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Reactions of palladium(II) and platinum(II) bis(azido) complexes with isocyanides: synthesis and structural characterization of palladium(II) and platinum(II) complexes containing carbodiimido (or bis(carbodiimido)) and bis(tetrazolato) ligands

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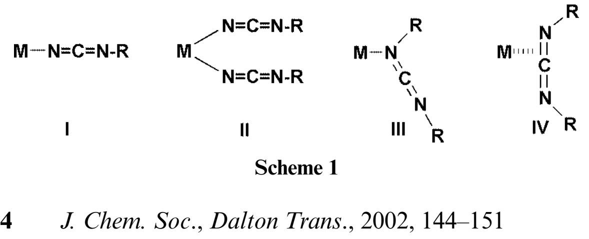
Bis(azido)palladium(II) complexes $Pd(N_3)_2L_2$ (L = PMe_3, PMe_2Ph, PEt_3, $PMePh_2$) reacted with two equivalents of 2,6-dimethylphenyl isocyanide to give the Pd(II) complexes, *trans*-$Pd[CN_4(R)](N{=}C{=}N{-}R)L_2$ (R = 2,6-$Me_2C_6H_3$, L = PMe_3, **1**; PMe_2Ph, **2**; PEt_3, **3**; $PMePh_2$, **4**) containing a carbodiimido ligand and a C-coordinated 5-membered tetrazolato ligand. X-Ray structures of **1** and **2** identified the formation of palladium(II) complexes with a carbodiimido group, in which a nitrogen of the linear N=C=N moiety is bonded to the metal center, and with a tetrazolato ring formed *via* 1,3-dipolar cycloaddition of the isocyanide to the coordinated azido bond. Heating the isolated complexes **1** and **3** at 60 °C for 5 h converted them into the bis(carbodiimido)palladium(II) complexes, *trans*-$Pd[N{=}C{=}N{-}R]_2L_2$ (R = 2,6-$Me_2C_6H_3$, L = PMe_3, **5**; PEt_3, **6**). The reactions of 2,6-dimethylphenyl isocyanide with $Pd(N_3)_2L_2$ (L = PMe_3, PEt_3) also gave the same complexes directly. Reaction of $Pd(N_3)_2$(dppe) with 2,6-dimethylphenyl isocyanide also caused the formation of the bis(carbodiimido) complex Pd[N=C=N–2,6-$Me_2C_6H_3]_2$(dppe), **7** in 75% yield. However, reactions of $M(N_3)_2(PMe_3)_2$ (M = Pd or Pt) with *tert*-butyl isocyanide resulted in the formation of bis(tetrazolato) compounds, $M[CN_4(R)]_2(PMe_3)_2$ (R = *tert*-butyl, M = Pd, **8**; Pt, **9**) by the cycloaddition of isocyanide to the coordinated azido bond. The same reactions with other isocyanides such as cyclohexyl and *n*-butyl isocyanides afforded bis(tetrazolato) complexes, *trans*-$M[CN_4(R)]_2L_2$ (M = Pd, R = C_6H_{11}, L = PMe_3: $\mathbf{10}_{anti,syn}$; M = Pd, R = *n*-Bu, L = PMe_3: $\mathbf{11}_{anti,syn}$; M = Pt, R = *n*-Bu, L = PMe_3: $\mathbf{12}_{anti,syn}$; M = Pt, R = *n*-Bu, L = PEt_3: $\mathbf{13}_{anti,syn}$), which show a mixture of *syn* and *anti* isomers in solution. Molecular structures of $\mathbf{11}_{anti}$, $\mathbf{12}_{anti}$, and $\mathbf{13}_{syn}$ have been determined by X-ray crystallography.

Introduction

Transition metal complexes containing a carbodiimido ligand, in which the nitrogen of the linear N=C=N ligand is directly bound to the metal, are considered to be potential catalysts for polymerization and/or precursors for metal nitrides and metal carbonitrides.[1] Despite their potential usefulness as catalysts and precursors, synthetic routes towards these complexes remain relatively unexplored. Currently, early transition metal or main group carbodiimido complexes are prepared by transmetallation of metal halides with trialkyltin (or silicon) carbodiimides,[1,2] but to date detailed synthetic methods for late transition metal carbodiimido complexes (type I and II) containing a linear N=C=N moiety with a metal–nitrogen bond have not been reported. However, the σ-bond formation (type III) through the nitrogen lone pair or π-coordination (type IV) *via* the C=N bond of organic carbodiimides (R–N=C=N–R) is relatively well-known as shown in Scheme 1. These complexes (type III and IV) are prepared from direct reactions of organic carbodiimides with metal complexes[3] and from oxidative addition of the carbodiimides to metal (0) or (I) complexes.[4–7]



Scheme 1

Werner and coworkers[8] and Hessell and Jones[9] have prepared η^2-carbodiimido complexes (type IV) of Rh and Co from the reaction of an organic azide and a metal-bound isocyanide, while Fisher and coworkers[10a] reported the formation of a type I complex from the reaction of isocyanide-bound complex $[(CO)_5CrCN(C_2H_5)_2][BF_4]$ with $[N(C_4H_9)_4]N_3$. In particular, Lewis and coworkers[11] reported a unique method for preparing the terminally bound carbodiimido complex $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)]$ from the reaction of $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)]$ with $PhNPPh_3$. In the early seventies Beck and coworkers[12] first observed the presence of a type I complex from the thermolysis of $AsPh_4[Au(CN_4CH_2C_6H_5)_4]$.

Recently we obtained type I carbodiimido palladium(II) complexes from the reactions of arylpalladium(II) azido complexes with 2,6-dimethylphenyl isocyanide.[13] These results suggested the possibility of conversion reactions of 2,6-dimethylphenyl isocyanide with coordinated azides to give general group 10 carbodiimido complexes. In an attempt to isolate various carbodiimido complexes we studied the reactions of palladium(II) and platinum(II) bis(azido) complexes with 2,6-dimethylphenyl isocyanide as well as other organic isocyanides. Earlier work by Beck and coworkers[12] showed that similar reactions of Pd(II)- and Pt(II)-bis(azido) complexes with various isocyanides gave bis(tetrazolato) complexes, but the

