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Synthesis, structures and properties of bis(carbodiimido) complexes of Ni(II), Pd(II) and Pt(II)

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Bis(azido)–Group 10 metal complexes ($M(N_3)_2L_2$) reacted with two equivalents of isocyanides (CNR) to give the corresponding bis(carbodiimido) complexes, $M(N{=}C{=}N{-}R)_2L_2$ {[$Pd(N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)_2L_2$]: L = PMe_3 (**1**), PEt_3 (**2**), PMe_2Ph (**3**); [$Pd(N{=}C{=}N{-}2,6\text{-}Et_2C_6H_3)_2L_2$]: L = PMe_3 (**4**); [$Ni(N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)_2L_2$]: L = PMe_3 (**5**), PEt_3 (**6**); [$Pt(N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)_2L_2$]: L = PMe_3 (**7**), PEt_3 (**8**)} in relatively high yields. Reaction schemes have been proposed on the basis of isolated intermediates such as $Ni[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$ (R = $2,6\text{-}Me_2C_6H_3$) (**9**), *trans*-$Pt[CN_4(R)]_2(PMe_3)_2$ (**10**), and $Pt[CN_4(R)](N{=}C{=}N{-}R)L_2$ (L = PMe_3 (**11**) or PEt_3, (**12**)). Molecular structures of **1**, **2**, **4**, **6**, **8**, and **11** have been determined by X-ray diffraction, demonstrating that the nitrogen of the carbodiimido (N=C=N) group is directly bonded to the metal center. The chelating phosphine analogues $M(N_3)_2$(L–L) {M = Pd or Ni; L–L = depe (1,2-bis(diethylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), or dppe (1,2-bis(diphenylphosphino)ethane)} reacted with isocyanides to also give the corresponding bis(carbodiimido) complexes, $M(N{=}C{=}N{-}R)_2$(L–L) {M = Pd: L–L = depe (**13**), dppp (**14**); M = Ni, L–L = dppe (**15**)} in high yields. Treating $Pd(N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)_2(PMe_3)_2$ (**1**) with two equivalents of benzoyl chloride (PhCOCl), phenyl chloroformate (PhOCOCl), and 2-thiophenecarbonyl chloride (C_4H_3SCOCl) gave organic cyanamides, $PhCON(CN)\text{-}2,6\text{-}Me_2C_6H_3$, $PhO(CO)N(CN)\text{-}2,6\text{-}Me_2C_6H_3$, and $C_4H_3SCON(CN)\text{-}2,6\text{-}Me_2C_6H_3$, respectively.

Introduction

Transition-metal complexes containing a carbodiimido (or bis(carbodiimido)) ligand, in which the nitrogen of a linear N=C=N fragment is directly bonded to the metal, have received a great deal of attention due to their potential applications as catalysts for polymerization, precursors for metal nitrides and metal carbonitrides, or intermediates for organic cyanamides.[1,2]

Early transition-metal or main-group complexes of the η^1-carbodiimido ligand are generally prepared by the transmetallation of metal halides with trialkylstannyl (or trialkylsilyl)carbodiimides.[1,3] Earlier work by Beck and co-workers revealed the existence of carbodiimido species based on spectral data of the thermolysis of $AsPh_4[Au(CN_4CH_2C_6H_5)_4]$.[4] Lewis and co-workers reported a unique method of preparing an end-on carbodiimido complex [$Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)$] from [$Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)$] and $PhNPPh_3$.[5] Fisher's group also prepared an η^1-carbodiimido complex by treating an isocyanide complex [$(CO)_5Cr(CNEt_2)$][BF_4] with [$N(C_4H_9)_4$]N_3.[6] Crutchley and co-workers reported several complexes of late transition metals such as Ni, Pd, Ru, and Cu containing a carbodiimido or bis(carbodiimido) ligand, which were prepared by metathesis reactions using thallium cyanamide derivatives.[7] Also, Robson and co-workers reported carbodiimido-bridged complexes of Ni(II) and Cu(II) from anionic cyanamide derivatives.[8] In addition, Fehlhammer and co-workers observed the existence of the carbodiimido group on the thermal treatment of [$RhCp^*(\mu\text{-}N_3)(N_3)$]$_2$ with ^{t}BuNC.[9] Although many studies of late transition-metal carbodiimides have been reported, chemical properties of Group 10 metal–carbodiimido complexes remain relatively unexplored. These complexes might be useful as potential intermediates or precursors in transition metal-catalyzed organic reactions.

