Unsymmetrical bidentate ligands of α-aminoaldimines leading to sterically controlled selectivity of geometrical isomerism in square planar coordination†

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Received 4th April 2008, Accepted 18th July 2008
First published as an Advance Article on the web 16th September 2008
DOI: 10.1039/b805674a

New α-aminoaldimines with the formula of $Et_2NCMe_2CH{=}NR$ (R = ^{i}Pr, ^{t}Bu, Ph) and their dichloro or diacetato complexes of Ni, Pd, Pt are prepared and structurally characterized. A nickel complex is in a distorted tetrahedral configuration, and the Pd and Pt complexes (**4–6**) are of square planar form. The α-aminoaldimines can chelate to the metal in a C_2-unsymmetric bidentate motif through the hetero functionalities of amine and imine, which show comparable *trans* influence. Square planar organometallic palladium derivatives bearing α-aminoaldimines, including Pd–methyl, Pd–acetyl, and Pd–(η^2-acetylnorboryl) (**7–10**), are also synthesized. The latter two species are a result of CO-insertion into Pd–methyl complexes and ensuing norbornene-insertion, respectively. The geometrical isomerism is found in the *trans* configuration in most studied cases. Such a stereoselectivity results from the thermodynamic stability governed predominantly by steric control. The stereoselectivity is also supported by DFT calculations.

Introduction

New auxiliary ligands often bring new chemical features to coordination chemistry. The bidentate ligands with hybrid hard and soft donors have been acquiring enormous attention, because they are anticipated to confer different electronic and steric effects to the metal center as well as reactivity of the complexes.[1] Some unsymmetrical bidentate ligands contain the same donor atom in hybrid functionalities.[2] Among them, those that coordinate through the functionalities of amine and imine are rarely studied.[3] Still, a few cases have proved to be useful for catalysis.[4] Others are found to be important to bio-functions.[5] Amino acids which can coordinate with metal through two hard groups of amine and carboxylate simultaneously can serve as natural unsymmetrical bidentate ligands.[6] The α-aminoaldimines, which are imino derivatives of amino acids, may be expected to provide chelation of non-C_2-symmetry through the two nitrogen donor atoms of the hetero functionalities of amine and imine. Such ligands might be suitable candidates for the examination of the individual power of electronic and steric influences in their coordination chemistry, particularly in the square planar mode.

There are at least several distinguishable aspects between amine and imine that are worthy of note. Amine is a typical σ-base containing a nitrogen donor atom of sp^3 configuration, often with bond angles of less than 110°. On the other hand, imine has both σ-donating and π-accepting character and has a nitrogen donor atom of sp^2 configuration, and gives significantly larger bond angles of around 120° with the adjacent ligand. In the square planar coordinating motif as shown in Chart 1, α-aminoaldimines constitute a non-planar five-membered ring with the metal ion. The amine holds two substituents, but the imine may only have one. The imino substituent can rotate along the N–C bond which lies in the molecular plane.[7] In contrast, the amino substituents are in tetrahedral fashion that directs out of molecular plane and potentially can provide an asymmetric environment.[8] Therefore, the coordination sites of A and B are expected to experience individual influence from the amine and imine functionalities.

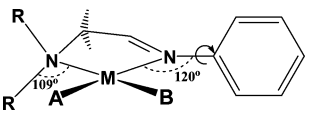

Chart 1 Square planar configuration with α-aminoaldimines.

In this article we report the synthesis and structures of the dichloro, diacetato, and some organometallic complexes of group 10 transition metals that bear new ligands of α-aminoaldimines. In the dichloro and diacetato species, the functionalities of amine and imine demonstrate comparable *trans* influence. In the organometallic derivatives, these unsymmetrical auxiliary ligands lead to geometrical stereoselectivity and geometrical isomerism that are attributed to the sterically controlled thermodynamic stability.

Results and discussion

Synthesis and spectroscopic characterization

The starting material, 2-bromo-2-methylpropanal (**1**),[9] was prepared by a reaction of bromine-1,4-dioxane and 2-methylpropanal in diethyl ether. The reaction slurry was constantly stirred till the disappearance of the orange color. The reaction solution was stirred for another 10 min, then extracted with ice-cold water. The resulting solution was dried with $MgSO_4$, and ether was removed

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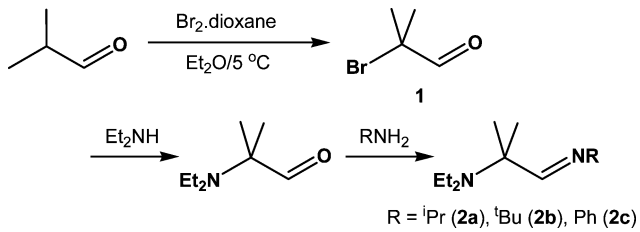
† CCDC reference numbers 682281, 683783–683791 (**3c**, **4a**, **4c**, **5b**, **5c**, **6c**, **7a**, **7c**, **8c** and **10c**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b805674a

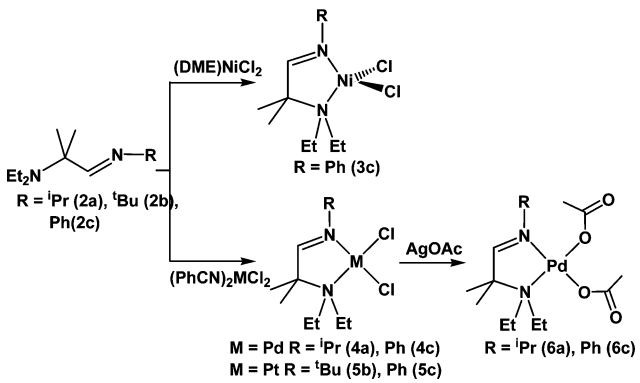
on a rotary evaporator. The brominated derivative **1** was usually ready for immediate use in the ensuing reaction.

There are two potential electrophilic sites in 2-bromo-2-methylpropanal (**1**). The reaction of **1** with secondary amine only leads to the substitution of bromine, presumably by radical-nucleophilic substitution, $S_{RN}1$, mechanism.[10] The new α-aminoaldimines in the form of $Et_2NCMe_2CH{=}NR$ (R = ^{i}Pr (**2a**), ^{t}Bu (**2b**), Ph (**2c**)) are synthesized first by substitution of diethylamine for bromine in **1**, and followed by condensation using primary amine or aniline, respectively, as shown in Scheme 1. The products are collected as viscous colorless liquids in good yields by means of distillation under reduced pressure. The structures of the new derivatives of α-aminoaldimines are mainly determined by spectroscopic methods.



Scheme 1 Synthesis of α-aminoaldimines.

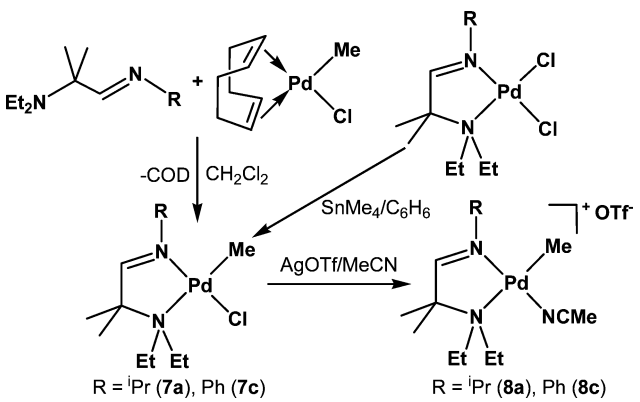
Compounds **2a**, **2b** or **2c** can serve as bidentate ligands with hybrid donor functionalities of amine and imine. The substitution reactions of **2a**, **2b** or **2c** with $(PhCN)_2MCl_2$ (M = Pd, Pt) leads to the neutral amine–imine complexes in the form of $[Et_2NCMe_2CH{=}NR]MCl_2$ (M = Pd, R = ^{i}Pr (**4a**), Ph (**4c**); M = Pt, R = ^{t}Bu (**5b**), Ph (**5c**)), as shown in Scheme 2. The yields for the palladium complexes are excellent, but relatively poor for the platinum complexes. Similar reaction of **2c** and $(DME)NiCl_2$ (DME = 1,2-dimethoxyethane) generate $[Et_2NCMe_2CH{=}NPh]NiCl_2$ (**3c**). Recrystallization of the violet inorganic product from CH_2Cl_2–Et_2O gives 62% yields and single crystals. The broadened NMR spectra of **3c** implicates a paramagnetic electronic configuration and tetrahedral molecular geometry.



Scheme 2 Synthesis of dichloro and diacetato complexes of Ni, Pd, or Pt.