Table 1 Color, yields and analytical data of **1**–**13**

Complex[a]	Color	Yield(%)	Analyses[b] C (%)	H (%)	N(%)
1 Pd[CN_4(R)](N=C=N–R)(PMe_3)$_2$	Pale yellow	79	49.92 (49.96)	6.19 (6.29)	14.31 (14.57)
2 Pd[CN_4(R)](N=C=N–R)(PMe_2Ph)$_2$	Pale yellow	57	58.34 (58.25)	5.82 (5.75)	11.42 (11.99)
3 Pd[CN_4(R)](N=C=N–R)(PEt_3)$_2$	Pale yellow	88	54.85 (54.50)	7.41 (7.32)	12.73 (12.71)
4 Pd[CN_4(R)](N=C=N–R)($PMePh_2$)$_2$	Yellow	63	63.96 (64.04)	5.43 (5.37)	10.24 (10.18)
5 Pd[N=C=N–R]$_2$(PMe_3)$_2$	Yellow	89	52.28 (52.51)	6.62 (6.61)	10.04 (10.21)
6 Pd[N=C=N–R]$_2$(PEt_3)$_2$	Yellow	74	56.91 (56.91)	7.72 (7.64)	8.66 (8.85)
7 Pd[N=C=N–R]$_2$(dppe)$_2$	Orange	75	66.43 (66.46)	5.31 (5.32)	6.81 (7.04)
8 Pd[CN_4(*tert*-butyl)]$_2$(PMe_3)$_2$	White	79	37.96 (37.76)	7.21 (7.13)	22.39 (22.02)
9 Pt[CN_4(*tert*-butyl)]$_2$(PMe_3)$_2$	White	71	32.38 (32.16)	6.12 (6.07)	18.94 (18.75)
10 Pd[CN_4(cyclohexyl)]$_2$(PMe_3)$_2$	White	86	42.51 (42.82)	7.17 (7.19)	19.59 (19.98)
11 Pd[CN_4(*n*-butyl)]$_2$(PMe_3)$_2$	White	85	37.79 (37.76)	7.14 (7.13)	21.78 (22.02)
12 Pt[CN_4(*n*-butyl)]$_2$(PMe_3)$_2$	White	92	32.07 (32.16)	6.07 (6.07)	18.59 (18.75)
13 Pt[CN_4(*n*-butyl)]$_2$(PEt_3)$_2$	White	62	38.99 (38.76)	7.20 (7.10)	16.40 (16.44)

[a] In complexes **1**–**7** R = 2,6-$Me_2C_6H_3$. [b] Calculated values are given in parentheses.

formation of carbodiimido or bis(carbodiimido) complexes by those reactions was unexplored.

In this work we report the unusual formation of several new complexes such as palladium(II) carbodiimido or bis(carbodiimido) complexes as well as palladium(II) and platinum(II) complexes containing bis(tetrazolato) ligands, whose structures were determined by X-ray diffraction studies.

Results and discussion

In a recent paper[13] we reported that reactions of arylpalladium(II) azido complexes with 2,6-dimethylphenyl isocyanide give arylpalladium(II) carbodiimido complexes, formulated as ArPd(N=C=N-2,6-Me_2-C_6H_3)(PMe_3)$_2$. Based on that result, we conducted the reactions of various bis(azido)palladium(II) complexes Pd(N_3)$_2$$L_2$ (L = PMe_3, PMe_2Ph, PEt_3, $PMePh_2$) with two equivalents of 2,6-dimethylphenyl isocyanide.

The reactions at room temperature afforded Pd(II) complexes containing a carbodiimido ligand (N=C=N) and a C-coordinated tetrazolato ring, *trans*-Pd[CN_4(R)](N=C=N–R)L_2 (R = 2,6-$Me_2C_6H_3$, L = PMe_3, **1**; PMe_2Ph, **2**; PEt_3, **3**; $PMePh_2$, **4**) as shown in eqn. (1).

Addition of the isocyanide to a solution of the azido complex caused immediate evolution of nitrogen gas and the reaction was monitored easily by the IR spectra which showed disappearance of an asymmetric stretching band $\nu(N_3)$ at *ca.* 2030 cm^{-1} and appearance of a new strong band at 2140–2170 cm^{-1} due to the carbodiimido group ν(N=C=N) of the products. The reactions occurred cleanly and gave no other possible products such as bis(tetrazolato) complexes, Pd[CN_4(R)]$_2$$L_2$ (R = 2,6-$Me_2C_6H_3$), or bis(carbodiimido) complexes, Pd[N=C=N–R]$_2$$L_2$ (R = 2,6-$Me_2C_6H_3$). Complexes **1**–**4** were isolated as pale yellow crystals and characterized by IR and NMR spectra as well as elemental analyses (see Tables 1 and 2). ^{1}H NMR signals in the range of 1.00–1.67 ppm of complexes **1**–**4** indicate the presence of tertiary alkyl phosphines. The $^{31}P\{^1H\}$ NMR spectra show a singlet which is consistent with the proposed *trans* structure. The $^{13}C\{^1H\}$ NMR spectra of **1**–**4** each show a broad triplet at δ 157–158 which is assigned to the tetrazolato carbon coordinated to the metal center. The carbon signals of the NCN group are observed in the δ 130 region with a weak intensity.

Molecular structures of **1** and **2** were determined by X-ray diffraction. Selected bond lengths and angles and crystallographic data are given in Tables 3 and 4. Figs. 1 and 2 show the ORTEP drawings of the complexes, *trans*-Pd[CN_4(R)](N=C=N–R)L_2 (R = 2,6-$Me_2C_6H_3$, L = PMe_3, PMe_2Ph), which have a slightly distorted square-planar coordination, containing two phosphines, a carbodiimido group, and a tetrazolato ring. The carbodiimido ligand and tetrazolato rings are at mutually *trans* positions. The ORTEP drawings clearly show that the nitrogen of the carbodiimido ligand is bonded to the Pd center and that the five-membered tetrazolato ring is coordinated to Pd through the carbon. The tetrazolato ligand is essentially planar, and the 2,6-dimethylphenyl ring bonded to the tetrazolato ring is twisted out of the tetrazolato ring with a dihedral angle of

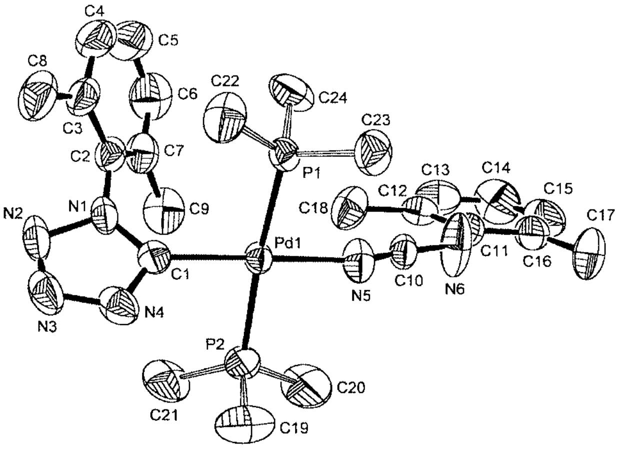
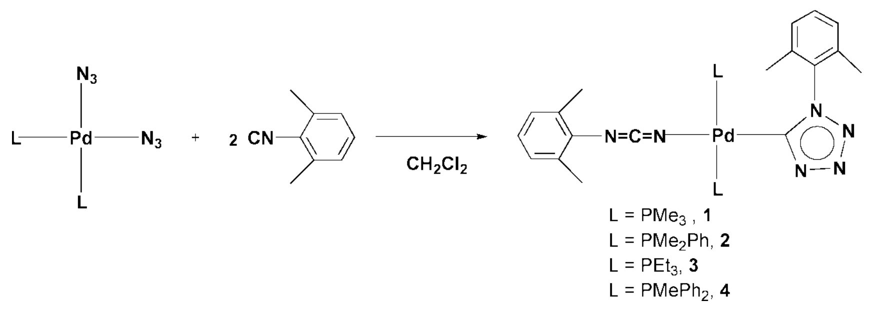


Fig. 1 ORTEP drawing[34] of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids.



