding acyl complexes ($Et_2NC_2H_4PPh_2$-κ^2N,P)(RCO)Pd–$Co(CO)_4$ (R = Me (**5a**), Ph (**5b**)). Rate of CO insertion for **2a** and **2b** is significantly faster than those for mononuclear methylpalladium complex, PdMeI($Et_2NC_2H_4PPh_2$-κ^2N,P) (**1a**), and methylpalladium–cobalt complex with a 1,2-bis(diphenylphosphino)ethane (dppe) ligand, (dppe-κ^2P,P')MePd–$Co(CO)_4$ (**6a**). **5a** smoothly reacts with nucleophiles such as diethylamine, methanol and benzenethiol to give corresponding amide, ester and thioester, respectively. These reactions of **5a** are also significantly faster than those of corresponding mononuclear analogues and the similar heterodinuclear complexes with symmetrical bidentate ligands such as 1,2-bis(diphenylphosphino)ethane or N,N,N',N'-tetramethylethylenediamine ligand.

Keywords: Heterodunuclear organopalladium complex; Unsymmetrical PN ligand; CO insertion

1. Introduction

Heterodinuclear organometallic complexes are expected to show cooperative effects of different metal centers [1]. We previously reported synthesis of hetrodinuclear organoplatinum or -palladium complexes with a symmetrical bidentate ligand such as 1,5-cyclooctadiene (cod), 1,2-bis(diphenylphosphino)ethane (dppe), N,N,N',N'-tetramethylethylenediamine (tmeda), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen), L_2RM–$M'L'_n$ (M = Pt, Pd; M′ = Mo, W, Mn, Re, Fe, Co; R = Me, Et, CH_2CMe_3, Ph, COMe, COPh, H; L_2 = cod, dppe, tmeda, bpy, phen; L′ = CO, Cp) [2]. They show unique reactions such as organic group transfer between different metal centers [2a,2c,2d,2h,2k,2o], significant acceleration of β-H elimination [2f,2i], and enhanced CO insertion reactions [2g,2l]. On the other hand, introduction of an unsymmetrical PN ligand into organometallic complex is expected to give higher selectivity and activity, because PN chelating ligand may provide a preferential vacant coordination site on metal center due to facile dissociation of the nitrogen atom. We recently reported synthesis of hetrodinuclear organoplatinum complex having a hemilabile ligand and reactions of heterodinuclear methylplatinum–molybdenum derivative, ($Et_2NC_2H_4PPh_2$-κ^2N,P)MePt–$MoCp(CO)_3$ with dimethyl acetylenedicarboxylate to give novel μ-platinacyclobutenone complexes ($Et_2NC_2H_4PPh_2$-κ^2N,P)MePt{μ-η^2:η^2-$C(O)C_2(CO_2Me)_2$}MoCp(μ-CO)(CO) [3]. In this work, we investigated the synthesis and reactions of novel heterodinuclear organopalladium complexes having an unsymmetrical PN ligand.

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2. Results and discussion

2.1. Synthesis of hetetrodinucular organopalladium–cobalt (or –molybdenum) complexes

A series of novel heterodinuclear organopalladium–cobalt (or –molybdenum) complexes having an unsymmetrical PN ligand were prepared by the metathetical reaction of PdRX($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*) (R = Me, Ph; X = I, NO_3) with corresponding carbonyl metallates such as $Na^+[MoCp(CO)_3]^-$ [4] and $Na^+[Co(CO)_4]^-$ [5]. Starting complexes PdRI($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*) (R = Me (**1a**), Ph (**1b**)) were prepared by the oxidative addition of methyl or phenyl iodide to $Pd_2(dba)_3 \cdot CHCl_3$ [6] (dba = dibenzylideneacetone) in the presence of 2-(diphenylphosphino)triethylamine [7] in 46% and 14% yield, respectively (Eq. (1)). These novel organopalladium complexes having an unsymmetrical PN ligand (**1a**,**b**) were characterized by NMR and IR spectroscopies and elemental analysis. Selected IR and NMR data of newly prepared compounds, **1a** and **1b**, are summarized in Table 1. The molecular structure of **1a** was determined by single crystal X-ray structure analysis, and the ORTEP drawing of **1a** is depicted in Fig. 1. The $^{31}P\{^1H\}$ NMR spectrum of **1a** shows a singlet at δ 42.4. In the ^1H NMR of **1a**, the methylene protons of the NCH_2CH_3 moiety appear as two doublets of quartets at δ 3.05 and 3.40, indicating that these methylene protons are diastereotopic. This fact is an indication of rigid coordination of both nitrogen and phosphorus atoms to the Pd center. The Pd–Me resonance is observed at δ 0.65 as a doublet with a small $^3J_{PH}$ value 3.9 Hz, suggesting that the Me ligand locates in the *cis* position to the phosphorus atom. This structural feature may be due to difference of relative *trans* influence of the coordinating atoms, where ligands having strong *trans* influence (Me and P) disfavor mutually *trans* positions to each other. Thus, the starting complex PdMeI($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*) (**1a**) in solution as well as in solid state has a square planar geometry depicted in Eq. (1). Analogous spectroscopic data are also obtained for PdPhI($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*) (**1b**).

Table 1
Selected IR and NMR data of mononuclear palladium complex, PdRI($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*) and heterodinuclear organopalladium–cobalt(or –molybdenum) complexes, ($Et_2NC_2H_4PPh_2$-κ^2*N*,*P*)RPd–ML_n (ML_n = $Co(CO)_4$, $MoCp(CO)_3$)