We have very recently reported the reactions of mono- or bis(azido) Pd(II) complexes with organic isocyanides to give novel Pd(II) complexes, which contain either a carbodiimido ligand (mono or bis) with an end-on N=C=N fragment or a C-bonded, 5-membered tetrazolato ligand, depending upon the reaction conditions.[10] These results prompted us to extend our synthetic scope to other Group 10 metal–carbodiimido complexes. Here we report a series of new bis(carbodiimido) Ni(II), Pd(II), and Pt(II) complexes, prepared by treating the corresponding bis(azido) complexes with isocyanides, along with their reactivity and structures.

Results and discussion

Preparations

Our recent paper revealed that the reactions of bis(azido)–Pd(II) complexes of the type $Pd(N_3)_2L_2$ (L = PMe_3 or PEt_3) with 2,6-dimethylphenyl isocyanide (CNR: R = $2,6\text{-}Me_2C_6H_3$) gave $Pd[CN_4(R)](N{=}C{=}N{-}R)L_2$ containing both an end-on carbodiimido and a C-bonded tetrazolato ring, and these complexes transformed into the bis(carbodiimido)–Pd(II) complexes, $Pd(N{=}C{=}N{-}R)_2L_2$ (L = PMe_3, (**1**); PEt_3(**2**)) by thermal activation.[10] On the basis of these results, we decided to employ the same synthetic strategy to prepare a complete set of bis(carbodiimido) complexes of a Group 10 triad of the type $M(N{=}C{=}N{-}R)_2L_2$, using bis(azido)–metal–phosphine complexes and isocyanides (eqn. (1)).

Bis(carbodiimido)–Group 10 metal complexes **3**–**8** were isolated in 45–83% yield and have been characterized by spectroscopy and elemental analysis (see Tables 1 and 2). The bis(carbodiimido) complex formation can be readily monitored by IR spectroscopy, which shows the disappearance of an asymmetric stretching band $\nu(N_3)$ at about 2030 cm^{-1} present in the starting compound and the appearance of a new strong band in the range of 2098–2179 cm^{-1} due to the carbodiimido group (N=C=N) of the product. ^{1}H and ^{13}C NMR spectra

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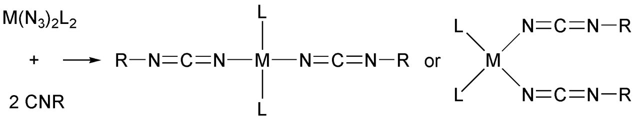
Table 1 Color, yield and analytical data for **3**–**15**