(1)

Table 2 NMR and IR data of the complexes (δ, J/Hz)

Complex	^{1}H NMR^a		^{13}C{^{1}H}^{b}	^{31}P{^{1}H}^{c}	ν(NCN)^d/cm^{-1}
	PR_3 (R = Me or Et)	Others			
1	1.17 (t, 18 H, $J = 4$)	2.26 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 6.69–6.73 (m, 1H), 6.91–6.93 (m, 2H), 7.21–7.34 (m, 3H)	13.8 (t, $J = 16$), 19.3, 20.3 (t, $J = 1$), 120.3, 127.8, 129.3, 129.4, 130.0 (br, NCN), 134.9, 135.4, 143.4, 157.9 ($J = 9.8$, CN_4)	−12.2	2140
2	1.45 (br, 12H)	1.77 (br s, 6H, CH_3), 2.13 (br s, 6H, CH_3), 6.65–6.71 (m, 1H), 6.84–6.87 (m, 2H), 6.98–7.01 (m, 2H), 7.11–7.19 (m, 1H), 7.24–7.36 (m, 6H), 7.46–7.52 (m, 4H)	19.1, 19.6 (t, $J = 1$), 120.1, 127.7, 128.7, 128.8, 128.9, 129.2, 130.5, 130.8, 130.9, 131.0, 132.6, 135.2, 143.3 (t, $J = 1$), 157.1 (br, CN_4)	−4.0	2170
3	1.00 (q, 18H), 1.50 (br, 12H)	2.31 (s, 12H, CH_3), 6.69–6.71 (m, 1H), 6.89–6.92 (m, 2H), 7.18–7.28 (m, 4H)	7.92, 15.1 (t, $J = 14$), 19.1, 20.6, 119.9, 127.6, 129.1, 129.4, 129.6 (br, NCN), 131.0, 135.1, 135.6, 143.8, 156.8 (br, CN_4)	18.4	2129
4	1.67 (t, 6H, $J = 4$)	1.59 (s, 6H, CH_3), 1.68 (s, 6H, CH_3), 6.50–6.68 (m, 4H), 6.93–6.96 (m, 2H), 7.18–7.50 (m, 20H)	12.7 (t, $J = 16$), 18.8, 19.2, 119.4, 127.2, 128.6, 128.7, 129.1 130.4, 130.8, 131.9, 132.8, 135.4, 143.3, 157.4 (br t, CN_4)	6.29	2128
5	1.44 (t, 18H, $J = 4$)	2.33 (s, 12H, CH_3), 6.75 (m, 2H, Ph), 6.92 (m, 4H, Ph)	12.8 (t, $J = 15$), 19.2, 120.9, 127.8, 131.1, 131.3 (NCN), 142.6 (br)	−10.4	2091
6	1.67 (br, 18H), 1.77 (m, 12H)	2.31 (s, 12H, CH_3), 6.72 (m, 2H, Ph), 6.93 (m, 4H, Ph)	7.89, 14.1 (t, $J = 13$), 19.0, 120.6, 127.7, 130.7 (NCN), 131.0, 142.9 (t, $J = 1$)	20.6	2081
7	2.35 (br s, 2H), 2.43 (br s, 2H)	2.05 (br s, 12H, CH_3), 6.55–6.60 (m, 2H), 6.73–6.75 (m, 4H), 7.35–7.51 (m, 12H), 7.70–7.77 (m, 8H)	25.6, 27.7 (d, $J = 15$), 28.1 (d, $J = 15$), 119.6, 126.6, 127.3, 127.5, 129.2, 129.1, 129.3, 129.5, 131.6, 132.3, 133.1, 133.2, 133.5, 133.6, 143.3	61.5	2090
8	1.08 (t, 18H, $J = 4$)	1.85 (s, 18H, CH_3)	14.4 (t, $J = 16$), 31.2, 57.8, 161.8 (br, CN_4)	−15.1	
9	1.18 (t, 18H, $J = 4$, $J_{Pt-H} = 32$)	1.88 (s, 18H, CH_3)	14.2 (t, $J = 19$), 31.2, 58.2, 157.1 (br, CN_4)	−20.8 ($J_{Pt-P} = 1297$)	
10$_{anti,syn}$	1.10 (br, 18H)	1.28 (br, 6H, –CH_2), 1.85–2.23 (m, 14H, –CH_2), 4.49 (m, 2H, –CH)	*anti*: 14.6 (t, $J = 16$), 25.5, 26.0, 34.1, 59.4, 165.6 (br t) *syn*: 15.0 (t, $J = 16$), 25.1, 26.0, 33.9, 58.3, 165.4 (br, CN_4)	−14.7 −15.4	
11$_{anti,syn}$	1.09 (br, 18H)	1.05 (br t, 6H, CH_3), 1.53 (m, 4H, –CH_2), 2.01 (m, 4H, –CH_2), 4.38 (m, 4H, –CH)	*anti*: 13.6, 14.4 (t, $J = 17$), 20.2, 32.1, 48.3, 166.4 (t, $J = 14$, CN_4) *syn*: 13.5, 14.1 (t, $J = 16$), 20.0, 32.5, 48.2, 166.4 (t, $J = 14$, CN_4)	−14.9 −13.9	
12$_{anti,syn}$	1.17 (t, 6H, $J = 7$)	1.04 (t, 6H, CH_3), 1.53 (m, 4H, CH*2*), 1.98 (m, 4H, CH_2), 4.36 (m, 4H, –CH_2)	*anti*: 13.8, 14.2 (t, $J = 13$), 20.4, 32.1, 48.3, 162.5 (t, $J = 12$, CN_4) *syn*: 13.7, 14.1 (t, $J = 19$), 20.2, 32.5, 48.2, 162.5 (t, $J = 12$, CN_4)	−19.4, $J_{Pt-P} = 2311$ −18.8, $J_{Pt-P} = 2316$	
13$_{anti,syn}$	1.05 (m, 18H), 1.39 (m, 12H)	1.55 (m, 4H, CH_2), 2.07 (m, 4H, CH_2), 4.36 (m, 4H, CH_2)	*anti*: 7.60, 13.7, 14.5 (t, $J = 17$), 20.5, 31.8, 46.6, 162.7 (t, $J = 8$, CN_4) *syn*: 7.66, 13.7, 14.8 (t, $J = 17$), 20.5, 31.7, 48.5, 162.7 (t, $J = 8$, CN_4)	9.67, $J_{Pt-P} = 2351$ 9.45, $J_{Pt-P} = 2338$	

[a] Obtained in $CDCl_3$ at 25 °C. Peak positions were referenced to internal $SiMe_4$. [b] Obtained in $CDCl_3$ at 25 °C. Peak positions were referenced to internal $SiMe_4$. [c] Obtained in $CDCl_3$ at 25 °C. Peak positions were referenced to external 85% H_3PO_4. Abbreviations: t, triplet; br, broad; br s, broad singlet; q, quartet; m, multiplet. [d] KBr.