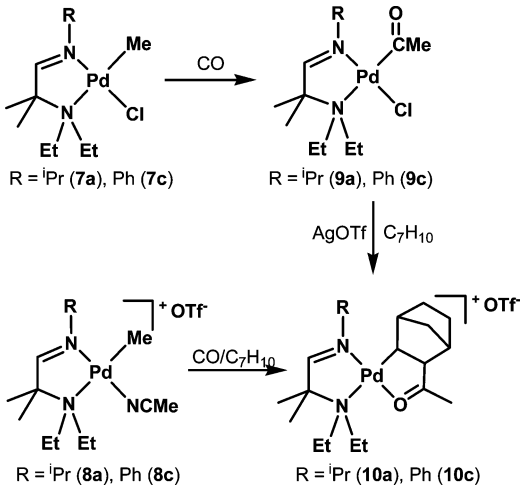
The distinct shift of the imino hydrogen signals in the ^{1}H NMR spectra and the imino carbon in the ^{13}C NMR spectra for the palladium and platinum complexes indicate the coordination mode of the ligand. The diastereotopic hydrogens of the amino methylene group, shown by the ^{1}H NMR, also support the tetrahedral configuration in the coordinating mode of amine.[11] Treating **4a** or **4c** with double molar amounts of silver acetate gives rise to the formation of diacetato complexes in the form of $[Et_2NCMe_2CH{=}NR]Pd(OAc)_2$ (R = ^{i}Pr (**6a**), Ph (**6c**)). The C=O stretching frequencies below 1700 cm^{-1} appear to be lower than the free acetates, and comparable to the coordinating fashion.[12] The C_2-unsymmetrical ligand results in the differentiation for the two acetato ligands. The two acetyloxy methyl groups in **6a** have close resonances in the ^{1}H NMR spectrum, implying small electronic difference between the amine and imine functionalities. For **6c**, there is only one carbonyl carbon identified in the ^{13}C NMR spectrum. However, two acetyloxy methyl signals in the ^{1}H and ^{13}C NMR spectra are observed. One is particularly upfield, presumably due to the ring current from the phenyl group on the *cis* imine.

Neutral organometallic complexes in the formula of $[Et_2NCMe_2CH{=}NR]Pd(Me)Cl$ (R = ^{i}Pr (**7a**), Ph (**7c**)) could be prepared either by substitution of α-aminoaldimines for COD (1,4-cyclooctadiene) in (COD)Pd(Me)Cl,[13] or by transmetallation using an organotin reagent[14] with $[Et_2NCMe_2CH{=}NR]PdCl_2$ (Scheme 3). The NMR data indicate that a single geometrical isomer is formed selectively. The Pd-bound methyl group of **7c** appears substantially upfield than that of **7a**, δ 0.46 *vs.* 0.73, implicating that methyl is likely *cis* to imine, and thus influenced by the ring current from the imino phenyl group. Chloride abstraction from **7a** or **7c** by silver triflate in acetonitrile results in the cationic species $\{[Et_2NCMe_2CH{=}NR]PdMe(NCMe)\}OTf$ (R = ^{i}Pr (**8a**), Ph (**8c**)). The stereochemistry of the *trans* isomerism is considered to be retained, since the Pd-bound methyl group in the NMR spectra for **8a** and **8c** resemble those for **7a** and **7c**, respectively.



Scheme 3 Synthesis of methylpalladium complexes.

Allowing CO to bubble through the solution of **7a** or **7c** readily results in a single product of neutral acetylpalladium complex **9a** or **9c**, respectively. A characteristic acyl CH_3 signal is at δ 2.44 in the ^{1}H NMR; and an acyl carbonyl is at δ 226.4 in the ^{13}C NMR for **9a**. For **9c**, the corresponding data are δ 2.10 and δ 223.0, respectively. Chloride abstraction from **8a** or **8c** using silver triflate in acetonitrile with the presence of norbornene leads to olefin insertion, yielding cationic acetylnorbornyl complexes **10a** or **10c**, respectively. Complexes **10a** and **10c** may alternatively be achieved from **8a** and **8c**, respectively ,with the presence of carbon monoxide and norbornene together, as illustrated in Scheme 4. The carbonyl stretching signals of low infrared frequencies, 1608 cm^{-1} for **10a** and 1605 cm^{-1} for **10c**, suggest that a coordinating mode



Scheme 4 CO and norbornene insertion of methylpalladium complexes.

through acyl oxygen might occur, as observed in many analogous prior cases.[15] It is noted again that some NMR resonances corresponding to the norbornyl hydrogen in **10c** are in the upfield region compared to **10a**. It is thus thought that the norbornyl group is *cis* to the imino functionality.

X-Ray structural analysis

Single crystals of **3c**, **4a**, **4c**, **5b**, **5c**, **6c**, **7a**, **7c**, **8c** and **10c** that are suitable for X-ray diffractions have been obtained. Crystallographic analyses provide unequivocal evidence for the molecular structures of these complexes which bear unsymmetrical amine–imine bidentates. The crystal data are listed in Table 1, and the selected bond lengths and bond angles are collected in Table 2.

In Fig. 1, the ORTEP drawing of complex **3c** is in a distorted tetrahedral configuration which explains its paramagnetism suggested by the broadened NMR signals. The amine–imine complexes of dichloropalladium, dichloroplatinum, and diacetatopalladium are all square planar. The representative ORTEP drawings of **4a**, **4c**, **5b** and **6c** are shown in Fig. 2 and 3; **8c** and **10c** are in Fig. 4 and 5, respectively.

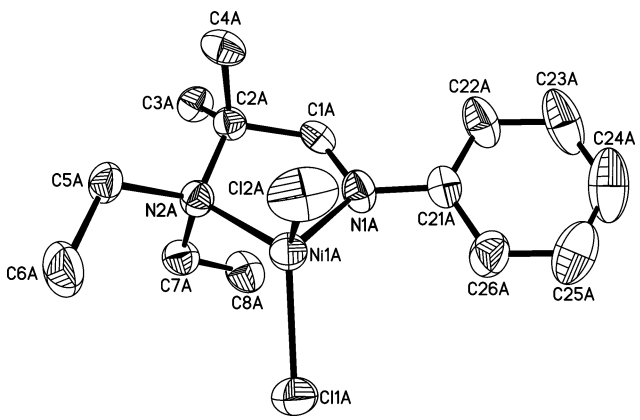


Fig. 1 ORTEP drawing of $[Et_2NCMe_2CH{=}NPh]NiCl_2$ (**3c**). All hydrogen atoms are omitted for clarity.

By viewing the data of **3c** in Table 2, the distance of the Ni–N2(sp^3) bond is longer than the Ni–N1(sp^2) bond (2.045 Å *vs.* 1.979 Å); and the distance of the amino C2–N2 bond is longer than the imino C1–N1 bond (1.520 Å *vs.* 1.297 Å), as expected. The N1–Ni–N2 angle is 83.5(1)°, nearly the same as that in Brookhart's diimine catalysts.[16] The Cl1–Ni–Cl2 angle is 115.65(5)°. In other Pd or Pt complexes of square planar geometry, the differences between the Pd–N1 bond and Pd–N2 bond are slightly larger than that in **3c** (about 0.1 Å *vs.* 0.07 Å). The imino C1–N1 bonds are generally shorter (about 1.27 Å *vs.* 1.30 Å) and the N1–M–N2 angles are generally smaller (about 80° *vs.* 84°) in **4a**, **4c**, **5b**, **5c** and **6c** than in **3c**. It is noted that in the square planar complexes of **4a**, **4c**, **5b**, **5c**, and **6c** the distances of two M–Cl or of two Pd–O bonds are all rather comparable, with the difference being less than about 0.01 Å. In the general sense, this phenomenon indicates that the amino group and the imino group hardly show significant difference in *trans* influence.[17]

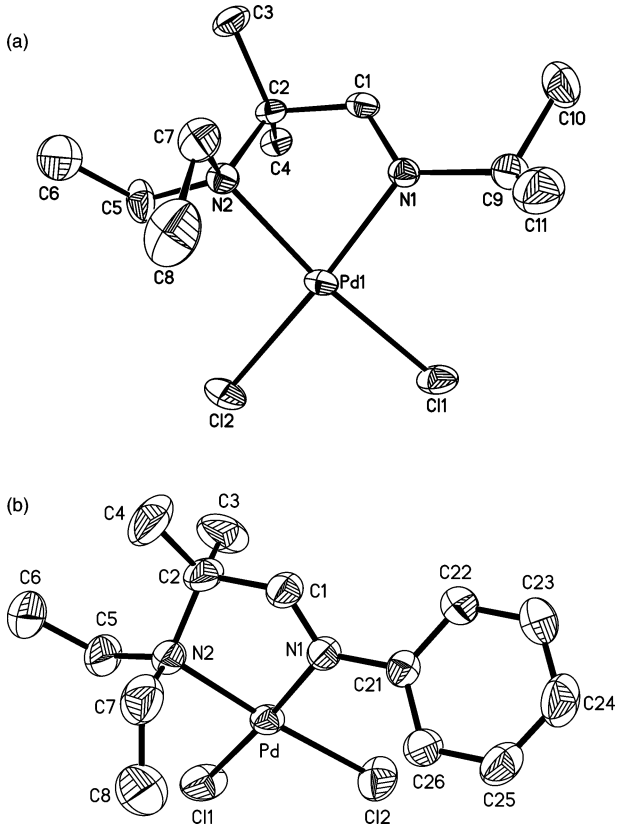


Fig. 2 ORTEP drawings of (a) $[Et_2NCMe_2CH{=}N^iPr]PdCl_2$ (**4a**), and (b) $[Et_2NCMe_2CH{=}NPh]PdCl_2$ (**4c**). All hydrogen atoms are omitted for clarity.