Complex[a]	Color	Yield (%)	Analyses[b] C (%)	H (%)	N (%)
3, $Pd(N{=}C{=}N{-}R)_2(PMe_2Ph)_2$	Yellow	78	60.28 (60.67)	6.06 (5.99)	8.20 (8.32)
4, $Pd(N{=}C{=}N{-}R)_2(PMe_3)_2$ (R = $2,6\text{-}Et_2C_6H_3$)	Yellow	58	55.23 (55.58)	7.41 (7.33)	9.14 (9.26)
5, $Ni(N{=}C{=}N{-}R)_2(PMe_3)_2$	Red	83	57.23 (57.51)	7.40 (7.24)	11.29 (11.28)
6, $Ni(N{=}C{=}N{-}R)_2(PEt_3)_2$	Red	80	61.48 (61.55)	8.43 (8.27)	9.77 (9.57)
7, $Pt(N{=}C{=}N{-}R)_2(PMe_3)_2$	White	53	45.27 (45.21)	5.77 (5.69)	8.81 (8.79)
8, $Pt(N{=}C{=}N{-}R)_2(PEt_3)_2$	White	45	50.31 (49.92)	6.84 (6.70)	7.68 (7.76)
9 $Ni[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$	Brown	43	54.36 (54.47)	6.71 (6.86)	15.67 (15.88)
10, $Pt[CN_4(R)]_2(PMe_3)_2$	White	76	41.29 (41.56)	5.31 (5.23)	15.65 (16.15)
11, $Pt[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$	White	54	42.68 (43.31)	5.42 (5.45)	12.31 (12.63)
12, $Pt[CN_4(R)](N{=}C{=}N{-}R)(PEt_3)_2$	White	92	47.58 (48.06)	6.56 (6.45)	11.40 (11.21)
13, $Pd(N{=}C{=}N{-}R)_2(depe)_2$	Yellow	78	55.45 (55.77)	7.07 (7.02)	9.09 (9.29)
14, $Pd(N{=}C{=}N{-}R)_2(dppp)_2$	Yellow	93	66.98 (66.79)	5.40 (5.48)	6.95 (6.92)
15, $Ni(N{=}C{=}N{-}R)_2(dppe)_2$	Orange	92	70.50 (70.70)	5.74 (5.66)	7.41 (7.50)

[a] R is $2,6\text{-}Me_2C_6H_3$, unless otherwise stated. [b] Calculated values are given in parentheses.

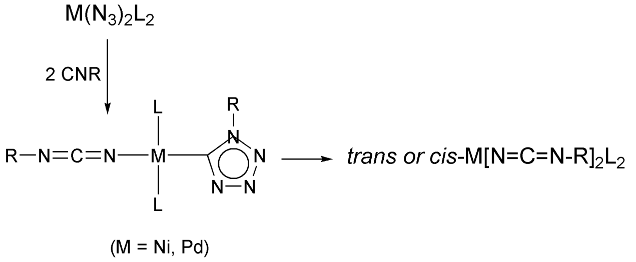


(1)

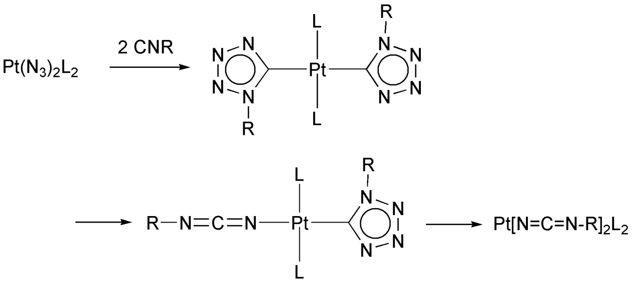
M = Pd: R = $2,6\text{-}Me_2C_6H_3$, L = PMe_3, **1**
R = $2,6\text{-}Me_2C_6H_3$, L = PEt_3, **2**
R = $2,6\text{-}Me_2C_6H_3$, L = PMe_2Ph, **3**
R = $2,6\text{-}Et_2C_6H_3$, L = PMe_3, **4**
M = Ni R = $2,6\text{-}Me_2C_6H_3$, L = PMe_3, **5**
R = $2,6\text{-}Me_2C_6H_3$, L = PEt_3, **6**
M = Pt, R = $2,6\text{-}Me_2C_6H_3$, L = PMe_3, **7**
R = $2,6\text{-}Me_2C_6H_3$, L = PEt_3, **8**

display a singlet due to the symmetric methyl groups of the 2,6-dimethylphenyl or 2,6-diethylphenyl group attached to the carbodiimido (N=C=N) group, suggesting a symmetric *trans* or *cis* structure of the carbodiimido complexes. ^{31}P NMR spectra of the complexes also support the proposed structures. The coordination geometry of these complexes, *trans* or *cis*, appears to be associated with the auxiliary ligands. For instance, PMe_3–bis(carbodiimido) complexes are observed to have a *cis* form both in solution and in the solid state. In contrast, the PEt_3 analogues appear to have only a *trans* form. Interestingly, complex **4** is observed as a mixture of *trans* and *cis* isomers of $Pd(N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)_2(PMe_2Ph)_2$ by spectroscopic analysis. Although we cannot give a clear-cut explanation for the existence of these isomers, the steric properties of PMe_2Ph compared with PMe_3 or PEt_3 might be operational in the formation of the isomers.