64.4(2) (for **1**) or 64.9(3)° (for **2**). Complexes **1** and **2** show quite similar structures, but the 2,6-$C_6H_3Me_2$ groups on the carbodiimido ligand across the molecular plane of the complexes show an approximately *syn* (for **1**) or *anti* (for **2**) conformation. Also, the orientation of the phosphine groups in each complex takes a staggered (for **1**) or an eclipsed (for **2**) conformation.

The carbodiimido group in each complex is approximately linear (NCN: 169.7(6)° and 171.4(10)°). The Pd–N distances (2.030(5) Å and 1.988(8) Å) of the carbodiimido ligand in compounds **1** and **2** are comparable with that (2.087(3) Å) found in *trans*-PdPh(N=C=N-2,6-$Me_2C_6H_3$)$(PMe_3)_2$.[13] However, these bonds are somewhat shorter than those found in palladium azide, *trans*-Pd(C_6H_4-*p*-Me)(N_3)$(PMe_3)_2$ (2.114(3) Å)[13] as well as palladium amide, *trans*-PdPh(NHPh)$(PMe_3)_2$ (2.116(13) Å),[14] indicating a partial π-bonding in the Pd–N bond. The Pd–N (1.988(8) Å) and Pd–C (1.969(9) Å) bond distances in **2** are shorter than those of **1** (2.030(5) Å and 2.006(5) Å) and those (2.087(3) Å and 2.014(3) Å) in *trans*-PdPh(N=C=N-2,6-$Me_2C_6H_3$)$(PMe_3)_2$, suggesting a weaker coordination of PMe_2-Ph compared with PMe_3. Interestingly, the bond distances between the nitrogen bound to the metal and center carbon in the carbodiimido groups of **1** (N5–C10) and **2** (N1–C17) are 1.156(7) Å and 1.150(11) Å, respectively, which are very close to the general C≡N bond length (1.16 Å),[15] whereas the other nitrogen–carbon bond distances are 1.235(8) Å (N6–C10 in **1**)

Table 3 Selected bond distances (Å) and bond angles (°) in **1** and **2**

1		**2**	
Pd1–C1	2.006(5)	Pd1–C26	1.969(9)
Pd1–N5	2.030(5)	Pd1–N1	1.988(8)
Pd1–P1	2.318(1)	Pd1–P1	2.334(2)
Pd1–P2	2.336(2)	Pd1–P2	2.329(2)
N1–C1	1.363(7)	N3–C26	1.352(11)
N1–N2	1.384(6)	N3–N4	1.393(10)
N2–N3	1.292(8)	N4–N5	1.309(11)
N3–N4	1.363(7)	N5–N6	1.350(11)
N4–C1	1.325(7)	N6–C26	1.367(11)
N5–C10	1.156(7)	N1–C17	1.150(11)
N6–C10	1.235(8)	N2–C17	1.274(11)
C1–Pd1–N5	175.6(2)	C26–Pd1–N1	175.5(3)
C1–Pd1–P1	95.9(1)	C26–Pd1–P1	98.9(2)
C1–Pd1–P2	87.3(2)	C26–Pd1–P2	89.0(3)
N5–Pd1–P1	87.0(2)	N1–Pd1–P1	85.7(2)
N5–Pd1–P2	90.2(2)	N1–Pd1–P2	86.5(2)
P1–Pd1–P2	172.72(6)	P2–Pd1–P1	171.54(8)
C1–N1–N2	108.3(5)	C26–N3–N4	110.1(8)
N3–N2–N1	105.6(5)	N5–N4–N3	106.4(9)
N2–N3–N4	111.6(5)	N4–N5–N6	109.0(9)
C1–N4–N3	107.0(5)	N5–N6–C26	110.2(8)
C10–N5–Pd1	158.2(5)	C17–N1–Pd1	168.9(8)
C10–N6–C11	132.7(6)	C17–N2–C18	131.9(8)
N4–C1–N1	107.4(5)	N3–C26–N6	104.1(8)
N5–C10–N6	169.7(6)	N1–C17–N2	171.4(10)

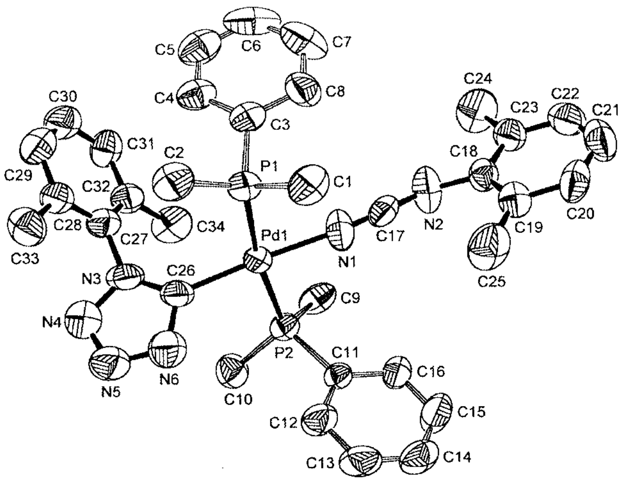
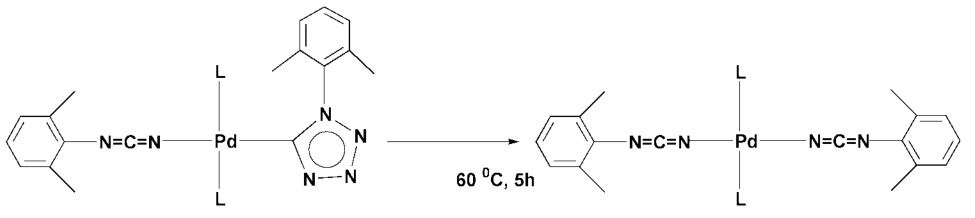


Fig. 2 ORTEP drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Table 4 X-Ray data collection and structure refinement for **1**, **2**, **11**, **12** and **13**