Complex	IR (νCO, cm^{-1})[a]	^1H NMR (ppm, rt)		^{31}P NMR (ppm, rt)
		R	NCH_2CH_3	
1a[b]		0.65 (d, $^3J_{PH} = 3.9$ Hz, 3H, CH_3)	1.20 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH_2CH_3) 3.05 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3) 3.40 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3)	42.4 (s)
1b[c]		6.5–6.7 (m, 3H, *m*- and *p*-C_6H_5) 6.93 (m, 2H, *o*-C_6H_5)	1.36 (t, $^3J_{HH} = 7.0$ Hz, 6H, NCH_2CH_3) 3.19 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.0$ Hz, 2H, NCH_2CH_3) 3.45 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.0$ Hz, 2H, NCH_2CH_3)	32.6 (s)
2a[d]	1866 (s) 1935 (s) 2014 (s)	0.95 (d, $^3J_{PH} = 4.8$ Hz, 3H, CH_3)	0.80 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH_2CH_3) 2.72 (dq, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3) 3.10 (dq, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3)	32.7 (s)
2b[d]	1876 (s) 1901 (s) 1961 (s) 2024 (s)	6.6–6.7 (m, 3H, *m*- and *p*-C_6H_5) 6.96 (brs, 2H, *o*-C_6H_5)	0.86 (t, $^3J_{HH} = 6.6$ Hz, 6H, NCH_2CH_3) 2.84 (br, 2H, NCH_2CH_3) 3.12 (br, 2H, NCH_2CH_3)	22.6 (s)
3b[b]	1789 (s) 1886 (s)	6.5–6.6 (m, 3H, *m*- and *p*-C_6H_5) 6.97 (d, $^3J_{HH} = 7.8$ Hz, 2H, *o*-C_6H_5)	1.19 (t, $^3J_{HH} = 6.9$ Hz, 6H, NCH_2CH_3) 3.2 (br, 4H, NCH_2CH_3)	23.9 (s)
5a[e]	1686 (s) 1875 (s) 1912 (s) 1945 (s) 2020 (s)	1.99 (s, 3H, $COCH_3$)	1.78 (t, $^3J_{HH} = 6.9$ Hz, 6H, NCH_2CH_3) 2.99 (br, 4H, NCH_2CH_3)	14.2 (s)
5b[e]	1645 (m) 1890 (s) 1932 (s) 1952 (s) 2027 (m)	7.0–7.3 (m, 5H, COC_6H_5)	1.25 (t, 6H, $^3J_{HH} = 7.2$ Hz, NCH_2CH_3) 3.1 (br, 4H, NCH_2CH_3)	14.6 (s)

[a] IR spectra were measured by KBr pellet method.

[b] NMR spectra were measured in acetone-d_6.

[c] In $CDCl_3$.

[d] In C_6D_6.

[e] In CD_2Cl_2.

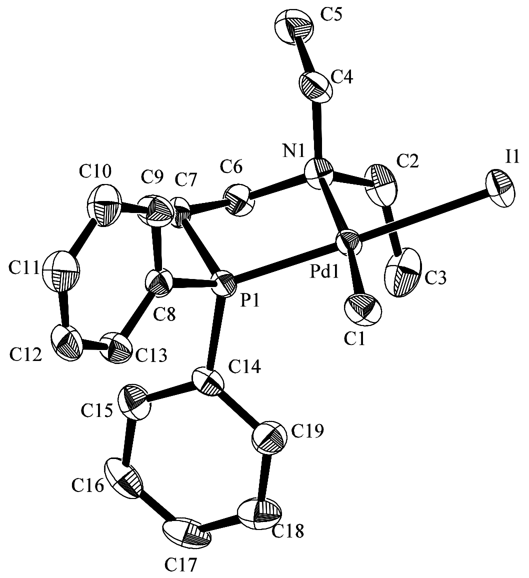
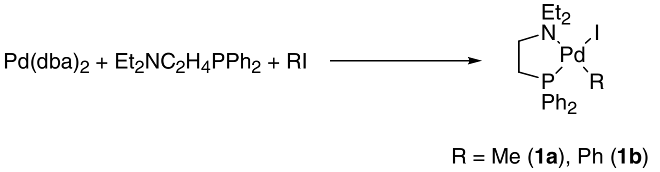
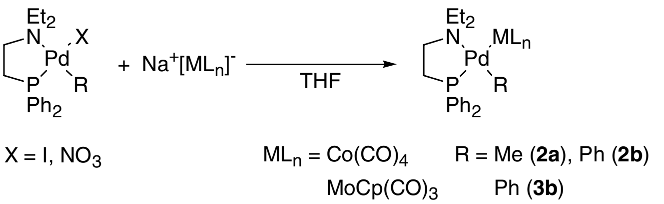


Fig. 1. ORTEP drawing of PdMeI($Et_2NC_2H_4PPh_2$-κ^2N,P) (**1a**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability. Selected bond distances (Å): Pd(1)–I(1) 2.679(3), Pd(1)–P(1) 2.194(3), Pd(1)–N(1) 2.228(3), Pd(1)–C(1) 2.011(3). Selected bond angles (°): I(1)–Pd(1)–N(1) 95.8(1), I(1)–Pd(1)–C(1) 90.5(2), P(1)–Pd(1)–N(1) 84.7(1), P(1)–Pd(1)–C(1), 89.0(2).



(1)

Metathetical reactions of PdRI($Et_2NC_2H_4PPh_2$-κ^2N,P) (R = Me (**1a**), Ph (**1b**)) with excess amounts of $Na^+[Co(CO)_4]^-$ in THF at −40 °C gave novel heterodinuclear organopalladium–cobalt complexes having an unsymmetrical PN ligand, ($Et_2NC_2H_4PPh_2$-κ^2N,P)RPd–$Co(CO)_4$ (R = Me (**2a**), Ph (**2b**)) in 45% and 46% yields, respectively (Eq. (2)).



(2)

Similarly, treatment of PdPh(NO_3)($Et_2NC_2H_4PPh_2$-κ^2N,P), prepared in situ from **1b** and $AgNO_3$, with $Na^+[MoCp(CO)_3]^-$ afforded phenylpalladium–molybdenum derivative (**3b**) in 76% yield. These novel hetrodinuclear organopalladium complexes having an unsymmetrical PN ligand, **2a**,**b** and **3b**, were characterized by NMR and IR spectroscopies and elemental analysis. Selected IR and NMR data of newly prepared compounds, **2a**,**b** and **3b**, are summarized in Table 1. Molecular structure of **2a** obtained by preliminary X-ray structure analysis is depicted in Fig. 2.

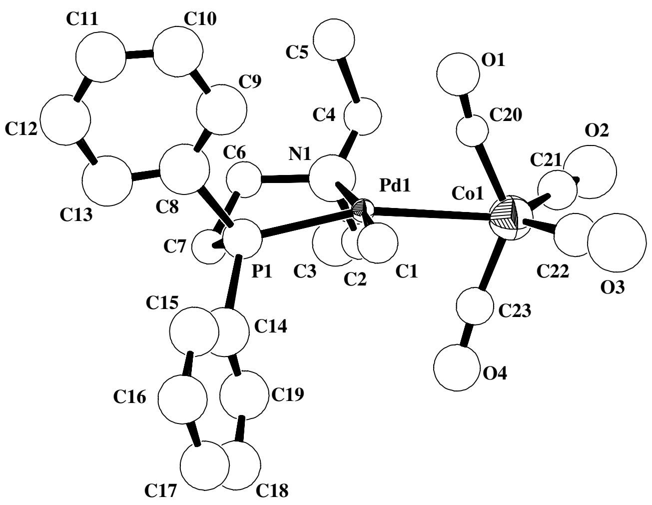


Fig. 2. The structure drawing of ($Et_2NC_2H_4PPh_2$-κ^2N,P)MePd–$Co(CO)_4$ (**2a**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