The structures of organometallic species **7a**, **7c**, **8c** and **10c** are all in the *trans* configuration, *i.e.* the metal–carbon bond is *trans* to the amino nitrogen, no matter if the substituent on the imino nitrogen is isopropyl or the phenyl group. Complex **10c** indicates that the norbornene insertion into the Pd–acyl bond takes place in the sole *syn*/*exo*-fashion.[18]

Further looking into the bond parameters as summarized in Table 3, a few trends may be noticed. The Pd–N2 bonds in the organometallic derivatives are substantially longer (>0.1 Å) than those in the dichloro derivatives. And, the differences between the Pd–N1 and Pd–N2 bonds are larger in the organometallic complexes than in the dichloro complexes (0.2 Å *vs.* 0.1 Å). This

Table 1 X-Ray crystal parameters and data collection

Compound	**3c**	**4a**	**4c**	**6c**	**5b**	**5c**	**7a**	**7c**	**8c**	**10c**
Formula	$C_{14}H_{22}Cl_2N_2Ni$	$C_{11}H_{24}Cl_2N_2Pd$	$C_{14}H_{22}Cl_2N_2Pd$	$C_{18}H_{28}N_2O_4Pd$	$C_{12}H_{26}Cl_2N_2Pt$	$C_{14}H_{22}Cl_2N_2Pt$	$C_{12}H_{27}ClN_2Pd$	$C_{15}H_{25}ClN_2Pd{\cdot}0.25CH_2Cl_2$	$C_{17}H_{28}N_3Pd{\cdot}CF_3SO_3$	$C_{23}H_{35}N_2OPd{\cdot}CF_3SO_3$
Formular wt	347.95	361.62	395.64	442,82	464.34	484.33	341.21	396.45	529.89	611.00
Crystal size/mm	0.3 × 0.25 × 0.2	0.05 × 0.1 × 0.4	0.5 × 0.4 × 0.3	0.2 × 0.2 × 0.07	0.25 × 0.2 × 0.15	0.3 × 0.25 × 0.1	0.1 × 0.1 × 0.2	0.45 × 0.25 × 0.25	0.4 × 0.35 × 0.1	0.15 × 0.2 × 0.25
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$Pbca$	$Pca2_1$	$P2_1/c$	$P2_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	11.4010(1)	7.241(2)	14.352(3)	12.955(2)	16.4203(3)	14.2861(2)	7.397(2)	8.168(4)	9.819(2)	13.150(3)
b/Å	22.9790(4)	13.163(5)	7.9957(8)	16.097(4)	7.4637(4)	8.0914(1)	15.509(5)	13.679(1)	10.897(3)	9.955(4)
c/Å	14.0160(2)	15.733(7)	14.633(3)	18.955(4)	12.9605(7)	14.6526(2)	7.866(2)	16.280(6)	22.110(3)	21.114(4)
α/°	90	90	90	90	90	90	90	88.19(2)	90	90
β/°	111.973(1)	90	91.40(2)	90	90	91.714 (1)	117.58(2)	82.95(4)	99.40(1)	100.40(2)
γ/°	90	90	90	90	90	90	90	85.21(3)	90	90
U/Å^3	3405.23(8)	1499.5(8)	1678.7(5)	3961(1)	1588.4(1)	1693.00(4)	799.9(4)	1798(1)	2334.0(8)	2719(1)
Z	8	4	4	8	4	4	2	4	4	4
ρ (calcd)/Mg m^{-3}	1.357	1.602	1.565	1.485	1.942	1.900	1.417	1.464	1.508	1.493
F(000)	1456	736	800	1824	896	928	352	810	1080	1256
T/K	295(2)	296(2)	295(2)	295(2)	295(2)	200(2)	295(2)	295(2)	295(2)	295(2)
μ/mm^{-1}	1.442	1.573	1.413	0.960	9.154	8.593	1.308	1.247	0.930	0.811
Transmission	0.737–0.806	0.620–0.928	0.672–0.726	0.666–0.784	0.122–0.280	0.180–0.285	0.851–0.892	0.6038–0.7457	0.663–0.796	0.767–0.860
θ/deg	3.04–26.60	2.02–27.50	1.42–27.47	2.14–25.00	2.73–27.45	1.43–25.0	2.63–27.50	1.93–25.00	1.87–25.00	1.70–25.00
h, k, l	−14–13, ±28, ±17	±9, −17–15, −20–12	±18, 10, 18	0–15, 0–19, 0–22	−21–19, −6–9, ±16	±16, ±9, ±17	−9–6, −19–20, −7–10	±9, 16, ±19	±11, 12, 26	±15, 11, 25
Reflns collected	43 966	8511	3851	3487	8029	17 802	5545	6321	4098	4776
Indep. reflections	7080	3436	3851	3487	3496	2986	3627	6321	4098	4776
R_{int}	0.0742	0.0441	0.0000	0.0000	0.0883	0.0270	0.0309	0.0000	0.0000	0.0000
Data/restraints	7080/0	3436/0	3851/0	3487/0	3496/1	2986/0	3627	6321	4098	4476
Parameters	443	154	177	232	155	155	153	372	268	321
$R1$ [$I > 2\sigma(I)$]	0.0439	0.0388	0.0245	0.0348	0.0517	0.0169	0.0316	0.0314	0.0352	0.0383
w$R2$ [$I > 2\sigma(I)$]	0.0830	0.0794	0.0666	0.0538	0.1242	0.0388	0.0600	0.0732	0.0881	0.1024
$R1$ (all data)	0.0950	0.0489	0.0317	0.1002	0.0730	0.0196	0.0410	0.0533	0.0656	0.0651
w$R2$ (all data)	0.1003	0.0831	0.0694	0.0631	0.1398	0.0448	0.0634	0.0795	0.0977	0.1126
Goodness of fit on F^2	1.022	1.070	1.054	1.000	1.029	1.160	1.026	1.017	1.022	1.026
Largest diff. peak and hole/e Å^{-3}	0.244 and −0.207	1.096 and −0.639	0.778 and −0.406	0.507 and −0.436	0.617 and −0.330	0.550 and −0.527	0.326 and −0.473	−0.503 and 0.70	0.617 and −0.330	−0.857 and 0.709

Table 2 Selected bond distances (Å) and angles (°)

[Et_2NCMe_2CH=NPh]$NiCl_2$ (**3c**)							
Ni–N1	1.979(3)	Ni–N2	2.045(2)	Ni–Cl1	2.217(1)	Ni–Cl2	2.206(1)
N1–C1	1.297(8)	N2–C2	1.520(5)	C1–C2	1.498(9)	N1–C21	1.428(4)
N2–C5	1.482(6)	N2–C7	1.531(6)				
N1–Ni–N2	83.5(1)	Cl1–Ni–Cl2	115.65(5)	Ni–N1–C1	112.8(4)		
Ni–N2–C2	106.5(2)	N1–C1–C2	120.4(6)	N2–C2–C1	107.4(4)		
C5–N2–Ni	112.6(3)	C7–N2–Ni	107.2(3)	C21–N1–Ni	125.6(2)		
[Et_2NCMe_2CH=N^{i}Pr]$PdCl_2$ (**4a**)							
Pd–N1	2.028(3)	Pd–N2	2.126(4)	Pd–Cl1	2.314(1)	Pd–Cl2	2.297(1)
N1–C1	1.263(6)	N2–C2	1.534(6)	C1–C2	1.493(6)	N1–C9	1.477(6)
N2–C5	1.493(7)	N2–C7	1.510(6)				
N1–Pd–N2	79.78(1)	Cl1–Pd–Cl2	89.31(6)	Pd–N1–C1	111.8(3)		
Pd–N2–C2	100.9(2)	N1–C1–C2	120.9(4)	N2–C2–C1	105.2(3)		
C5–N2–Pd	115.9(3)	C7–N2–Pd	107.6(3)	C9–N1–Pd	124.8(3)		
[Et_2NCMe_2CH=NPh]$PdCl_2$ (**4c**)							
Pd–N1	2.026(2)	Pd–N2	2.115(2)	Pd–Cl1	2.2822(7)	Pd–Cl2	2.2947(8)
N1–C1	1.268(3)	N2–C2	1.528(3)	C1–C2	1.507(3)	N1–C21	1.435(3)
N2–C5	1.505(3)	N2–C7	1.517(4)				
N1–Pd–N2	80.03(8)	Cl1–Pd–Cl2	88.61(3)	Pd–N1–C1	112.9(2)		
Pd–N2–C2	103.0(2)	N1–C1–C2	120.4(2)	N2–C2–C1	105.4(2)		
C5–N2–Pd	112.58(2)	C7–N2–Pd	106.5(2)	C21–N1–Pd	127.2(2)		
[Et_2NCMe_2CH=N^{t}Bu]$PtCl_2$ (**5b**)							
Pt–N1	2.03(1)	Pt–N2	2.12(1)	Pt–Cl1	2.310(4)	Pt–Cl2	2.304(4)
N1–C1	1.31(2)	N2–C2	1.54(2)	C1–C2	1.47(2)	N1–C9	1.50(2)
N2–C5	1.51(2)	N2–C7	1.52(2)				
N1–Pt–N2	80.1(5)	Cl1–Pt–Cl2	84.8(2)	Pt–N1–C1	112(1)		
Pt–N2–C2	103(7)	N1–C1–C2	121(1)	N2–C2–C1	106(1)		
C5–N2–Pt	111.3(8)	C7–N2–Pt	109(1)	C9–N1–Pt	128.6(8)		
[Et_2NCMe_2CH=NPh]$PtCl_2$ (**5c**)							
Pt–N1	2.016(3)	Pt–N2	2.119(3)	Pt–Cl1	2.303(1)	Pt–Cl2	2.311(1)
N1–C1	1.281(5)	N2–C2	1.537(5)	C1–C2	1.504(5)	N1–C21	1.447(5)
N2–C5	1.522(6)	N2–C7	1.524(6)				
N1–Pt–N2	80.3(1)	Cl1–Pt–Cl2	88.04(4)	Pt–N1–C1	114.0(3)		
Pt–N2–C2	104.1(2)	N1–C1–C2	120.1(3)	N2–C2–C1	105.7(3)		
C5–N2–Pt	111.3(3)	C7–N2–Pt	107.5(3)	C21–N1–Pt	126.7(2)		
[Et_2NCMe_2CH=NPh]$Pd(OAc)_2$ (**6c**)							
Pd–N1	1.996(4)	Pd–N2	2.075(4)	Pd–O1	2.012(3)	Pd–O3	2.012(3)
N1–C1	1.271(6)	N2–C2	1.520(6)	C1–C2	1.502(6)	N1–C21	1.437(6)
N2–C5	1.491(6)	N2–C7	1.524(5)				
N1–Pd–N2	81.0(2)	O1–Pd–O3	85.8(1)	Pd–N1–C1	114.6(3)		
Pd–N2–C2	104.3(3)	N1–C1–C2	118.2(5)	N2–C2–C1	105.7(4)		
C5–N2–Pd	109.7(3)	C7–N2–Pd	107.4(3)	C21–N1–Pd	125.8(3)		
[Et_2NCMe_2CH=N^{i}Pr]Pd(Me)Cl (**7a**)							
Pd–N1	2.046(3)	Pd–N2	2.250(3)	Pd–C9	2.022(4)	Pd–Cl1	2.306(1)
N1–C1	1.282(6)	N2–C2	1.531(5)	C1–C2	1.478(8)	N1–C21	1.485(7)
N2–C5	1.500(5)	N2–C7	1.485(5)				
N1–Pd–N2	78.3(1)	Cl1–Pd–C9	88.2(1)	Pd–N1–C1	112.8(3)		
Pd–N2–C2	100.5(2)	N1–C1–C2	122.7(3)	N2–C2–C1	106.1(3)		
C5–N2–Pd	111.9(2)	C7–N2–Pd	107.3(2)	C21–N1–Pd	125.1(3)		
[Et_2NCMe_2CH=NPh]Pd(Me)Cl (**7c**)							
Pd–N1	2.040(3)	Pd–N2	2.270(3)	Pd–C9	2.018(4)	Pd–Cl1	2.310(2)
N1–C1	1.268(5)	N2–C2	1.520(5)	C1–C2	1.498(8)	N1–C21	1.444(5)
N2–C5	1.494(5)	N2–C7	1.485(5)				
N1–Pd–N2	78.3(1)	Cl1–Pd–C9	87.5(1)	Pd–N1–C1	115.1(3)		
Pd–N2–C2	103.2(2)	N1–C1–C2	122.9(3)	N2–C2–C1	107.0(3)		
C5–N2–Pd	110.7(2)	C7–N2–Pd	106.4(2)	C21–N1–Pd	126.9(2)		
{[Et_2NCMe_2CH=NPh]Pd(Me)(NCMe)}OTf (**8c**)							
Pd–N1	2.027(3)	Pd–N2	2.230(3)	Pd–C9	2.007(4)	Pd–N3	2.001(4)
N1–C1	1.266(5)	N2–C2	1.509(5)	C1–C2	1.490(5)	N1–C21	1.437(5)
N2–C5	1.501(5)	N2–C7	1.505(5)	N3–C10	1.123(5)		
N1–Pd–N2	79.1(1)	N3–Pd–C9	86.9(2)	Pd–N1–C1	113.3(3)		
Pd–N2–C2	101.6(2)	N1–C1–C2	122.6(4)	N2–C2–C1	107.1(3)		
C5–N2–Pd	109.9(2)	C7–N2–Pd	108.1(2)	C21–N1–Pd	127.0(2)		
C10–N3–Pd	174.3(4)						