As shown in eqn. (1), the bis(azido)–Pd(II)- and Ni(II)-complexes at 60 °C for 5 h undergo reactions to give the bis(carbodiimido) species, with no other possible products such as mono(tetrazolato) or bis(tetrazolato) complexes arising from the C-coordinated tetrazolato formation by the 1,3-dipolar cycloaddition of the isocyanide to the azido ligand. These reactions seem to involve the initial formation of the C-coordinated bis(tetrazolato) complex, $M[CN_4(R)]_2L_2$. One of the tetrazolato rings then transforms to an end-on NCN–R fragment with the elimination of N_2 to give the intermediate $M[CN_4(R)](N{=}C{=}N{-}R)L_2$, which contains a tetrazolato ring and a carbodiimido ligand. Finally, the subsequent N_2 elimination occurs on a second tetrazolato ring to give the bis(carbodiimido) complex (Scheme 1). In a previous paper,[10] we have shown the formation of the intermediates $Pd[CN_4(R)](N{=}C{=}N{-}R)L_2$ (R = $2,6\text{-}Me_2C_6H_3$; L = PMe_3 or PEt_3) and their conversion to the bis(carbodiimido) complexes. In this work, we have also isolated the nickel intermediate, $Ni[CN_4(R)](N{=}C{=}N{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$ (**9**) and its conversion at 60 °C to the bis(carbodiimido) complex, $Ni(N{=}C{=}N{-}R)_2(PMe_3)_2$ (**5**) in 96% yield. These results support the proposed reaction scheme that proceeds *via* the intermediate $M[CN_4(R)](N{=}C{=}N{-}R)L_2$. Interestingly, those reactions below 50 °C give a mixture of the two species, $M[CN_4(R)](N{=}C{=}N{-}R)L_2$ and $M(N{=}C{=}N{-}R)_2L_2$. Therefore, we conclude that the reaction at 60 °C is suitable for the preparation of bis(carbodiimido) complexes.



Scheme 1



Scheme 2

Reactions of bis(azido)–platinum(II) complexes with 2,6-dimethylphenyl isocyanide proceed *via* a similar reaction scheme as shown in Scheme 2. However, the reaction scheme shows that platinum tetrazolato intermediates appear to be thermally more stable than the nickel and palladium ones, which has been proposed on the basis of the isolated compounds **7**, **8**, and **10**–**12**. Reaction of $Pt(N_3)_2(PMe_3)_2$ with 2 equiv. 2,6-dimethylphenyl isocyanide at room temperature gives a bis(tetrazolato) complex, *trans*-$Pt[CN_4(2,6\text{-}Me_2C_6H_3)]_2(PMe_3)_2$ (**10**), and the subsequent thermal activation at 60 °C for 5 h transforms it into $Pt[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$ (**11**), which contains both a tetrazolato ring and a carbodiimido ligand. Direct reactions of $Pt(N_3)_2L_2$ (L = PMe_3 or PEt_3) with 2,6-dimethylphenyl isocyanide at 60 °C for 5 h also produce the same complexes, $Pt[CN_4(R)](N{=}C{=}N{-}R)L_2$ {(L = PMe_3(**11**), PEt_3(**12**)) in high yields. A further thermal treatment (stirring) at 80 °C for 24 h leads to the conversion of $Pt[CN_4(R)](N{=}C{=}N{-}R)L_2$ into the ultimate bis(carbodiimido) complexes, *trans*- or *cis*-$Pt(N{=}C{=}N{-}R)_2L_2$ (compounds **7** and **8**). Direct reactions of $Pt(N_3)_2L_2$ (L = PMe_3 or PEt_3) with 2,6-dimethylphenyl

Table 2 NMR and IR data (δ, *J*/Hz)