IR spectrum of phenylpalladium–molybdenum complex (**3b**) shows strong ν(CO) bands at ca. 1780–1890 cm^{-1}, which are similar to those for the known anionic Mo(0) complexes $[MoCp(CO)_3]^-$ rather than neutral M(II) complexes such as $MoMeCp(CO)_3$ [4]. The cobalt derivatives, **2a** and **2b**, also show similar ν(CO) bands (1866–2024 cm^{-1}) as anionic Co(–I) complex, $Na^+[Co(CO)_4]^-$ [5]. These data suggest that the actual oxidation states of the palladium and connecting metals such as molybdenum and cobalt are close to be Pd(II) and Mo(0) or Co(–I), which are consistent with the observed geometry of each metal, although the formal oxidation states are Pd(I) and Mo(I) or Co(0).

The $^{31}P\{^1H\}$ NMR spectra of **2a**,**b** and **3b** show a singlet around ca. 23–33 ppm, which are lower field from free ligand, indicating coordination of phosphorus atoms to the Pd center. The Pd–Me resonance of **2a** is observed at δ 0.95 as a doublet with a small $^3J_{PH}$ value (4.8 Hz), suggesting that the Me ligand locates in *cis* position to the phosphorus atom. In the ^1H NMR spectra, the methylene protons of the NCH_2CH_3 moiety for palladium–cobalt complexes **2a** and **2b** were observed diastereotopically, suggesting rigid coordination of the nitrogen atom to the Pd center. In contrast, the methylene protons of molybdenum complex **3b** appeared as a broad singlet, suggesting involvement of some dynamic processes (vide infra).

When PdMeI($Et_2NC_2H_4PPh_2$-κ^2N,P) (**1a**) was treated with $Na^+[MoCp(CO)_3]^-$, heterometallic tetranuclear complex, $[PdMoCp(\mu\text{-}CO)_3(Et_2NC_2H_4PPh_2\text{-}\kappa^1P)]_2$ (**4**), was formed in 15% yield, in stead of desired heterodinuclear methylpalladium–molybdenum complex, ($Et_2NC_2H_4PPh_2$-κ^2N,P)MePd–$MoCp(CO)_3$ (**3a**) [8] (Eq. (3)). X-ray structure analysis of the crystal of **4** fortunately revealed the molecular structure, and the ORTEP drawing of **4** is depicted in Fig. 3. Fate of the methyl group during the reaction was not clear, though evolution of very small amount of ethylene was observed.

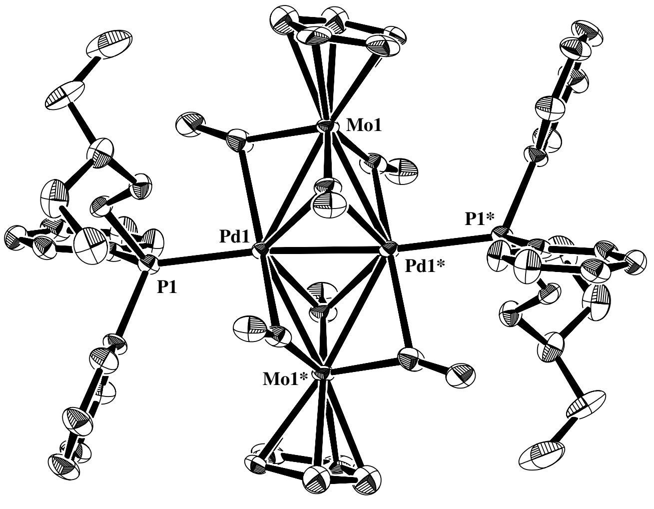
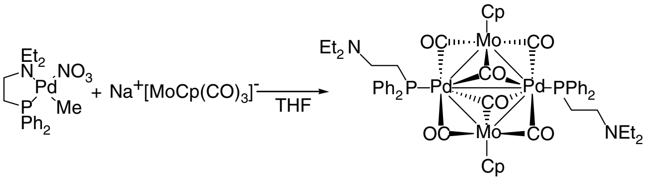


Fig. 3. ORTEP drawing of $[PdMoCp(CO)_3(Et_2NC_2H_4PPh_2\text{-}\kappa^1P)]_2$ (**4**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

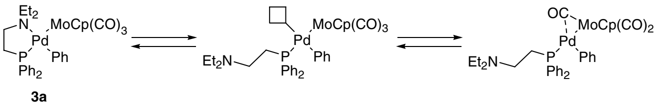


4

(3)

2.2. Dynamic behavior of the PN chelate ligand in heterodinuclear organopalladium complexes

Variable-temperature ^1H NMR of phenylpalladium–molybdenum complex **3b** shows a dynamic behavior of the resonances due to diastereotopic methylene protons of the coordinating diethylamino moiety (Fig. 4). The methylene protons of the ethyl group in **3b** appear as a broad singlet at room temperature. On lowering the temperature as shown in Fig. 4, the signal initially broadens and then gradually splits into two peaks. At 253 K, two doublets of quartets with equal intensity appear due to couplings between the diastereotopic geminal protons which further couple to the methyl protons. On the other hand, the Cp resonance and phosphorous spectrum shows no notable change in this temperature range. This is conveniently interpreted by the facile and reversible Pd–N bond rupture, which loses magnetic inequivalency of the methylene protons (Eq. (4)).



3a

(4)

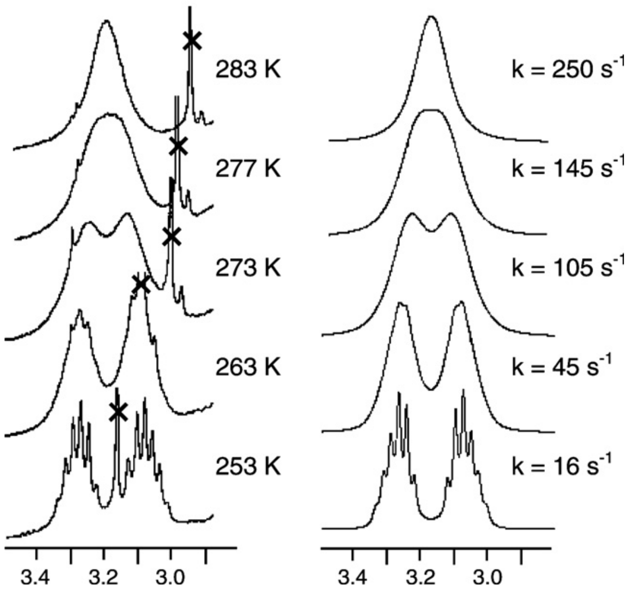
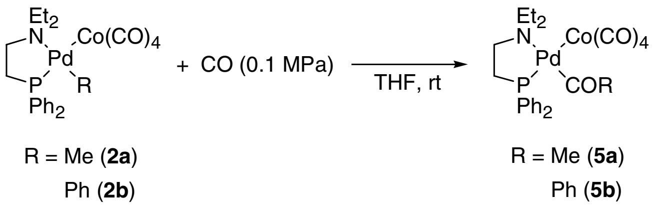


Fig. 4. Variable-temperature ^1H NMR spectra of the diastereotopic methylene protons in NEt_2 moiety of **3b** in acetone-d_6. Observed spectra: left, simulated spectra: right.