Table 2 (*Contd.*)

{[Et_2NCMe_2CH=NPh]Pd[C(O)Me(C_7H_{10})]}OTf (**10c**)							
Pd–N1	2.019(3)	Pd–N2	2.227(3)	Pd–C9	2.008(4)	Pd–O1	2.045(3)
N1–C1	1.280(5)	N2–C2	1.513(5)	C1–C2	1.501(6)	N1–C21	1.438(5)
N2–C5	1.481(5)	N2–C7	1.488(5)	O1–C16	1.240(6)		
N1–Pd–N2	79.2(1)	O1–Pd–C9	83.6(2)	Pd–N1–C1	113.7(3)		
Pd–N2–C2	101.5(2)	N1–C1–C2	121.4(4)	N2–C2–C1	106.2(3)		
C5–N2–Pd	107.9(3)	C7–N2–Pd	109.4(2)	C21–N1–Pd	126.7(3)		
C14–C9–Pd	109.0(3)	C16–O1–Pd	115.2(3)				

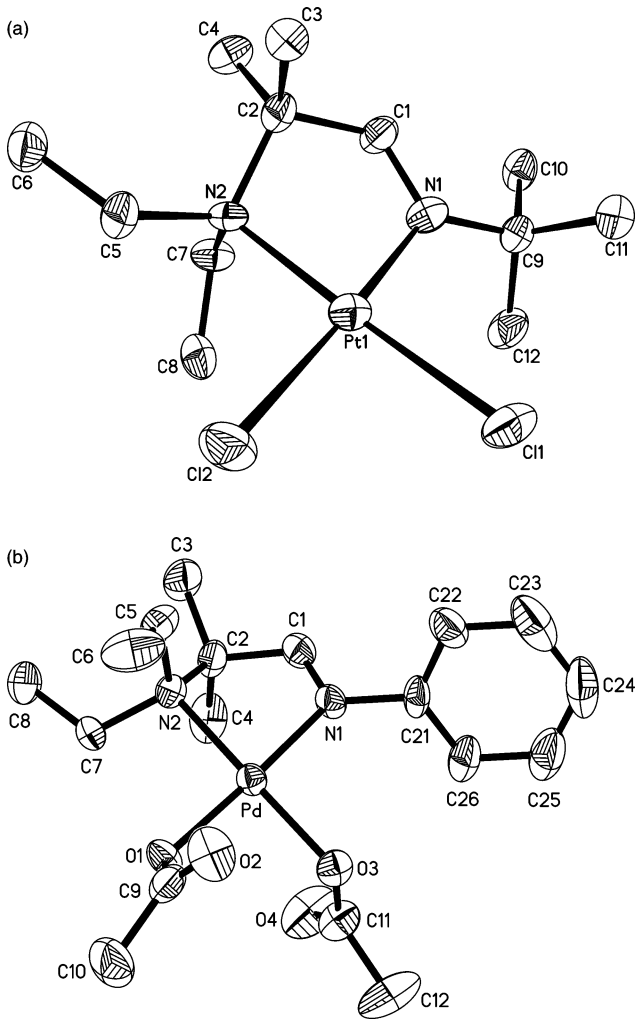


Fig. 3 ORTEP drawings of (a) [Et_2NCMe_2CH=N^{t}Bu]$PtCl_2$ (**5b**), and (b) [Et_2NCMe_2CH=NPh]$Pd(OAc)_2$ (**6c**). All hydrogen atoms are omitted for clarity.

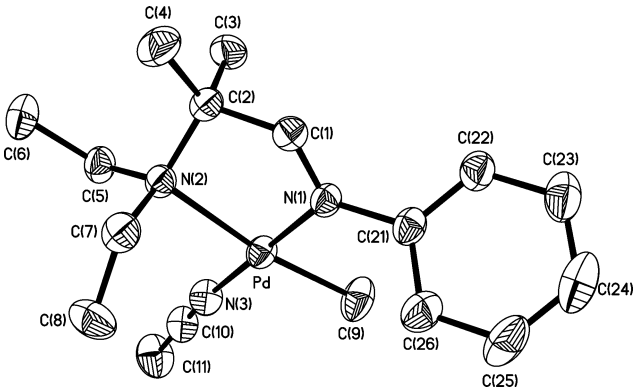


Fig. 4 ORTEP drawing of {[Et_2NCMe_2CH=NPh]Pd(Me)(NCMe)}-OTf (**8c**). All hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at the 30% probability level.

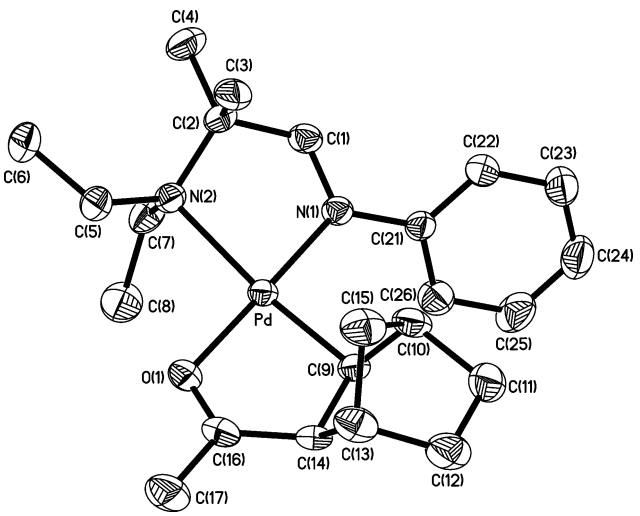


Fig. 5 ORTEP drawing of {[Et_2NCMe_2CH=NPh]Pd[C(O)Me(C_7H_{10})]}-OTf (**10c**). All hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at the 30% probability level.

is attributed to the large *trans* influence of the Pd-bound methyl. Despite the slight lengthening of the Pd–N1 and Pd–N2 bonds in the organometallic complexes, the bite-angles of N1–Pd–N2 in **7a** and **7c** are smaller (1–2°) than in the corresponding dichloro complexes **4a** and **4c**, respectively; however, they are slightly larger than in the methylchloro analogues of the diimino complexes.[19]

Geometrical isomerism

All the prepared organometallic derivatives with the title ligands show a single geometrical isomer of the *trans* configuration, even the products from the reaction of CO or olefin insertion as illustrated in Scheme 4. The stereo-retention of CO insertion and norbornene insertion may be explained either by a pathway involving a five-coordinate intermediacy,[20] or isomerization *via* amine dissociation and re-coordination.[21]