	1	**2**	**11**	**12**	**13**
Formula	$C_{24}H_{36}N_6P_2Pd$	$C_{34}H_{40}N_6P_2Pd$	$C_{16}H_{36}N_8P_2Pd$	$C_{16}H_{36}N_8P_2Pt$	$C_{22}H_{48}N_8P_2Pt$
M	576.93	701.06	508.87	597.56	681.71
Temperature/K	293(2)	293(2)	294(2)	296(2)	294(2)
Crystal size/mm^3	0.48 × 0.40 × 0.32	0.60 × 0.46 × 0.07	0.30 × 0.40 × 0.44	0.58 × 0.10 × 0.06	0.10 × 0.20 × 0.50
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$	$Pbca$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.078(2)	10.064(1)	6.376(1)	6.369(1)	10.153(2)
b/Å	11.772(3)	16.446(3)	15.657(1)	15.643(1)	11.872(2)
c/Å	13.628(4)	40.816(5)	12.671(2)	12.686(1)	12.910(2)
a/°	—	—	—	—	94.864(9)
β/°	109.12(2)	—	92.422(9)	92.50(1)	102.154(8)
γ/°	—	—	—	—	93.323(9)
V/Å^3	1375.9(6)	6756(2)	1263.7(2)	1262.6(2)	1511.1(4)
Z	2	8	2	2	2
d_{cal}/g cm^{-3}	1.393	1.379	1.337	1.572	1.498
μ/mm^{-1}	0.813	0.677	0.877	5.700	4.773
F(000)	596	2896	528	592	688
T_{min}	0.3360	0.5032	0.2274	0.0322	0.2766
T_{max}	0.3895	0.5230	0.2768	0.0545	0.4086
No. of reflns measured	2704	5827	2399	2382	5584
No. of unique reflns	2538	5827	2192	2174	5261
No. of reflns with $I > 2\sigma(I)$	2469	3044	2009	1607	4784
No. of parameters refined	298	389	125	125	307
Max., in $\Delta\rho$/e Å^{-3}	0.330	1.279	0.621	0.890	1.178
Min., in $\Delta\rho$/e Å^{-3}	−0.406	−1.165	−0.379	−0.682	−1.078
GOF on F^2	1.032	1.012	1.015	1.133	1.036
R	0.0275	0.0669	0.0282	0.0311	0.0295
$wR_2{}^a$	0.0724	0.1344	0.0760	0.0705	0.0719
R (all data)	0.0285	0.1502	0.0308	0.0478	0.0349
$wR_2{}^a$ (all data)	0.0734	0.1717	0.0784	0.0788	0.0745

[a] $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.



L = PMe_3, **5**
L = PEt_3, **6**

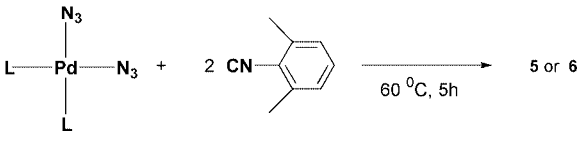
(2)

and 1.274(11) Å (N2–C17 in **2**), suggesting a double bond character. These asymmetric NCN linkages are similar to those found in the early transition metal complexes such as $Cp_2Ti(NCNPh)_2$[1] and $(CO)_5CrNCN(C_2H_5)_2$.[10]

As shown in eqn. (1), the formation of the carbodiimide group using the isocyanide seems to involve initial formation of the C-coordinated bis(tetrazolato) ligand. One of the tetrazolato rings then eliminates a molecule of N_2 to give the product. Another possibility to be considered in the formation of the tetrazolato ring involves the prior dissociation of the azido anion. This is followed by isocyanide coordination to the metal center and then nucleophilic attack by the azide anion.[12,16] The carbodiimido formation from $Pd(N_3)_2(PMePh_2)_2$ with the isocyanide is slower than that from $Pd(N_3)_2(PMe_3)_2$ or $Pd(N_3)_2(PEt_3)_2$, probably because of weaker basicity or steric effects of $PMePh_2$ compared with PMe_3 and PEt_3. Although we could not provide conclusive information on the formation of the carbodiimido complexes, electronic or steric effects of phosphines seem to operate on the formation of carbodiimido complexes. In order to gain insight into the mechanism of the carbodiimide group we have carried out the following reaction, as shown in eqn. (2).

Gently heating a solution of *trans*-$Pd[CN_4(R)](N{=}C{=}N\text{–}R)L_2$ (R = 2,6-$Me_2C_6H_3$, L = PMe_3, PEt_3) at 60 °C for 5 h in THF–CH_2Cl_2 (3 : 1 ratio) caused the formation of the bis(carbodiimido) complexes, *trans*-$Pd[N{=}C{=}N\text{–}R]_2L_2$ (R = 2,6-$Me_2C_6H_3$, L = PMe_3, **5**; PEt_3, **6**). The bis(carbodiimido) complexes **5** and **6** were obtained as yellow crystalline solids and were fully characterized by elemental analysis and IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. IR spectra of the complexes show a characteristic band ($\nu_{N=C=N}$) at 2091 and 2081 cm^{-1}, for **5** and **6**, respectively, which are slightly shifted to a lower frequency than that of the starting materials. Also, the two ^1H NMR signals due to the inequivalent methyl substituents of the starting materials are changed to a singlet with a correct integration ratio. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the complexes are consistent with the proposed symmetrical structure.

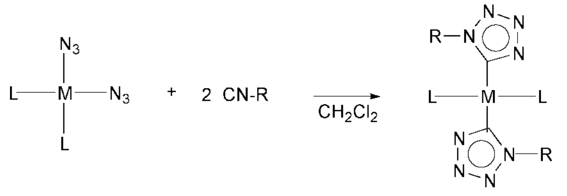
Direct reaction of $Pd(N_3)_2L_2$ (L = PMe_3, PEt_3) with 2,6-dimethylphenyl isocyanide at 60 °C for 5 h caused the formation of the same bis(carbodiimido) complexes *trans*-$Pd[N{=}C{=}N\text{–}R]_2L_2$ (R = 2,6-$Me_2C_6H_3$, L = PMe_3, **5**; PEt_3, **6**) in high yields, as shown in eqn. (3).



(3)

The obtained complexes were identified with IR, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopy. We have also attempted the reaction of $Pd(N_3)_2(dppe)$ with two equivalents of 2,6-dimethylphenyl isocyanide under the same conditions. The reaction gave a bis(carbodiimido) complex, $Pd[N{=}C{=}N\text{–}2,6\text{-}Me_2C_6H_3]_2(dppe)$, **7** in 75% yield as shown in eqn. (4). However, in this instance the reaction can also occur slowly at room temperature.