Such hemilabile behavior had been reported for some mononuclear platinum or palladium complexes with PN [9] or bidentate nitrogen ligand [10], and heterodinuclear phenylplatinum complex having a 2-(diphenylphosphino)triethylamine [3a]. From the line shape analysis of these VT NMR spectra of **3b** by gNMR, dissociation rate constants of the amino group at various temperatures were estimated both in acetone-d_6 and toluene-d_8, giving kinetic parameters as follows: $\Delta G^{\ddagger}_{273} = 56.0 \pm 0.6\ \text{kJ mol}^{-1}$, $\Delta H^{\ddagger} = 51.3 \pm 0.1\ \text{kJ mol}^{-1}$, $\Delta S^{\ddagger} = -17.3 \pm 1.6\ \text{J mol}^{-1}\ \text{K}^{-1}$ in acetone-d_6 and $\Delta G^{\ddagger}_{273} = 56.9 \pm 0.6\ \text{kJ mol}^{-1}$, $\Delta H^{\ddagger} = 53.6 \pm 0.1\ \text{kJ mol}^{-1}$, $\Delta S^{\ddagger} = -11.8 \pm 1.7\ \text{J mol}^{-1}\ \text{K}^{-1}$ in toluene-d_8. It is notable that the $\Delta S^{\ddagger}$ values in both acetone and toluene solvents are slightly negative, even though the process is considered to be an intramolecular dissociative one. The process possibly involves coordination of intramolecular bridging of the carbonyl ligand to stabilize the resulting coordinatively unsaturated species. The methylene protons of the ethyl group in **2a** and **2b** appear as well-separated two signals at ambient temperature, indicating no such dynamic behavior.

2.3. CO insertion into carbon–palladium bond of heterodinuclear organopalladium–cobalt complexes

Reaction of the heterodinucler organopalladium–cobalt complexes having an unsymmetrical PN ligand (**2a**,**b**) toward CO insertion was investigated (Eq. (5)). Treatment of the methylpalladium complex **2a** with atmospheric CO at room temperature led to the formation of an acetyl complex, $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)(MeCO)Pd–Co(CO)_4$ (**5a**). Under the similar conditions, phenylpalladium complex **2b** gave a CO insertion product $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$-$(PhCO)Pd–Co(CO)_4$ (**5b**) in 75% yield.



(5)

Novel acylpalladium–cobalt complexes, **5a**,**b**, were characterized by NMR and IR spectroscopies and elemental analysis. IR spectra of these acyl complexes display strong ν(C=O) band due to the PdCOR group at 1686 (**5a**) or 1645 (**5b**) cm^{-1} and a few strong ν(C≡O) bands at 1875–2000 cm^{-1} whose frequencies are close to the broad peaks of anionic metal carbonyls $Na^+[Co(CO)_4]^-$.

CO insertion reactions for methyl or phenylpalladium complexes were monitored by NMR, employing the samples of the complexes with concentrations of ca. 0.02 M in CD_2Cl_2 at 24 ± 1 °C and 0.1 MPa CO (ca. 9-fold). Fig. 5 represents time–yield curves of CO insertion to give corresponding acyl complexes. The methylpalladium–cobalt complex having an unsymmetrical PN ligand (**2a**) gave a significantly higher activity than the corresponding mononuclear palladium complex **1a** and the methylpalladium–cobalt complex with dppe ligands, (dppe-κ^2P,P')-MePd–$Co(CO)_4$ (**6a**) [2g,21]. The CO insertion reaction of phenyl derivative **2b** was significantly faster than methyl complex **2a**. The significant acceleration for the CO insertion reaction may be attributable to facile formation of a vacant coordination site by the preferential dissociation of nitrogen ligand in **2a** or **2b** though such site locates *trans* to Me or Ph. Hence, it is clearly shown that the CO insertion is enhanced by both the $Co(CO)_4$ group and unsymmetrical PN ligand. Mononuclear acetylpalladium complexes having an unsymmetrical PN ligand, Pd(COMe)I($Et_2NC_2H_4PPh_2$-κ^2N,P) (**7a**), was characterized by NMR and IR spectroscopies as well as single crystal X-ray structure analysis, and the ORTEP drawing of **7a** is depicted in Fig. 6.

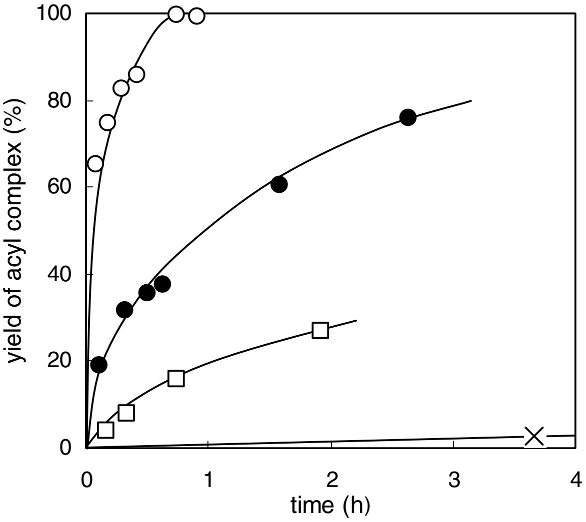


Fig. 5. Time–yield curves of acylpalladium complex formed by CO insertion into carbon–palladium bond of methyl- or phenylpalladium complexes at 24 ± 1 °C: ($Et_2NC_2H_4PPh_2\kappa^2N,P$)(MeCO)Pd–$Co(CO)_4$ (**5a**, ●), ($Et_2NC_2H_4PPh_2$-κ^2N,P)(PhCO)Pd–$Co(CO)_4$ (**5b**, ○), Pd(COMe)I($Et_2NC_2H_4PPh_2$-κ^2N,P) (**7a**, ×), and (dppe-κ^2P,P')(MeCO)Pd–$Co(CO)_4$ (**8a**, □).