In complexes **7a** and **7c**, the *trans* isomerism appears to be not affected by the isopropyl or phenyl group on the imine. Such a stereoselectivity is attributed to steric hindrance between the methyl ligand in **7** or **8**, acetyl in **9** or norbornyl in **10** and the ethyl substituents of amine functionality that could destabilize the

Table 3 Selected bond parameters from crystallographic analysis

Complex	Pd–N1 (Å)	Pd–N2 (Å)	N1–Pd–N2 (°)	L1–Pd–L2[a] (°)
4a	2.028(3)	2.126(4)	79.8(1)	89.31(6)
4c	2.026(2)	2.115(2)	80.03(8)	88.61(3)
trans-**7a**	2.046(3)	2.250(3)	78.3(1)	88.2(1)
trans-**7c**	2.040(3)	2.270(3)	78.3(1)	87.5(1)
trans-**8c**	2.027(3)	2.230(3)	79.1(1)	86.9(2)
trans-exo-**10c**	2.019(3)	2.227(3)	79.2(1)	83.6(2)

[a] L1: the donor atom *trans* to imine; L2: the donor atom *trans* to amine.

cis form.[22] The two methyl substituents on the α-carbon (C2) of aminoaldimines might enhance this hindrance. On the other hand, the imino functionality in which the trigonal planar disposition around the N(sp^2) is supposed to be more tolerable to the steric strain than the N(sp^3). Besides, teriary amines are known to be hemi-labile.[23] It is reasonable to assume that the *trans* isomerism is a thermodynamic result of isomerization *via* amine dissociation and re-coordination.

Calculational analysis

In order to seek theoretical support for the stereoselectivity to the *trans* geometrical isomers, DFT calculations of the energy differences between the *trans* and *cis* isomers of **7a**, **7c**, **8c**, **9c** and the *trans*/*cis-exo*/*endo* forms for **10c** have been carried out.

The results regarding the calculated relative stability between the isomers are consistent with the experimental observations. As the data listed in Table 4 shows, the neutral complexes of *trans*-**7a**, *trans*-**7c**, and *trans*-**9c** are more stable than their corresponding *cis* isomers by 4.08, 5.21, and 4.78 kcal mol^{-1}, respectively. For the cationic complex **8c**, the *trans* form is more favorable by only 2.62 kcal mol^{-1}. For **10c**, the *trans-syn*/*exo*, *trans-syn*/*endo*, and the *cis-syn*/*exo* configurations have been compared. The *cis-exo* form is 5.51 kcal mol^{-1}, while the *trans-endo* form is 1.47 kcal mol^{-1} less stable than the *trans-exo* form that is the sole isomer observed by X-ray diffractions.

Table 4 DFT calculations for the relative stability of organopalladium stereoisomers

Complex	*trans* (kcal mol^{-1})	*cis* (kcal mol^{-1})
7a	0	4.08
7c	0	5.21
8c	0	2.62
9c	0	4.78
10c-*exo*	0	5.51
10c-*endo*	1.47[a]	—

[a] Relative to **10c**-*trans-exo*.

The structural parameters from the theoretical approach are listed in Table 5. It is shown that all of the biting angles of N1–Pd–N2 are about 3° smaller than the data from X-Ray analysis. But the angles of L1–Pd–L2 are matched well. Comparing the theoretical structures for the geometrical isomers of **7a**, **7c**, **8c** and **9c**, the larger bond lengths between Pd–N1 and Pd–N2 in the *trans* species rather than in *cis* could be attributed to the *trans* influence. However, it is difficult to ascribe the favorable stability of the *trans* form to electronic or steric effect according to these data.

In the case of **10c**, the bond parameters of *trans-exo* derivative between the calculated and the experimental data are rather comparable. In the *trans-endo* form, the hindrance appears to be mainly resulting from a methyl on the α-carbon of the bidentate ligand and the H of nobornyl bridge. The closest H···H distance is 2.313 Å (whilst 3.025 Å in *trans-exo*), as shown in Fig. 6(a) and 6(b). In the *cis-exo* form, multiple H···H hindrances likely result from the interaction between the amino ethyl groups and the norbornyl group. In Fig. 6(c), three sets of H···H distance within 2.3 Å are found. It indicates that the respective steric effects from

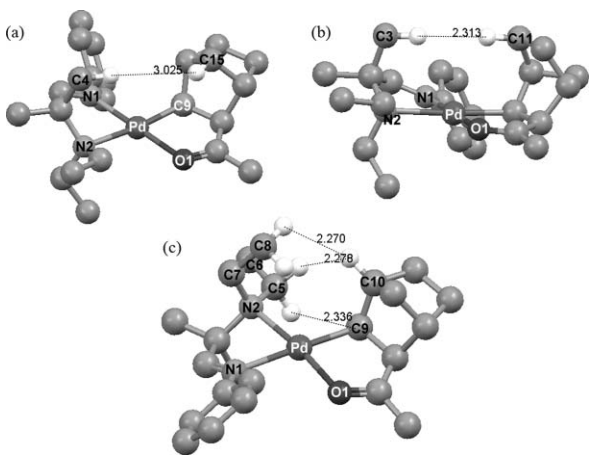


Fig. 6 Calculated steric hindrance in **10c** of (a) *trans-exo*, (b) *trans-endo*, (c) *cis-exo*.

Table 5 Selected bond parameters from calculations

Complex	Pd–N1 (Å)	Pd–N2 (Å)	C1=N1 (Å)	Pd–L1[a] (Å)	Pd–L2[b] (Å)	N1–Pd–N2 (°)	L1–Pd–L2 (°)
cis-**7a**	2.201	2.337	1.259	2.072(*L1* = *C9*)	2.369(*L2* = *Cl1*)	74.99	88.07
trans-**7a**	2.138	2.416	1.268	2.071(*L1* = *C9*)	2.366(*L2* = *Cl1*)	74.99	88.16
cis-**7c**	2.273	2.335	1.269	2.077(*L1* = *C9*)	2.369(*L2* = *Cl1*)	74.39	85.12
trans-**7c**	2.131	2.421	1.275	2.073(*L1* = *C9*)	2.369(*L2* = *Cl1*)	75.15	88.22
cis-**8c**	2.223	2.260	1.265	2.080(*L1* = *C9*)	2.064(*L2* = *N3*)	76.15	87.27
trans-**8c**	2.105	2.371	1.273	2.083(*L1* = *C9*)	2.065(*L2* = *N3*)	76.23	86.76
cis-**9c**	2.318	2.432	1.265	1.986(*L1* = *C9*)	2.420(*L2* = *Cl1*)	73.18	83.67
trans-**9c**	2.197	2.500	1.271	1.995(*L1* = *C9*)	2.400(*L2* = *Cl1*)	73.66	88.07
cis-exo-**10c**	2.115	2.334	1.269	2.079(*L1* = *C9*)	2.146(*L2* = *O1*)	76.06	81.46
trans-endo-**10c**	2.224	2.279	1.275	2.089(*L1* = *C9*)	2.133(*L2* = *O1*)	74.73	80.81
trans-exo-**10c**	2.113	2.334	1.274	2.073(*L1* = *C9*)	2.123(*L2* = *O1*)	76.74	81.52

[a] L1: the donor atom *trans* to imine. [b] L2: the donor atom *trans* to amine.

the amino and imino functionalities of such aldimines are crucial to the geometrical isomerism in the square planar configuration.

Concluding remarks

New unsymmetric bidentate ligands of α-aminoaldimines in the formula of $Et_2NCMe_2CH{=}NR$ are synthesized. A tetrahedral dichloronickel(II) complex and square planar dichloro and diacetato complexes of palladium or platinum are synthesized. The amine and imine functionalities show comparable *trans* influence. Square planar organometallic complexes of palladium with selective geometrical isomerism favored by the *trans* configuration are acquired. Such a stereoselectivity is a result of the thermodynamic option governed predominantly by the steric control from the hetero-donating functionalities of the ligand. In more specific words, the bulkier ligands prefer to coordinate *cis* to the imine group rather than amine group in the studied cases, so that the steric hindrance could be minimized.

Experimental section

Synthesis and spectral characterization

General procedures. Commercially available reagents were purchased and used without further purification unless otherwise indicated. Organic solvents were dried from purple solutions of benzophenone ketyl or over P_2O_5 under nitrogen, and distilled immediately prior to use. Air-sensitive material was manipulated under a nitrogen atmosphere in a glove box or by standard Schlenk techniques. The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were measured on Bruker AC-200, AC-300, or AC-400 spectrometer. The corresponding frequencies for ^{13}C NMR spectra were 50.324 and 75.469 MHz, or 100.625 MHz respectively. Values upfield of ^1H and ^{13}C data are given in δ relative to tetramethylsilane (δ 0.00) in $CDCl_3$ or to benzene in d^6-benzene (7.15, C_6H_6; 128.7, C_6H_6). Mass spectrometric analyses were collected on a Finnigan TSQ-46C or JEOL SX-102A spectrometer. Elemental analysis was done on a Perkin-Elmer 2400 CHN analyzer.

$BrCMe_2CHO$ (1). Orange bromine–1,4-dioxane adduct (32.7 g, 0.132 mol) was added in several aliquots to 2-methylpropanal (10 g, 0.139 mol) in 50 mL of diethyl ether at 5 °C. The orange slurry was continuously stirred until the disappearance of the color. The resulting solution was stirred for 10 min more, and then extracted three times with ice-cold water. The solution was dried with $MgSO_4$ and ether was removed on a rotary evaporator. The yield was 70%. IR (KBr): ν_{CO} 1733 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.34 (s, 1H, C*H*O), 1.77 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ 192.8 (*C*HO), 63.8 (*C*Me_2Br), 26.5 (*C*H_3); MS (FAB, *m*/*z*): 151 (M^+).