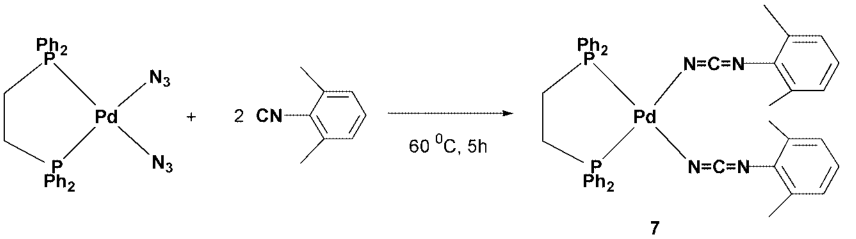
We carried out similar reactions of bis(azido) Pd(II) and Pt(II) complexes with *tert*-butyl and cyclohexyl isocyanides in CH_2Cl_2 as shown in eqn. (5).



(5)

M = Pd L = PMe_3, R = tert-Butyl ; **8**
M = Pt L = PMe_3, R = tert-Butyl ; **9**
M = Pd L = PMe_3, R = Cyclohexyl ; **10**

The reactions (eqn. (5)) did not give the expected carbodiimido complexes but bis(tetrazolato) Pd(II) and Pt(II) complexes with C-coordinated tetrazolato rings through 1,3-dipolar cycloaddition of the isocyanide into the coordinated azido bond in high yields. Earlier work by Beck and coworkers[12] showed that the azido complexes $M(N_3)_2(PPh_3)_2$ (M = Pd, Pt) react with excess amounts of alkyl isocyanide to give complexes $[Ph_3P(R\text{–}NC)M(CN_4R)_2]$ (R = C_6H_{11}, $C_6H_5CH_2$, C_6H_5) in which one phosphine has been replaced by an isocyanide. However, in our case, reactions (eqn. (5)) do not give any isocyanide-adduct complexes. Complexes **8**–**10** are characterized by IR, NMR, and elemental analyses (see Tables 1 and 2). The $^{13}C\{^1H\}$ NMR spectra in the complexes exhibit a triplet or a broad singlet at δ 162.0–166.4 with a coupling with two magnetically equivalent phosphorus atoms, indicating C-coordination of the tetrazolato ring to the metal center. The $^{31}P\{^1H\}$ spectra of the complexes also support the proposed *trans* structure. Interestingly, the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra of **10** apparently show the presence of *syn* and *anti*-isomers according to the orientation of substitutents on the tetrazolato ring. The $^{13}C\{^1H\}$ NMR spectrum of **10** exhibits eight signals due to the cyclohexyl group substituted on the tetrazolato ring as *anti* and *syn* species and also shows two triplets due to the corresponding PMe_3 with virtual coupling. The $^{31}P\{^1H\}$ spectrum also shows two singlets due to *anti* and *syn* species. The relative abundance ratio of the isomers (*anti*/*syn*), illustrated by the $^{31}P\{^1H\}$ spectrum, is 1 : 0.79. In contrast, no other isomers of complexes **8** and **9** are observed because rotation of the Pd–C (or Pt–C) bond in the C-coordinated tetrazolato ring for *syn*



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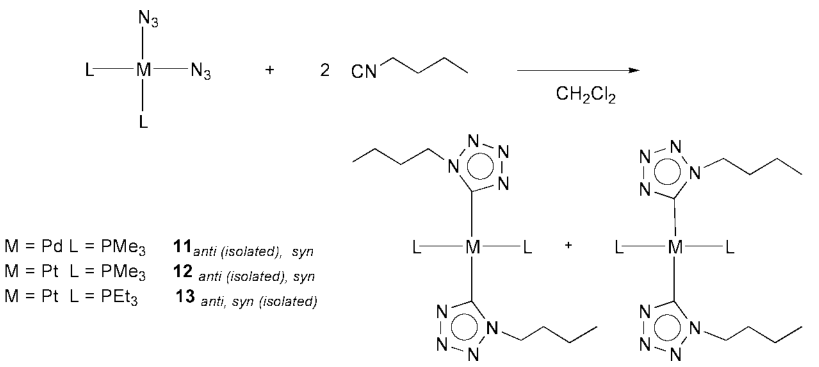
(4)



(6)

and *anti* isomer formation might be influenced by the steric hindrance of the substituents on the tetrazolato ring.

It is well known that the cycloaddition of organic nitriles to coordinated azides produces N-coordinated tetrazolato compounds containing several linkage isomers formed by the N(1) or N(2)-coordination to one of the nitrogen atoms on the tetrazolato ring.[17–27] In contrast, similar studies on the cycloaddition of organic isocyanides with coordinated azides to form the C-coordinated tetrazolato compounds are rarer than those of N-tetrazolato compounds, because there is no such linkage isomer in the metal–carbon bond formation.[28,29] Moreover, there is only one example concerning a C-coordinated tetrazolato compound, $[Au(CN_4R)_4]^-$ ($R = i\text{-}C_3H_7$)[30] which is structurally characterized and suggests an *anti* and *syn* conformation of the substituent attached to the tetrazolato ring in the molecule. In order to obtain more detailed information about the conformation of the C-coordinated tetrazolato compounds in the solution and solid state we chose the following cycloaddition using *n*-butyl isocyanide as shown in eqn. (6).

These reactions occur rapidly to give bis(tetrazolato) Pd(II) and Pt(II) complexes, **11**–**13** as white solids in high yields. The $^{13}C\{^1H\}$ NMR spectra of the complexes show a triplet (J = 8–14 Hz) at δ 162.5–166.4 due to the carbon of the C-coordinated tetrazolato ring. Four pairs of singlets and two triplets with very close chemical shifts, which are assigned to the corresponding *n*-butyl carbons and PMe_3 as *anti* and *syn* isomers, are also observed. Also, each of the two singlets in the $^{31}P\{^1H\}$ NMR spectra of the complexes indicates a mixture of the *syn* and *anti* conformers with the *trans* structure. All spectroscopic data support the presence of the *syn* and *anti* conformers in solution at room temperature. The relative ratios of the isomers (*anti*/*syn*) in the complexes **11**–**13** are 1.0/0.72, 1.0/0.64 and 1.0/0.27, respectively, which are measured by integration of the peaks in the $^{31}P\{^1H\}$ NMR spectra. The higher abundance of the *anti* isomer rather than the *syn* isomer may be explained by a sterically favorable geometry which minimizes steric repulsion between the two phosphine ligands and two *n*-butyl groups attached to the tetrazolato ring in the solution.