By analogy of our previously proposed mechanism for enhanced CO insertion of methylpalladium–cobalt complex with dppe [2l], a possible mechanism for this CO insertion is proposed (Scheme 1). At first, coordinated nitrogen atom of PN ligand reversibly dissociates and is displaced by CO to give ($Et_2NC_2H_4PPh_2$-κ^1P)(CO)MePd–$Co(CO)_4$. Similar complex is known in the reaction of platinum derivative with carbon monoxide [3a]. Then, as previously proposed in CO insertion into methylpalladium–cobalt complex with dppe [2g,2l], methyl migration from Pd to Co initially takes place, followed by fast CO insertion into the Co–Me bond, and then migration of the resulting acetyl group at Co to Pd. Coordination of CO ligand to Pd in ($Et_2NC_2H_4PPh_2$-κ^1P)(CO)MePd–$Co(CO)_4$ would accelerate methyl migration from Pd to Co. Probably, the higher reactivity of phenyl complex (**2b**) for CO insertion is due to weaker coordination of nitrogen atom to Pd by *trans* effect of phenyl group, which is indicated by peak broadening of methylene signal of NCH_2CH_3 in ^1H NMR.

2.4. Reactions of acetylpalladium–cobalt complexes with nucleophiles

Reactions of the acetyl complex **5a** with nucleophiles such as diethylamine, methanol and benzenethiol were

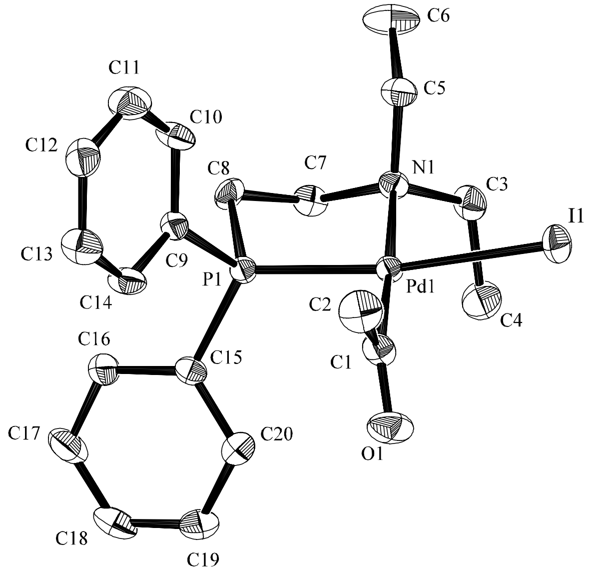
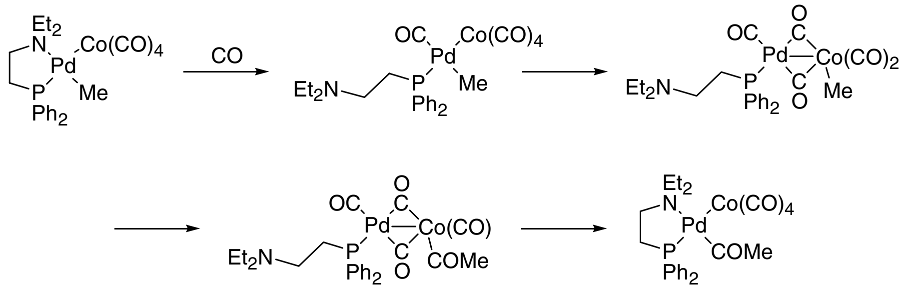


Fig. 6. ORTEP drawings of Pd(COMe)I($Et_2NC_2H_4PPh_2$-κ^2N,P) (**7a**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability. Selected bond distances (Å): Pd(1)–I(1) 2.6703(6), Pd(1)–P(1) 2.253(1), Pd(1)–N(1) 2.271(4), Pd(1)–C(1) 1.982(4), C(1)–C(2) 1.490(7), C(1)–O(1) 1.214(6). Selected bond angles (°): I(1)–Pd(1)–N(1) 96.03(9), I(1)–Pd(1)–C(1) 88.8(1), P(1)–Pd(1)–N(1) 84.67(9), P(1)–Pd(1)–C(1) 92.1(1), Pd(1)–C(1)-O(1) 119.2(4), Pd(1)–C(1)–C(2) 118.8(3), O(1)–C(1)–C(2) 121.9(4).



Scheme 1.

Table 2
Reactions of acetylpalladium complexes with nucleophiles[a]

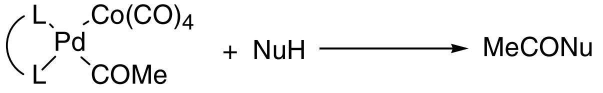
Entry	Complex	Nucleophile	Yield (%)
1	**5a**	Et_2NH	87
2[b]	**5a**	MeOH	79
3[c]	**5a**	PhSH	93
4	**7a**	Et_2NH	0
5	**8a**	Et_2NH	15
6	**9a**	Et_2NH	Trace

[a] Reaction conditions: acetylpalladium complex (0.006 mmol), nucleophiles (0.03 mmol), C_6D_6 (0.5 ml), 50 °C, 24 h.

[b] Acetone-d_6 (0.5 ml), rt, 4 days.

[c] Acetone-d_6 (0.5 ml), rt, 30 min.

investigated, and the results are summarized in Table 2. Treatment of **5a** with diethylamine at 50 °C for 24 h in C_6D_6 gave *N*,*N*-diethyl acetamide in 87% yield (Table 2, entry 1). Similarly, the reaction of **5a** with methanol and benzenethiol at room temperature in acetone-d_6 afforded methyl acetate and phenyl thioacetate in 79% and 93% yields, respectively (entries 2 and 3). It is interesting to note that under the same reaction conditions, (dppe-$\kappa^2 P,P'$)(MeCO)Pd–Co(CO)$_4$ (**8a**) [2g,21] showed much less reactivity toward Et_2NH (15%), and (tmeda-$\kappa^2 N,N'$)-(MeCO)Pd–Co(CO)$_4$ (**9a**) [2k] and Pd(COMe)I(Et_2N-$C_2H_4PPh_2$-$\kappa^2 N,P$) (**7a**) showed almost no reactivity (entries 4–6). The present higher reactivity of **5a** may also attribute to the facile dissociation of PN ligand, though the detail mechanisms are not clear at present.