Et_2NCMe_2CHO. In a round-bottom flask was placed $BrCMe_2CHO$ (14 g, 92 mmol) in 30 mL of diethyl ether. The solution was first cooled to 0 °C. Et_2NH (17 g, 233 mmol) was added dropwise. The mixture was then stirred for 4 h to allow the reaction to complete. After the removal of amine salt, the solution was distilled to give a viscous yellow liquid product in 88% yield (11.7 g). IR (KBr): ν_{CO} 1739 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.39 (s, 1H, C*H*O), 2.50 (q, J_{H-H} = 7.1 Hz, 4H, NCH_2CH$_3$), 1.07 (s, 6H, C(CH_3)$_2$), 1.02 (t, J_{H-H} = 7.1 Hz, 6H, NCH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 205.5 (*C*HO), 66.7 (*C*(CH$_3$)$_2$), 43.4 (N*C*H$_2$CH$_3$), 18.9 (C(*C*H$_3$)$_2$), 16.0 (NCH$_2$*C*H$_3$); MS (FAB, *m*/*z*): 143 (M^+).

$Et_2NCMe_2CH{=}N^iPr$ (2a). In a round-bottom flask was placed Et_2NCMe_2CHO (4.33 g, 30.3 mmol) and isopropylamine (1.9 g, 32.8 mmol) in 100 mL of benzene. The solution was stirred with 4 Å molecular sieves at 25 °C. Distillation under vacuum gave colorless liquid product in 49% yield (2.7 g). IR (KBr): ν_{CN} 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (s, 1H, C*H*=N), 3.27 (h, J_{H-H} = 6.8 Hz, 1H, NC*H*(CH$_3$)$_2$), 2.50 (q, J_{H-H} = 7.2 Hz, 4H, NCH_2CH$_3$), 1.12 (s, 6H, C(CH_3)$_2$), 1.10 (d, J_{H-H} = 6.8 Hz, 6H, NCH(CH_3)$_2$), 1.00 (t, J_{H-H} = 7.2 Hz, 6H, NCH$_2$CH_3);^{13}C NMR ($CDCl_3$): δ 168.3 (*C*=N), 61.1 (*C*(CH$_3$)$_2$), 61.0 (N*C*H(CH$_3$)$_2$), 43.2 (N*C*H$_2$CH$_3$), 23.9 (C(*C*H$_3$)$_2$), 22.0 (NCH(*C*H$_3$)$_2$), 16.4 (NCH$_2$*C*H$_3$); MS (FAB, *m*/*z*): 185.2 (M^+ + 1).

$Et_2NCMe_2CH{=}N^tBu$ (2b). Using $^tBuNH_2$ and following the similar procedure as the preparation for **2a** gave the product of **2b** in a yield of 76%. ^1H NMR ($CDCl_3$): δ 7.48 (s, 1H, C*H*=N), 2.51 (q, J_{H-H} = 7.1 Hz, 4H, NCH_2CH$_3$), 1.13 (s, 9H, C(CH_3)$_3$), 1.12 (s, 6H, C(CH_3)$_2$), 1.02 (t, J_{H-H} = 7.1 Hz, 6H, NCH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 165.0 (*C*H=N), 61.44 (*C*(CH$_3$)$_3$), 56.16 (*C*(CH$_3$)$_2$), 43.30 (N*C*H$_2$CH$_3$), 29.63 (C(*C*H$_3$)$_3$), 21.73 (C(*C*H$_3$)$_2$), 16.40 (NCH$_2$*C*H$_3$).

$Et_2NCMe_2CH{=}NPh$ (2c). In a round-bottom flask was added Et_2NCMe_2CHO (7.0 g, 49 mmol) and then aniline (7.6 g, 82 mmol) in 150 mL of benzene. The solution was refluxed under nitrogen with Dean–Stark set-up. The product was isolated as a viscous colorless liquid by distillation under vacuum. The yield was 66% (11.8 g). IR (KBr): ν_{CN} 1648 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.75 (s, 1H, C*H*=N), 7.35–6.99 (m, 5H, phenyl-*H*), 2.61 (q, J_{H-H} = 7.0 Hz, 4H, NCH_2CH$_3$), 1.28 (s, 6H, C(CH_3)$_2$), 1.06 (t, J_{H-H} = 7.0 Hz, 6H, NCH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 172.6 (*C*=N), 151.8, 130–112 (phenyl-*C*), 63.0 (*C*(CH$_3$)$_2$), 43.8 (N*C*H$_2$CH$_3$), 21.8 (C(*C*H$_3$)$_2$), 15.8 (NCH$_2$*C*H$_3$); MS (FAB, *m*/*z*): 219.2 (M^+ + 1). Anal. calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83%. Found: C, 76.43; H, 10.01; N, 12.32%.

$[Et_2NCMe_2CH{=}NPh]NiCl_2$ (3c). (DME)$NiCl_2$ (300 mg, 1 mmol) and **2c** (327 mg, 1.5 mmol) were placed in a round-bottom flask under nitrogen. Predried CH_2Cl_2 (15 mL) was transferred under vacuum. The orange solution turned to violet within 10 min. The reaction was allowed to complete at 25 °C. After removal of the supernatant solid, the reaction solution was concentrated. Addition of dry Et_2O resulted in the solid product, and the yield of **1a** was 62% (270 mg) after recrystallization from CH_2Cl_2–Et_2O.

$[Et_2NCMe_2CH{=}N^iPr]PdCl_2$ (4a). To a 20 mL CH_2Cl_2 solution containing $(PhCN)_2PdCl_2$ (547 mg, 1.428 mmol) was added the ligand **2a** (270 mg, 1.467 mmol). The solution was stirred at 25 °C for 45 min, then was concentrated. Addition of diethyl ether gave the yellow precipitate in 93% yield (480 mg). Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–Et_2O. IR (KBr pellet): ν_{CN} 1655 cm^{-1}; ^1H NMR (CD_3CN): δ 7.36 (s, 1H, C*H*=N), 4.54 (h, J_{H-H} = 6.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 3.13, 2.99 (m, J_{H-H} = 7.2, 14.6 Hz, 4H, NCH_2CH$_3$), 1.82 (s, 6H, C(CH_3)$_2$), 1.49 (t, J_{H-H} = 7.2 Hz, 6H, NCH$_2$CH_3), 1.31 (d, J_{H-H} = 6.6 Hz, 6H, NCH(CH_3)$_2$);^{13}C NMR (CD_3CN): δ 176.8 (*C*=N), 75.0 (*C*(CH$_3$)$_2$), 56.7 (N*C*H(CH$_3$)$_2$), 49.2 (N*C*H$_2$CH$_3$),

23.3 ($C(CH_3)_2$), 21.9 ($NCH(CH_3)_2$), 13.1 (NCH_2CH_3); MS (FAB, *m/z*): 327.0 ($M^+ + 1 - Cl$). Anal. calcd for $C_{11}H_{24}Cl_2N_2Pd$: C, 36.53; H, 6.69; N, 7.75%. Found: C, 35.74; H, 6.57; N, 7.62%.

[Et$_2$NCMe$_2$CH=NPh]PdCl$_2$ (4c). Using similar procedures as for **4a**, the reaction of $(PhCN)_2PdCl_2$ (395 mg, 0.969 mmol) and ligand **2c** (235 mg, 1.078 mmol) gave the yellow precipitate of **4c** in 95% yield (389 mg). Single crystals were grown from CH_2Cl_2–Et_2O cosolvents. IR (KBr): ν_{CN} 1627 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.57 (s, 1H, C*H*=N), 7.48–7.20 (m, 5H, phenyl-*H*), 3.22, 3.07 (br, J_{H-H} = 7.1 Hz, 2H, 2H, NCH_2CH_3), 1.88 (s, 6H, $C(CH_3)_2$), 1.54 (t, J_{H-H} = 7.1 Hz, 6H, NCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 183.1 (*C*=N), 128.7, 128.6, 123.2 (phenyl-*C*), 74.7 ($C(CH_3)_2$), 49.5 (NCH_2CH_3), 23.1 ($C(CH_3)_2$), 13.3 (NCH_2CH_3); MS (FAB, *m/z*): 323.1 ($M^+ - 2Cl$), 359 ($M^+ - Cl$). Anal. calcd for $C_{14}H_{22}Cl_2N_2Pd$: C, 42.50; H, 5.60; N, 7.08%. Found: C, 41.66; H, 5.09; N, 6.91%.

[Et$_2$NCMe$_2$CH=N^{t}Bu]PtCl$_2$ (5b). A similar procedure as the preparation for **5c** gave the product in a yield of 42%. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–Et_2O. IR (KBr): ν_{CN} 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.84 (s, 1H, C*H*=N), 3.19, 3.12 (m, J_{H-H} = 7.0 Hz, 2H, 2H, NCH_2CH_3), 1.83 (s, 6H, $C(CH_3)_2$), 1.58 (s, 9H, $C(CH_3)_3$), 1.43 (t, J_{H-H} = 7.0 Hz, 6H, NCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 177.0 (*C*H=N), 76.2 ($C(CH_3)_2$), 50.2 (NCH_2CH_3), 30.1 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 22.1 ($C(CH_3)_2$), 12.9 (NCH_2CH_3); MS (FAB, *m/z*): 464.1 ($M^+ - Cl$).