The molecular structures of **11**–**13** have been determined by X-ray crystallography. The ORTEP drawings of these complexes with the atom-numbering scheme are shown in Figs. 3–5, respectively. Selected bond lengths and angles are listed in Table 5. Compounds **11** and **12** are isostructural. The molecular structures of **11** and **12** clearly indicate that the two tetrazolato rings are mutually *trans* and oriented perpendicular to the coordination plane containing the two PMe_3 groups and the two carbons (C4 and C4A). The central metal lies on the crystallographic inversion point, by which the *n*-butyl substituents attached to the tetrazolato rings are oriented in the opposite direction (*anti* orientation). In contrast, the *n*-butyl groups attached to the tetrazolato ring in **13** indicate a *syn* orientation in spite of the expected steric repulsion between the *n*-butyl substituents and the two PEt_3 groups. Thus, the P1–Pt–P2 (167.88(5)°) fragment of **13** is severely bent compared with the linear fragments of P1–Pd–P1A (180.0(0)°) in **11** and P1–Pt–P1A (180.0(8)°) in **12**. The C-coordinated tetrazolato ring of complexes **11**–**13** is nearly planar. Bond distances (C–N and N–N) in the tetrazolato rings lie in the range 1.280–1.389 Å, indicating a slight π-electron localization in the tetrazolato ring. This deviation is relatively larger than that in similar N-coordinated counterparts such as *trans*-$(Ph_3P)_2Pd(N_4C\text{-}C_6H_5)_2$ (1.300–1.347 Å)[18] and *cis*-$(PhMe_2P)_2Pd(N_4C\text{-}CH_3)_2$ (1.296–1.366 Å and 1.327–1.351 Å).[31] In this work, we have

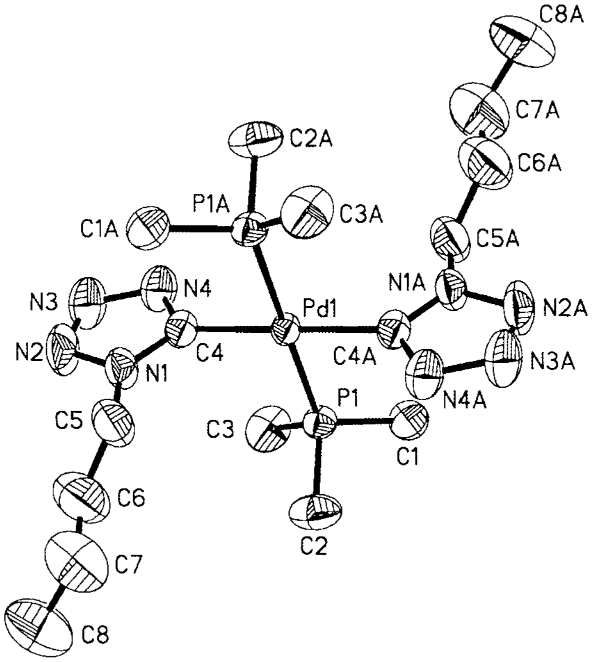


Fig. 3 ORTEP drawing of **11** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Symmetry-equivalent atoms (denoted by an A) are generated by the crystallographic inversion center located at the Pd1 atom.

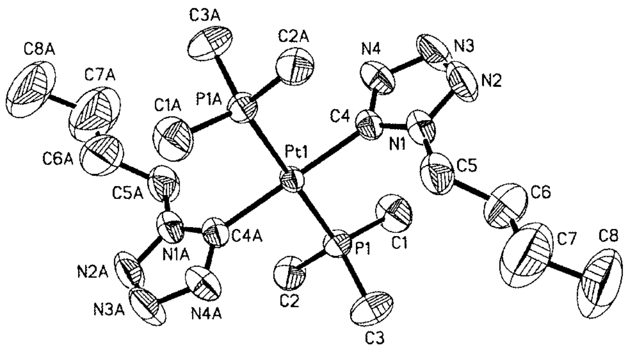


Fig. 4 ORTEP drawing of **12** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Symmetry-equivalent atoms (denoted by an A) are generated by the crystallographic inversion center.

Table 5 Selected bond distances (Å) and bond angles (°) in **11**–**13**

11		**12**		**13**			
Pd1–C4	2.034(3)	Pt1–C4	2.033(6)	Pt–C18	2.033(5)	Pt–C13	2.056(5)
Pd1–P1	2.3072(6)	Pt1–P1	2.304(2)	Pt–P2	2.303(1)	Pt–P1	2.307(1)
N1–C4	1.350(4)	N1–C4	1.340(8)	N1–N2	1.345(8)	N1–C13	1.356(7)
N1–N2	1.352(3)	N1–N2	1.341(8)	N2–N3	1.275(9)	N3–N4	1.379(8)
N2–N3	1.280(4)	N2–N3	1.294(9)	N4–C13	1.327(7)	N5–C18	1.338(7)
N3–N4	1.365(4)	N3–N4	1.389(8)	N5–N6	1.362(7)	N6–N7	1.280(8)
N4–C4	1.331(4)	N4–C4	1.338(8)	N7–N8	1.360(7)	N8–C18	1.334(7)
C4–Pd1–P1	91.84(8)	C4–Pt1–P1	91.7(2)	C18–Pt–C13	178.82(16)	C18–N5–N6	107.4(5)
C4–N1–N2	109.6(3)	C4–N1–N2	111.0(6)	C18–Pt–P2	90.82(12)	N7–N6–N5	110.8(5)
N3–N2–N1	106.2(2)	N3–N2–N1	106.2(6)	C18–Pt–P1	91.84(12)	N6–N7–N8	105.6(5)
N2–N3–N4	111.0(3)	N2–N3–N4	110.1(6)	P2–Pt–P1	167.88(5)	C18–N8–N7	110.7(5)
C4–N4–N3	106.8(3)	C4–N4–N3	106.2(6)	N2–N1–C13	109.7(6)	N4–C13–N1	106.6(5)
N4–C4–N1	106.4(2)	N4–C4–N1	106.5(6)	N3–N2–N1	106.5(5)	N8–C18–N5	105.6(4)
N4–C4–Pd1	126.3(2)	N4–C4–Pt1	125.3(5)	N2–N3–N4	111.0(5)		
N1–C4–Pd1	127.2(2)	N1–C4–Pt1	128.2(5)	C13–N4–N3	106.2(5)		

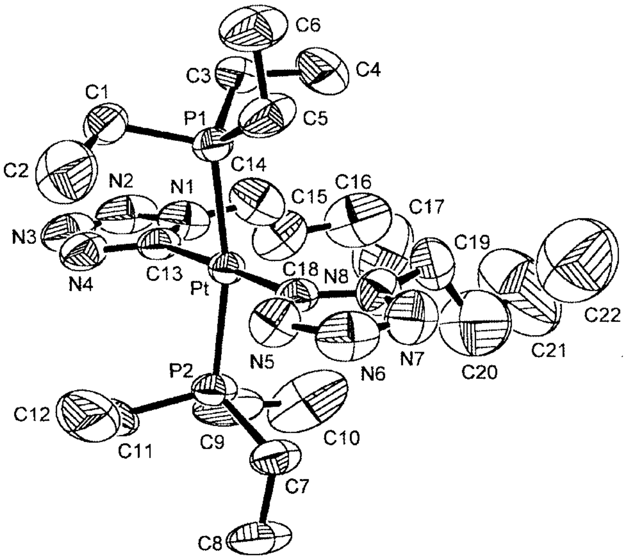


Fig. 5 ORTEP drawing of **13** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

confirmed the existence of the stereoisomers of bis(tetrazolato) complexes. To the best of our knowledge, this is the first example of the isolation of *syn–anti* conformers of the tetrazolato–transition metal complexes in the solid state.