(6)

L_2 = $Et_2NC_2H_4PPh_2$ (**5a**)
dppe (**8a**)
tmeda (**9a**)

3. Conclusions

In the present study, synthesis of novel heterodinuclear organopalladium–cobalt (or –molybdenum) complexes having an unsymmetrical PN ligand ($Et_2NC_2H_4PPh_2$-$\kappa^2 N,P$)RPd–ML$_n$ (ML$_n$ = Co(CO)$_4$; R = Me (**2a**), Ph (**2b**), ML$_n$ = MoCp(CO)$_3$; R = Ph (**3b**)) was described. Heterodinucler organopalladium–cobalt complexes (**2a**,**b**) are shown to react with CO, giving corresponding acyl complexes ($Et_2NC_2H_4PPh_2$-$\kappa^2 N,P$)(RCO)Pd–Co(CO)$_4$ (R = Me (**5a**), Ph (**5b**)). Similar acceleration by PN ligand was previously observed for CO insertion of the methylplatinum derivative [3a]. The CO insertion reaction of phenyl derivative **2b** was significantly faster than methyl complex **2a**. Probably, this higher reactivity of phenyl complex (**2b**) for CO insertion is depending on weaker coordination of nitrogen atom to Pd. The reactions of **5a** with Et_2NH are significantly faster than those of corresponding mononuclear analogues and the similar heterodinuclear complexes with a symmetrical bidentate ligand such as dppe or tmeda. The unsymmetrical PN ligand in heterodinucler organopalladium–cobalt complex is considered to play an important role in accelerating CO insertion of palladium–carbon bond as well as nucelophilic attack to acyl carbon center.

4. Experimental

4.1. General

All manipulations were carried out under dry nitrogen or argon atmosphere using standard Schlenk and vacuum line techniques [11]. Solvents were refluxed over and distilled from appropriate drying agents under N_2: benzene, toluene, hexane, and THF from sodium benzophenone ketyl; acetone from drierite; CH_2Cl_2 from P_2O_5. Deuterated solvents were degassed by three freeze–pump–thaw cycles and then vacuum transferred from appropriate drying agents (C_6D_6 and toluene-d_8 from sodium wire, acetone-d_6 from drierite, CD_2Cl_2 and $CDCl_3$ from P_2O_5).

$Pd_2(dba)_3 \cdot CHCl_3$ [6], $Et_2NC_2H_4PPh_2$ [7], $Na^+[MoCp(CO)_3]^-$ [4] and $Na^+[Co(CO)_4]^-$ [5] were prepared according to the literature methods with minor modifications. $AgNO_3$ and CO (99.9%) were used as received. NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^1H, 121.6 MHz for ^{31}P). Chemical shifts were reported in ppm downfield from TMS for ^1H and from

85% H_3PO_4 in D_2O for ^{31}P. IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr disks. Elemental analyses were carried out with a Perkin–Elmer 2400 series II CHN analyzer. Molar electric conductivity was measured on a TOA Conduct Meter CM 7B. Line shape analysis was performed with the gNMR program [12] by fitting of the exchange rate and resonance frequency.

4.2. Synthesis of $PdRI(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$

4.2.1. $PdMeI(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (**1a**)

To a benzene solution of $Pd_2(dba)_3 \cdot CHCl_3$ (791.3 mg, 0.7657 mmol) was added $Et_2NC_2H_4PPh_2$ (0.38 ml, 1.8 mmol) and methyl iodide (0.12 ml, 1.9 mmol) at room temperature. The reaction mixture was stirred at room temperature for overnight. After filtration through an alumina pad, the filtrate was evaporated to dryness in vacuo giving orange solid, which was washed with hexane. Recrystallization from CH_2Cl_2/hexane gave orange crystals. Yield 46% (374.9 mg, 0.7024 mmol). Anal. Calc. for $C_{19}H_{27}INPPd$: C, 42.76; H, 5.10; N, 2.62. Found: C, 42.43; H, 4.85; N, 2.50%. ^1H NMR (acetone-d_6, rt): δ 0.65 (d, $^3J_{PH} = 3.9$ Hz, 3H, $PdCH_3$), 1.20 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH_2CH_3), 2.5–2.9 (m, 4H, PCH_2CH_2N), 3.05 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 3.40 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 7.52–7.64 (m, 6H, *m*- and *p*-Ph), 7.72–7.80 (m, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR (acetone-d_6, rt): δ 42.4 (s).

4.2.2. $PdPhI(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (**1b**)

PhI was used instead of MeI. This compound was obtained as orange crystals from CH_2Cl_2/hexane. Yield 14% (86.7 mg, 0.145 mmol). Anal. Calc. for $C_{24}H_{29}INPPd$: C, 48.38; H, 4.91; N, 2.35. Found: C, 48.24; H, 5.30; N, 2.34%. ^1H NMR ($CDCl_3$, rt): δ 1.36 (t, $^3J_{HH} = 7.0$ Hz, 6H, NCH_2CH_3), 2.4–2.7 (m, 4H, PCH_2CH_2N), 3.19 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.0$ Hz, 2H, NCH_2CH_3), 3.45 (dq, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.0$ Hz, 2H, NCH_2CH_3), 6.5–6.7 (m, 3H, *m*- and *p*-Ph (Pd-Ph)), 6.93 (m, 2H, *o*-Ph (Pd-Ph)), 7.3–7.8 (10H, m, Ph(P-Ph)). $^{31}P\{^1H\}$ NMR ($CDCl_3$, rt): δ 32.6 (s).

4.3. Synthesis of heterodinucler organopalladium complexes having an unsymmetrical PN ligand

A typical procedure for $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)MePd\text{–}Co(CO)_4$ (**2a**) is given. To a THF solution of $PdMeI(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (108.3 mg, 0.2040 mmol), a THF solution of $Na^+[Co(CO)_4]^-$ (35.2 mg, 0.182 mmol) was added at −80 °C and the mixture was stirred at −40 °C for 3 h. All volatile matters were removed by evaporation and the resulting brown-yellow solid was extracted with toluene at −30 °C. After the filtered solution was concentrated under reduced pressure at −20 °C, an excess hexane was added. The solution was cooled to −30 °C to give pale yellow needles of **2a**. The product was filtered, and washed with hexane, and dried under vacuum at room temperature. Yield 45% (52.6 mg, 0.0910 mmol). Anal. Calc. for $C_{23}H_{27}CoNO_4PPd$: C, 47.81; H, 4.71; N, 2.42. Found: C, 48.16; H, 4.81; N, 3.05%. IR (KBr, cm^{-1}): 2014(s), 1935(s), 1866(s). ^1H NMR (C_6D_6, rt): δ 0.80 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH_2CH_3), 0.95 (d, $^3J_{PH} = 4.8$ Hz, 3H, $PdCH_3$), 1.7–1.9 (m, 4H, PCH_2CH_2N), 2.72 (dq, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 3.10 (dq, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 7.0 (m, 6H, *m*- and *p*-Ph), 7.5 (m, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, rt): δ 32.7 (s).