[Et$_2$NCMe$_2$CH=NPh]PtCl$_2$ (5c). To a 20 mL benzene solution containing $(PhCN)_2PtCl_2$ (50 mg, 0.1 mmol) was added the ligand **2c** (125 mg, 0.57 mmol). The solution was refluxed for 24 h, then was concentrated. Addition of diethyl ether gave the yellow precipitate in 20% yield (10 mg). Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–Et_2O. ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H, C*H*=N), 7.37–7.08 (m, 5H, phenyl-*H*), 3.46, 3.28 (m, J_{H-H} = 7.1 Hz, 2H, 2H, NCH_2CH_3), 1.81 (s, 6H, $C(CH_3)_2$), 1.52 (t, J_{H-H} = 7.1 Hz, 6H, NCH_2CH_3).

[Et$_2$NCMe$_2$CH=N^{i}Pr]Pd(OAc)$_2$ (6a). Treating a solution of **4a** (144 mg, 0.398 mmol) in 15 mL CH_2Cl_2 with AgOAc (133 mg, 0.797 mmol) under N_2 atmosphere. The solution was stirred at 25 °C for 50 min, then was concentrated after the removal of AgCl precipitates. Addition of diethyl ether gave the yellow solid product in 78% yield (127 mg). IR (KBr): ν_{CO}, ν_{CN} 1658, 1626, 1596 cm^{-1}; ^{1}H NMR (CD_3CN, 200 MHz): δ 7.16 (s, 1H, C*H*=N), 3.61 (h, J_{H-H} = 6.6 Hz, 1H, $CH(CH_3)_2$), 2.97, 2.72 (qd, qd, J_{H-H} = 7.3 Hz, J_{gem} = 12.6 Hz, 2H, 2H, NCH_2CH_3), 1.87, 1.84 (s, s, 3H, 3H, $C(O)CH_3$), 1.83 (s, 6H, $C(CH_3)_2$), 1.52 (t, J_{H-H} = 7.1 Hz, 6H, NCH_2CH_3), 1.24 (d, J_{H-H} = 6.6 Hz, 6H, $CH(CH_3)_2$); MS (FAB, *m/z*): 349.1 ($M^+ - OAc$).

[Et$_2$NCMe$_2$CH=NPh]Pd(OAc)$_2$ (6c). Using similar procedures as for **6a**, the reaction of **4c** (141.7 mg, 0.358 mmol) and AgOAc (119.6 mg, 0.717 mmol) gave the yellow precipitate of **6c** in 95% yield (150 mg). Single crystals were grown from *n*-hexane–MeOH co-solvents. IR (KBr): ν_{CO}, ν_{CN} 1631, 1605, 1579 cm^{-1}; ^{1}H NMR (CD_3CN): δ 7.41 (s, 1H, C*H*=N), 7.29 (br, s, 5H, phenyl-*H*), 3.13, 2.87 (qd, qd, J_{H-H} = 7.2 Hz, J_{gem} = 13.0 Hz, 2H, 2H, NCH_2CH_3), 1.97 (s, 6H, $C(CH_3)_2$), 1.91 (s, 3H, $C(O)CH_3$), 1.63 (t, J_{H-H} = 7.2 Hz, 6H, NCH_2CH_3), 1.45 (s, 3H, $C(O)CH_3$); ^{13}C NMR ($CDCl_3$): δ 179.5 (*C*=O), 177.8 (*C*=N), 145.2, 128.9, 122.5 (phenyl-*C*), 74.4 ($C(CH_3)_2$), 47.7 (NCH_2CH_3), 23.3 ($C(CH_3)_2$), 22.7, 22.3 ($C(O)CH_3$), 12.2 (NCH_2CH_3); MS (FAB, *m/z*): 382.1 ($M^+ - OAc$).

[Et$_2$NCMe$_2$CH=N^{i}Pr]Pd(Me)Cl (7a). To a 15 mL CH_2Cl_2 solution containing (COD)Pd(Me)Cl (241.6 mg, 0.911 mmol) was added **2a** (176 mg, 0.957 mmol). The solution was stirred at 25 °C for 1 h, then concentrated. Addition of diethyl ether gave the yellow precipitate in 83% yield (258 mg). Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–Et_2O. IR (KBr pellet): ν_{CN} 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 1H, C*H*=N), 3.88 (h, J_{H-H} = 6.6 Hz, 1H, $NCH(CH_3)_2$), 2.91, 2.86 (m, J_{H-H} = 7.4, 16.8 Hz, 4H, NCH_2CH_3), 1.56 (s, 6H, $C(CH_3)_2$), 1.26 (dd, J_{H-H} = 7.4, 7.4 Hz, 6H, NCH_2CH_3), 1.24 (d, J_{H-H} = 6.6 Hz, 6H, $NCH(CH_3)_2$), 0.73 (s, 3H, $PdCH_3$); ^{13}C NMR ($CDCl_3$): δ 176.6 (*C*=N), 66.6 ($C(CH_3)_2$), 55.0 ($NCH(CH_3)_2$), 43.8 (NCH_2CH_3), 23.4 ($C(CH_3)_2$), 22.2 ($CH(CH_3)_2$), 11.9 (NCH_2CH_3), –4.48 ($PdCH_3$); MS (FAB, *m/z*): 307.1 ($M^+ - Cl$). Anal. calcd for $C_{12}H_{27}ClN_2Pd$: C, 42.24; H, 8.21; N, 7.98%. Found: C, 42.22; H, 8.25; N, 8.07%.

[Et$_2$NCMe$_2$CH=NPh]Pd(Me)Cl (7c). Using similar procedures as for **7a**, the reaction of (COD)Pd(Me)Cl (200 mg, 0.75 mmol) and **2c** (173 mg, 0.79 mmol) gave the yellow precipitate of **7c** in 68% yield (620 mg). Alternatively, a reaction of **4c** (86 mg, 0.217 mmol) and $SnMe_4$ (46 mg, 0.257 mmol) was carried out in CH_2Cl_2 at 25 °C for 13 h. After filtration with Celite the reaction solution was concentrated. Addition of diethyl ether gave the yellow solid product in 68% yield (56 mg). Single crystals were grown from CH_2Cl_2–Et_2O co-solvents. IR (KBr pellet): ν_{CN} 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.74 (s, 1H, C*H*=N), 7.38–7.24, 7.02–6.97 (m, m, 3H, 2H, C_6H_5), 3.01, 3.02 (q, J_{H-H} = 7.3 Hz, 2H, NCH_2CH_3), 1.68 (s, 6H, $C(CH_3)_2$), 1.33 (t, J_{H-H} = 7.3 Hz, 6H, NCH_2CH_3), 0.46 (s, 3H, $PdCH_3$); ^{13}C NMR ($CDCl_3$): δ 182.9 (*C*=N), 147.8, 129.0, 127.8, 122.1 (phenyl-*C*), 66.7 ($C(CH_3)_2$), 44.1 (NCH_2CH_3), 23.3 ($C(CH_3)_2$), 12.0 (NCH_2CH_3), 0.80 ($PdCH_3$); MS (FAB, *m/z*): 323. ($M^+ - Cl - CH_3$). Anal. calcd for $C_{15}H_{25}ClN_2Pd$: C, 48.01; H, 6.71; N, 7.47%. Found: C, 47.84; H, 6.57; N, 7.75%.

{[Et$_2$NCMe$_2$CH=N^{i}Pr]Pd(Me)(NCMe)}OTf (8a). **7a** (50 mg, 0.147 mmol) was treated with AgOTf (38 mg, 0.148 mmol) in CH_3CN for 15 min, then AgCl precipitate was filtered off. The residue was a dark brown oil. ^{1}H NMR ($CDCl_3$): δ 7.72 (s, 1H, C*H*=N), 3.70 (h, J_{H-H} = 6.6 Hz, 1H, $CH(CH_3)_2$), 2.97, 2.65 (m, J_{H-H} = 7.0 Hz, J_{gem} = 14.1 Hz, 2H, 2H, NCH_2CH_3), 2.38 (s, 3H, $NCCH_3$), 1.58 (s, 6H, $C(CH_3)_2$), 1.27 (t, J_{H-H} = 7.0 Hz, 6H, NCH_2CH_3), 1.19 (d, J_{H-H} = 6.6 Hz, 6H, $CH(CH_3)_2$), 0.63 (s, 3H, $PdCH_3$);^{13}C NMR (CD_3CN): δ 181.2 (*C*=N), 121 (*C*≡N), 67.9 (*C*CH_3), 55.9 ($CH(CH_3)_2$), 44.2 (NCH_2CH_3), 23.1 ($C(CH_3)_2$), 21.7 ($CH(CH_3)_2$), 11.7 (NCH_2CH_3), 3.2 ($NCCH_3$), –0.7 ($PdCH_3$); MS (FAB, *m/z*): 346.1 ($M^+ - OTf$).