In this work, we have shown that bis(azido)palladium(II) complexes react with 2,6-dimethylphenyl isocyanide to give unique palladium(II) complexes, *trans*-Pd[CN$_4$(R)](N=C=N–R)-L$_2$ (R = 2,6-Me$_2$C$_6$H$_3$, L = tertiary phosphine) containing a carbodiimido and a tetrazolato ligand. We have also found that heating the palladium(II) complexes at 60 °C results in formation of the bis(carbodiimido)palladium(II) complexes, *trans*-Pd[N=C=N–R]$_2$L$_2$ (R = 2,6-Me$_2$C$_6$H$_3$, L = tertiary phosphine). Thus, we have demonstrated that the direct reaction of bis(azido)palladium(II) complexes with 2,6-dimethylphenyl isocyanide results in the formation of bis(carbodiimido)palladium(II) complexes with phosphine ligands. These results provide an efficient preparation for the bis(carbodiimido)palladium(II) complex. Although several transition metal compounds of π-coordinated (η^2) carbodiimide are known, those mono or bis(carbodiimido) compounds of group 10 metals with a linear N=C=N moiety have not been reported. Among the amido-type ligands, the carbodiimido ligands are sterically less hindered around the metal center and thus may have a potent possibility for the polymerization of carbodiimido ligands. The functionality of the complexes having a mono or bis(carbodiimido) group seems to be of interest as reaction intermediate in synthetic organic reactions catalyzed by group 10 metals.

Experimental

General, materials and measurements

All manipulations of air-sensitive compounds were performed under an N$_2$ or argon atmosphere using standard Schlenk techniques. Solvents were distilled from Na-benzophenone. The analytical laboratories at the Basic Science Institute of Korea and at Kangnung National University carried out elemental analyses. IR spectra were recorded on Hitachi 270-30 and Perkin-Elmer BX spectrophotometers. NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectra were obtained on Bruker-300 and -500 MHz and on JEOL Lamda 300 MHz spectrometers. Chemical shifts were referenced to an internal Me$_4$Si standard and to an external 85% H$_3$PO$_4$ standard. Pd(N$_3$)$_2$L$_2$ (L = PMe$_3$, PEt$_3$, PMePh$_2$, PMe$_2$Ph, dppe) and Pt(N$_3$)$_2$L$_2$ (L = PMe$_3$, PEt$_3$) were prepared from ligand exchange reactions of Pd(N$_3$)$_2$(tmeda)[32] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and Pt(N$_3$)$_2$-(COD)[32] (COD = 1,5-cyclooctadiene) with corresponding tertiary or chelated phosphine ligands, respectively.

Preparations

Complexes 1–4. To a Schlenk flask containing Pd(N$_3$)$_2$-(PMe$_3$)$_2$ (0.138 g, 0.40 mmol) were added CH$_2$Cl$_2$ (5 cm^3) and 2,6-dimethylphenyl isocyanide (0.106 g, 0.81 mmol) in that order. The initial yellow solution immediately turned to pale yellow with evolution of nitrogen. After stirring for 3 h at room temperature, the reaction mixture was fully evaporated under vacuum and then the resulting solid was washed with hexane. Recrystallization from CH$_2$Cl$_2$–hexane gave pale yellow crystals of *trans*-Pd[CN$_4$(R)](N=C=N–R)(PMe$_3$)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$), **1** (0.183 g).

Complexes **2**, **3**, and **4** were analogously prepared.

Complexes 5 and 6. Complex **1** (0.101 g, 0.18 mmol) was dissolved in a 3 : 2 mixture of THF–CH$_2$Cl$_2$ (5 cm^3). The mixture was heated at 60 °C for 5 h. The initial yellow solution slowly turned to orange. After stirring, the solvent was removed completely, and the resulting residue was solidified with ether and hexane as a yellow powder. Recrystallization from CH$_2$Cl$_2$–hexane gave yellow crystals of *trans*-Pd[N=C=N–R]$_2$(PMe$_3$)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$), **5** (0.085 g).

Complex **6** was analogously prepared from complex **3**.

Complexes **5**–**7** were prepared independently from the reactions of bis(azido) complexes Pd(N$_3$)$_2$(PMe$_3$)$_2$, Pd(N$_3$)$_2$(PEt$_3$)$_2$ and Pd(N$_3$)$_2$(dppe), respectively, with 2,6-dimethylphenyl isocyanide under the conditions described above.

Complexes 8–10. To a Schlenk flask containing Pd(N$_3$)$_2$-(PMe$_3$)$_2$ (0.343 g, 1.00 mmol) were added CH$_2$Cl$_2$ (15 cm^3) and *tert*-butyl isocyanide (0.238 cm^3, 2.10 mmol) in that order. The initial yellow solution immediately turned colorless. After stirring for 1 h at room temperature, the reaction mixture was fully evaporated under vacuum and then the resulting solid was washed with hexane (10 cm^3). Recrystallization from CH_2Cl_2–hexane gave white crystals of *trans*-Pd[CN_4(*tert*-butyl)]$_2$(PMe_3)$_2$, **8** (0.401 g).

Complexes **9** and **10** were analogously prepared.

Complexes 11–13. To a Schlenk flask containing $Pd(N_3)_2$-(PMe_3)$_2$ (0.364 g, 1.06 mmol) were added CH_2Cl_2 (30 cm^3) and *n*-butyl isocyanide (0.234 cm^3, 2.23 mmol) in that order. The initial yellow solution immediately turned colorless. After stirring for 1 h at room temperature, the reaction mixture was fully evaporated under vacuum and then the resulting solid was washed with hexane (3 × 3 cm^3). Recrystallization from CH_2Cl_2–hexane gave white crystals of *trans*-Pd[CN_4(*n*-butyl)]$_2$-(PMe_3)$_2$, **11** (0.459 g).

Complexes **12** and **13** were analogously prepared.

X-Ray structure determination

All X-ray data were collected using a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 25–36 reflections in the range $10.0° < 2\theta < 25.0°$. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with Ψ-scan data. All calculations were carried out using the SHELX-97 programs.[33] The structures were solved by direct methods and refined by full-matrix least-squares calculations of F^2 values, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located in the difference Fourier maps and refined isotropically. The crystal data and details of the structure refinement of **1**, **2**, **11**, **12**, and **13** are summarized in Table 4.

CCDC reference numbers 167462–167466.

See http://www.rsc.org/suppdata/dt/b1/b103916b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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