4.3.1. $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)PhPd\text{–}Co(CO)_4$ (**2b**)

This compound was obtained as orange crystals from THF/hexane. Yield 46% (41.5 mg, 0.0649 mmol). Anal. Calc. for $C_{28}H_{29}CoNO_4PPd \cdot C_4H_8O$: C, 53.98; H, 5.24; N, 1.97. Found: C, 54.02; H, 5.14; N, 2.05%. IR (KBr, cm^{-1}): 2024(s), 1961(s), 1901(s), 1876(s). ^1H NMR (C_6D_6, rt): δ 0.86 (t, $^3J_{HH} = 6.6$ Hz, 6H, NCH_2CH_3), 1.3–1.5 (m, 4H, PCH_2CH_2N), 2.84 (br, 2H, NCH_2CH_3), 3.12 (br, 2H, NCH_2CH_3), 6.6–6.7 (m, 3H, *m*- and *p*-Ph (Pd-Ph)), 6.96 (brs, 2H, *o*-Ph (Pd-Ph)), 7.2–7.5 (m, 10H, Ph (P-Ph)). $^{31}P\{^1H\}$ NMR (C_6D_6, rt): δ 22.6 (s).

4.3.2. $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)PhPd\text{–}MoCp(CO)_3$ (**3b**)

This compound was obtained as orange crystals from THF/hexane. Yield 76% (108.5 mg, 0.1520 mmol). Anal. Calc. for $C_{32}H_{34}MoNO_3PPd$: C, 53.83; H, 4.80; N, 1.96. Found: C, 53.90; H, 5.12; N, 1.96%. IR (KBr, cm^{-1}): 1886(s), 1789(s). ^1H NMR (acetone-d_6, rt): δ 1.19 (t, $^3J_{HH} = 6.9$ Hz, 6H, NCH_2CH_3), 2.6–2.8 (m, 4H, PCH_2CH_2N), 3.2 (br, 4H, NCH_2CH_3), 4.63 (s, 5H, Cp), 6.5–6.6 (m, 3H, *m*- and *p*-Ph (Pd-Ph)), 6.97 (d, $^3J_{HH} = 7.8$ Hz, 2H, *o*-Ph (Pd-Ph)), 7.4-7.5 (m, 10H, Ph (P-Ph)). $^{31}P\{^1H\}$ NMR (acetone-d_6, rt): δ 23.9 (s).

4.3.3. $[PdMoCp(CO)_3(Et_2NCH_2CH_2PPh_2\text{-}\kappa^1P)]_2$ (**4**)

This compound was obtained by the same procedure as above as white crystals from benzene/hexane, but characterized by spectroscopically as well as by X-ray structure analysis. Yield 15% (6.3 mg, 0.0099 mmol). IR (KBr, cm^{-1}): 1833(s), 1767(s). ^1H NMR (C_6D_6, rt): δ 1.02 (t, $^3J_{HH} = 7.1$ Hz, 6 H, NCH_2CH_3), 2.55 (q, $^3J_{HH} = 7.1$ Hz, 4H, NCH_2CH_3), 2.78 (m, 2H, PCH_2CH_2N), 3.12 (m, 2H, PCH_2CH_2N), 4.64 (s, 5H, Cp), 6.9-7.2 (m, 6H, *m*- and *p*-Ph (P-Ph)), 7.6 (m, 4H, *o*-Ph (P-Ph)). $^{31}P\{^1H\}$ NMR (C_6D_6, rt): δ 12.9 (s).

4.4. Synthesis of acylpalladium complexes by CO insertion

A typical preparative procedure of $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)(MeCO)Pd\text{–}Co(CO)_4$ (**5a**) is given. **2a** (51.7 mg, 0.0894 mmol) was dissolved in THF under N_2 in a Schlenk tube and the solution was degassed. CO (0.1 MPa) was introduced into the Schlenk tube and the orange solution turned to red after stirring for 16 h. After filtration of the reaction mixture, the filtered solution was evaporated to dryness. The resulting solids were extracted with THF and addition of hexane to the concentrated solution of extracts gave yellow needles. The crystals were washed with cold hexane and dried under vacuum. Yield 19% (10.2 mg, 0.0168 mmol). Anal. Calc. for $C_{24}H_{27}CoNO_5PPd$: C, 47.58; H, 4.49; N, 2.31. Found: C, 47.44; H, 4.62; N, 2.32%. IR (KBr, cm^{-1}): 2020(s), 1945(s), 1912(s), 1875(s), 1686(s). ^1H NMR (CD_2Cl_2, rt): δ 1.78 (t, $^3J_{HH} = 6.9$ Hz, 6H, NCH_2CH_3), 1.99 (s, 3 H, $PdCOCH_3$), 2.4-2.6 (m, 4H, PCH_2CH_2N), 2.99 (br, 4H, NCH_2CH_3), 7.6 (m, 6H, *m*- and *p*-Ph), 7.8 (m, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ 14.2 (s).

4.4.1. $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)(PhCO)Pd\text{–}Co(CO)_4$ (**5b**)

This compound was obtained as yellow powder from THF/hexane. Yield 75% (55.2 mg, 0.0827 mmol). Anal. Calc. for $C_{29}H_{29}CoNO_5PPd$: C, 52.15; H, 4.38; N, 2.10. Found: C, 52.64; H, 4.62; N, 2.15%. IR (KBr, cm^{-1}): 2027 (m), 1952 (s), 1932 (s), 1890 (s), 1645 (m). ^1H NMR (C_6D_6, rt): δ 1.25 (t, 6H, $^3J_{HH} = 7.2$ Hz, NCH_2CH_3), 2.4–2.6 (m, 4H, PCH_2CH_2N), 3.1 (br, 4H, NCH_2CH_3), 7.0–7.3 (m, 5H, Ph (PdCO-Ph)), 7.5–8.0 (m, 10H, Ph (P-Ph)). $^{31}P\{^1H\}$ NMR (C_6D_6, rt): δ 14.6 (s).