{[Et$_2$NCMe$_2$CH=NPh]Pd(Me)(NCMe)}OTf (8c). **7c** (166 mg, 0.44 mmol) was treated with AgOTf (114 mg, 0.444 mmol) in CH_3CN for 15 min. The solution was filtered to remove the precipitate of AgCl and was concentrated. Addition of diethyl ether gave the yellow solid of **8c** in 93% yield (201 mg). Single crystals were grown from CH_2Cl_2–Et_2O co-solvents. IR (KBr pellet): ν_{CN} 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 1H, C*H*=N), 7.40–7.28, 7.05–7.01 (m, m, 3H, 2H, C_6H_5), 3.13, 2.87 (m, m, J_{H-H} = 7.1 Hz, J_{H-H} = 7.1 Hz, 2H, NCH_2CH_3), 2.44 (s, 3H, $NCCH_3$), 1.74 (s, 6H, $C(CH_3)_2$), 1.37 (t, J_{H-H} = 7.1 Hz, 6H,

NCH_2CH_3), 0.44 (s, 3H, $PdCH_3$); ^{13}C NMR ($CDCl_3$): δ 187.2 (*C*=N), 146.5, 129.3, 128.5, 122.3 (phenyl-*C*), 68.1 ($C(CH_3)_2$), 44.7 (NCH_2CH_3), 23.2 ($C(CH_3)_2$), 12.1 (NCH_2CH_3), 3.8 ($PdCH_3$), 3.5 ($NCCH_3$); MS (FAB, *m*/*z*): 380.1 (M^+ – OTf). Anal. calcd for $C_{18}H_{28}F_3N_3O_3SPd$: C, 40.80; H, 5.33; N, 7.93%. Found: C, 40.71; H, 5.26; N, 7.70%.

[Et_2NCMe_2CH=N^{i}Pr]PdC(O)MeCl (9a). A 1 mL solution of $CDCl_3$ containing **7a** (31 mg, 0.091 mmol) was bubbled with CO for 15 min. The yellowish green solution was monitored with ^1H NMR: δ 7.52 (s, 1H, C*H*=N), 3.66 (h, $J_{H\text{-}H}$ = 6.4 Hz, 1H, $NCH(CH_3)_2$), 2.78, 2.64 (m, $J_{H\text{-}H}$ = 7.2, 14.5 Hz, 2H, 2H, NCH_2CH_3), 2.44 (s, 3H, $PdC(O)CH_3$), 1.53 (s, 6H, $C(CH_3)_2$), 1.20 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, NCH_2CH_3), 1.15 (d, $J_{H\text{-}H}$ = 6.4 Hz, 6H, $NCH(CH_3)_2$);^{13}C NMR ($CDCl_3$): δ 226.4 (C=O), 176.8 (*C*=N), 65.5 ($C(CH_3)_2$), 59.0 ($NCH(CH_3)_2$), 42.9 (NCH_2CH_3), 36.0 ($C(O)CH_3$), 23.6 ($C(CH_3)_2$), 22.1 ($CH(CH_3)_2$), 11.8 (NCH_2CH_3); MS (FAB, *m*/*z*): 333.0 (M^+ – Cl).

[Et_2NCMe_2CH=NPh]PdC(O)MeCl (9c). To a 20 mL CH_2Cl_2 containing **7c** (254 mg, 0.677 mmol), was bubbled with CO for 20 min. The solution was concentrated. Addition of diethyl ether gave the yellow precipitate of **9c** in 83% yield (226 mg). IR (KBr): ν_{CN} 1638 cm^{-1}, ν_{CO} 1716 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.68 (s, 1H, C*H*=N), 7.31–7.23, 7.07–7.02 (m, m, 3H, 2H, C_6H_5), 2.93–2.81 (m, $J_{H\text{-}H}$ = 7.3 Hz, 4H, NCH_2CH_3), 2.10 (s, 3H, $PdC(O)CH_3$), 1.66 (s, 6H, $C(CH_3)_2$), 1.35 (t, $J_{H\text{-}H}$ = 7.3 Hz, 6H, NCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 223.0 (*C*=O), 182.3 (*C*=N), 149.1, 129.1, 128.0, 121.4 (phenyl-*C*), 65.7 ($C(CH_3)_2$), 43.4 (NCH_2CH_3), 33.6 ($PdC(O)CH_3$), 23.5 ($C(CH_3)_2$), 12.1 (NCH_2CH_3); MS (FAB, *m*/*z*): 367.1 (M^+ – Cl).

{[Et_2NCMe_2CH=N^{i}Pr]Pd[C(O)Me(C_7H_{10})]}OTf (10a). Complex **9a** was first prepared from **7a** (113.6 mg, 0.333 mmol) and CO *in situ* at 0 °C. The reaction solution was flushed by nitrogen for 15 min, followed by 2 mL CH_3CN, norbornene (nbe) (31.5 mg, 0.335 mmol), and AgOTf (86 mg, 0.335 mmol) in sequence. The solution was stirred at 0 °C for 3 h. After removal of AgCl precipitate, the solution was concentrated. Addition of diethyl ether gave the whitish precipitate in 75% yield (137 mg). IR (KBr): ν_{CN} 1643 cm^{-1}, ν_{CO} 1608 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.87 (s, 1H, C*H*=N), 3.62 (m, 1H, $NCH(CH_3)_2$), 3.15, 3.04, 2.85 (m, 1H, 1H, 1H, NCH_2CH_3 + nbe), 2.68 (br, 1H, nbe), 2.47 (br, 2H, nbe), 2.33 (m, 4H, nbe and $C(O)CH_3$), 1.96 (br, 1H, nbe), 1.82 (s, 6H, $C(CH_3)_2$), 1.53 (br, 3H, NCH_2CH_3 + nbe), 1.40 (br, 3H, NCH_2CH_3), 1.34 (br, 8H, $NCH(CH_3)_2$ + nbe), 1.16 (br, 4H, NCH_2CH_3 + nbe);^{13}C NMR ($CDCl_3$): δ 238, 180.9, 103.4, 70.5, 68.3, 57.8, 49.5, 44.6, 43.3, 43.2, 36.8, 29.5, 29.1, 27.3, 25.6, 24.0, 20.8, 20.6, 12.8, 10.7; MS (FAB, *m*/*z*): 427.1 (M^+ – OTf). Anal. calcd for $C_{21}H_{37}F_3N_2O_4SPd$: C, 43.71; H, 6.46; N, 4.85%. Found: C, 42.71; H, 6.28; N, 4.92%.

{[Et_2NCMe_2CH=NPh]Pd[C(O)Me(C_7H_{10})]}OTf (10c). Using similar procedures as for **10a**, reaction of **7c** (101 mg, 0.269 mmol) gave the white solid **10c** in 67% yield (111 mg). The single crystals were grown by evaporating off $CHCl_3$. IR (KBr): ν_{CN} 1624 cm^{-1}, ν_{CO} 1605 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.02 (s, 1H, C*H*=N), 7.38–7.18 (m, 5H, phenyl-*H*), 3.24, 3.12, 3.02, 2.73 (m, 1H, 1H, 1H, 1H, NCH_2CH_3), 2.54, 2.36 (d, d, $J_{H\text{-}H}$ = 6.3 Hz, $J_{H\text{-}H}$ = 3.7 Hz, 1H, 1H, nbe), 2.32 (s, 3H, $C(O)CH_3$), 2.07 (dd, 1H, $J_{H\text{-}H}$ = 6.3, 2.1 Hz, nbe), 1.67 (d, $J_{H\text{-}H}$ = 10.3 Hz, 1H, nbe), 1.92, 1.64 (s, s, 3H, 3H, $C(CH_3)_2$), 1.52, 1,25 (t, t, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 7.3 Hz, 3H, 3H, NCH_2CH_3), 1.44 (tt, $J_{H\text{-}H}$ = 12.4, 4.6 Hz, 1H, nbe), 1.33 (d, $J_{H\text{-}H}$ = 3.7 Hz, 1H, nbe), 1.12 (m, 2H, nbe), 0.85 (tt, $J_{H\text{-}H}$ = 12.4, 4.6 Hz, 1H, nbe), 0.37 (m, 1H, nbe); ^{13}C NMR ($CDCl_3$): δ 238.8 (*C*=O), 186.4 (C=N), 146.9, 129.1, 128.4, 122.5 (phenyl-*C*), 70.7, 68.2, 53.3, 44.9, 43.9, 43.2, 42.1, 36.5, 29.2, 28.0, 27.3, 25.0, 21.1, 12.9, 11.2.

X-Ray crystallographic analysis

Diffraction data were measured on a Nonius CAD-4, SmartCCD, or Nonius KappaCCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.7103 Å). No significant decay was observed during the data collection. The data were processed on a PC using the SHELXTL refinement software package.[24] The structures were solved using the direct method and refined by full-matrix least-squares on the F^2 value.

All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were identified by calculation and refined using a riding mode, and their contributions to structure factors were included. Atomic scattering factors were taken from the International Tables of Crystallographic Data, Vol IV.[25] Computing programs are from the NRC VAX package. Crystallographic data and selected atomic coordinates and bond parameters are collected in Tables 1–3. The rest of the data are supplied in the ESI.†

Computational details

All configurations were optimized by first using molecular mechanics MM+ (ArgusLab 4.01) and then with Amsterdam Density Functional (ADF 2004.01) without any restriction to symmetry and restrains. For the structures with crystallographic data, direct optimization was applied. The Vosko–Wilk–Nusair (VWN) parameterization of the electron gas for local density approximation (LDA) and exchange–correlation functionals from Becke–Lee–Yang–Parr (BLYP) for the generalized gradient approximation (GGA) were used. Relativistic zero-order regular approximation (ZORA) was applied.

For palladium, a standard triple-zeta Slater-type orbitals (STOs) basis set with one set of polarization functions was applied as implemented in the ADF basis set library (ADF database ZORA/TZP). The 1s–4p electrons were treated with the frozen core approximation. For main-group elements (C, N, O, H) a standard double-zeta Slater-type orbitals (STOs) basis set with one set of polarization functions was applied as implemented in the ADF basis set library (ADF database ZORA/DZP). The 1s electrons were treated with frozen core approximation. All structures shown correspond to minimum points on the potential surface. No symmetry constraints were used.

Acknowledgements

We thank the National Science Council, Taiwan, ROC, and the NSC-NWO joint project for the financial support.

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