4.4.2. $Pd(COMe)I(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (**7a**)

This compound was obtained as yellow powder from acetone/hexane. Yield 93% (127.8 mg, 0.2275 mmol). Anal. Calc. for $C_{29}H_{29}CoNO_5PPd$: C, 42.76; H, 4.84; N, 2.49. Found: C, 42.70; H, 4.58; N, 2.59%. IR (KBr, cm^{-1}): 1650 (m). ^1H NMR (C_6D_6, rt): δ 0.97 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH_2CH_3), 1.6–1.8 (m, 4H, PCH_2CH_2N), 2.67 (br, 2H, NCH_2CH_3), 3.08 (m, 2H, NCH_2CH_3), 7.0–7.5 (m, 10H, Ph (P-Ph)). $^{31}P\{^1H\}$ NMR (C_6D_6, rt): δ 20.3 (s).

4.5. NMR tube reactions for CO insertion of organopalladium complex

A typical procedure for **2a** is given. C_6D_6 (0.5 mL) was vacuum-transferred to an NMR tube (5 mmϕ × 180 mm) containing **2a** (5.1 mg, 0.0088 mmol), and Ph_3CH was added as an internal standard to the solution ([**2a**] = 0.018 M). The solution was degassed by freeze–pump–thaw cycles and CO (0.1 MPa) was introduced. The sample tube was placed in NMR probe at 24 ± 1 °C, and ^1H NMR spectra were periodically measured to follow the CO insertion reaction at 24 ± 1 °C.

4.6. Reactions of acetylpalladium–cobalt complexes with nucleophiles

A typical procedure for **5a** with Et_2NH is given. Complex **5a** (3.6 mg, 0.0053 mmol) was placed in an NMR tube with Ph_3CH as an internal standard, and C_6D_6 (0.5 mL) was added under N_2 atmosphere. Et_2NH (2.7 μL, 0.026 mmol) was added to the solution by hypodermic syringe and then heated at 50 °C for 24 h. Products were quantitatively analyzed by ^1H NMR.

4.7. X-ray structure analyses of $PdMeI(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (**1a**), $(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)MePd\text{–}Co(CO)_4$ (**2a**), $[PdMoCp(CO)_3(Et_2NC_2H_4PPh_2\text{-}\kappa^1P)]_2$ (**4**) and $Pd(COMe)I(Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P)$ (**7a**)

Diffraction experiments were performed on a Rigaku four-circle diffractometer RASA-7R diffractometer with graphite-monochromatized Mo Kα radiation (0.71069 Å). A single crystal was selected by use of a polarized microscope and mounted in a capillary tube (GLASS, 0.7 mmϕ), which was sealed by small flame torch. The unit cells were determined by the automatic indexing of the 20 centered reflections. The structures were solved and refined by a full matrix least-square procedure using the texsan crystal solution package (Rigaku) operating on a SGI O2 workstation [13]. An absorption correction for **1a**, **4**, and **7a** was applied with the program ψ-scan. The structures of **1a** and **4** were solved by direct methods, and the structures of **7a** were solved by Patterson methods (SAPI). For these complexes, all non-hydrogen atoms were found on difference Fourier maps, and refined anisotropically expect C5 and C6 of **4**, and all hydrogen atoms were located in the calculated positions, which were not refined. Due to low quality of the crystal of **2a**, non-hydrogen atoms expect Pd1 and Co1 atoms were refined with isotropic displacement parameters, and Ph rings and CO ligands were treated as fixed groups, and all hydrogen atoms were located in the calculated positions, which were not refined. Therefore, no structural feature was discussed in the text. Selected bond distances (Å) for **2a**: Pd(1)–Co(1) 2.667(3), Pd(1)–P(1) 2.233(6), Pd(1)–N(1) 2.27(2), Pd(1)–C(1) 1.98(2), Pd(1)–C(20) 2.42(12), Pd(1)–C(23) 2.70(10). Selected bond angles (°) for **2a**: Co(1)–Pd(1)–N(1) 96.8(5), Co(1)–Pd(1)–C(1) 88.3(6), P(1)–Pd(1)–N(1) 85.2(5), P(1)–Pd(1)–C(1) 89.3(6). Crystal data for **1a**: $C_{19}H_{27}INPPd$, FW = 533.71, *orthorhombic*, *Pbca*, $a = 13.2$ (1) Å, $b = 25.17(9)$ Å, $c = 12.21(8)$ Å, $V = 4057(43)$ Å^3, $Z = 8$, $D_{calc} = 1.744$ g cm^{-3}, μ(Mo Kα) = 25.12 cm^{-1}, $2\theta_{max} = 56.0$ °, 5293 reflections measured (5263 unique), 4271 observations with $I > 3.00\sigma(I)$, R (R_w) = 0.028 (0.063), GOF = 1.86. Crystal data for **2a**: $C_{23}H_{27}CoNO_4PPd$, FW = 577.78, *monoclinic*, $P2_1$, $a = 8.442(5)$ Å, $b = 14.761(6)$ Å, $c = 12.244(7)$ Å, $\beta = 102.61$ (5)°, $V = 1488(1)$ Å^3, $Z = 2$, $D_{calc} = 1.289$ g cm^{-3}, μ(Mo Kα) = 12.39 cm^{-1}, $2\theta_{max} = 55.0°$, 3778 reflections measured (3718 unique), 3226 observations with $I > 3.00\sigma(I)$, R (R_w) = 0.125 (0.178), GOF = 1.68. Crystal data for **4**: $C_{26}H_{29}MoNO_3PPd$, FW = 636.83, *triclinic*, $P\bar{1}$, $a = 10.73(5)$ Å, $b = 12.81(3)$ Å, $c = 10.56(4)$ Å, $\alpha = 90.2(3)°$, $\beta = 117.9(3)°$, $\gamma = 76.6(3)°$, $V = 1238(9)$ Å^3, $Z = 2$, $D_{calc} = 1.707$ g cm^{-3}, μ(Mo Kα) = 13.24 cm^{-1}, $2\theta_{max} = 55.4$ °, 6018 reflections measured (5707 unique), 4466 observations with $I > 3.00\sigma(I)$, R (R_w) = 0.063 (0.102), GOF = 1.14. Crystal data for **7a**: $C_{20}H_{27}OINPPd$, FW = 561.72, *orthorhombic*, $Pna2_1$, $a = 17.120(3)$ Å, $b = 7.890(3)$ Å, $c = 15.736(3)$ Å, $V = 2125(1)$ Å^3, $Z = 4$, $D_{calc} = 1.755$ gcm^{-3}, μ(Mo Kα) = 24.10 cm^{-1}, $2\theta_{max} =$

55.0 °, 2798 reflections measured (2529 unique), 2385 observations with $I > 3.00\sigma(I)$, R (R_w) = 0.020 (0.024), GOF = 1.09.

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Appendix A. Supplementary material

CCDC 633363, 633364, 633365 and 633366 contain the supplementary crystallographic data for **1a**, **2a**, **4** and **7a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.029.

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