Complex	^1H NMR[a]		$^{13}C\{^1H\}$[b]	$^{31}P\{^1H\}$[c]	$\nu(NCN)$[d]/cm^{-1}
	PR_3 (R = Me or Et)	others			
3 *trans*	1.70 (t, 12H, *J* = 4)	2.15 (s, 12H, CH_3)	11.7 (t, *J* = 16, CH_3) 19.0, 120.7, 127.7, 128.8 (t, *J* = 5) 130.5, 130.6,131.1 131.5, 132.3, 142.6,	−3.9	2179
cis	1.59 (br, 12H)	2.32 (s, 12H, CH_3) 6.65–6.74 (m, 2H) 6.84–6.88 (m, 4H) 7.23–7.41 (m, 8H) 7.57–7.64 (m, 2H)	14.2 (t, *J* = 36),19.4 120.1, 127.6, 129.0 130.5, 130.7, 131.1, 131.9, 132.6, 143.1	4.1	
4	1.42 (t, 18 H, *J* = 4)	1.23 (t, 12H, *J* = 8, CH_3) 2.75 (q, 8H, CH_2) 6.82–6.87 (m, 2H) 6.95–6.97 (m, 4H)	12.6 (t, *J* = 8), 14.7, 25.5, 121.4, 126.0, 129.3, 129.4 131.2 (br, NCN) 137.2, 141.2	10.4	2100
5	1.29 (brs, 18H)	2.29 (s, 12H, CH_3) 6.70–6.75 (m, 2H) 6.90–6.93 (m, 4H)	12.2, 19.1, 120.6, 127.7, 130.8, 132.8 (br, NCN) 143.1	−15.6	2148
6	1.29 (brs, 18H) 1.56 (brs, 12H)	2.25 (s, 12H, CH_3) 6.69 (m, 2H) 6.88–6.90 (m, 4H)	8.0, 13.7 (t, *J* = 12), 19.0,120.5, 127.6, 130.9, 133.2 (br, NCN) 143.4(t, *J* = 2)	13.2	2105
7	1.67 (dd, 18H, *J* = 5)	2.29 (s, 12H, CH_3) 6.65–6.70 (m, 2H) 6.83–6.86 (m, 4H)	15.7, 16.3 (J_{Pt-C} = 45), 19.3, 120.4, 127.6, 130.0 (br, NCN) 142.5	−29.3 (J_{Pt-P} = 3288)	2132
8	1.17 (q, 18H, *J* = 8) 1.85 (m, 12H, *J* = 4)	2.31 (s, 12H, CH_3) 6.69–6.74 (m, 2H) 6.91–6.93 (m, 4H)	7.66, 13.9 (t, *J* = 16), 19.0, 120.4, 127.7, 131.0, 143.1	16.0 J_{Pt-P} = 2397	2098
9	1.07 (brs, 18H)	2.28 (s, 12H, CH_3) 2.48 (s, 12H, CH_3) 6.67–6.72 (m, 1H) 6.89–6.92 (m, 2H) 7.26–7.31 (m, 3H)	13.0, 19.2, 20.7 120.3, 127.8, 129.1, 129.6, 130.8, 130.9 (s, NCN), 134.5, 135.6, 143.3, 165.5 (s, CN_4)	−10.3	
10	1.05 (t, 18H, J_{Pt-H} = 30) 7.22–7.27 (m, 4H)	2.10 (s, 12H, CH_3) 7.08–7.11 (m, 2H) 129.1, 135.1, 135.8,	15.0 (t, *J* = 19), 20.3,129.0, 162.0 (t, CN_4, *J* = 12)	−19.2 J_{Pt-P} = 2454	
11	1.25 (t, 18H, *J* = 4 J_{Pt-H} = 28)	2.27 (s, 6H, CH_3) 2.32 (s, 6H, CH3) 6.69–6.74 (m, 1H) 6.91–6.94 (m, 2H) 7.19–7.32 (m, 3H)	13.6 (t, *J* = 19), 19.3, 20.6, 120.4, 127.8, 129.3, 129.6 (s, NCN), 131.0, 135.2, 135.5, 143.0, 145.2, 164.9 (s, CN_4)	14.5 J_{Pt-P} = 2440	2147
12	1.00 (q, 18H, *J* = 8) 1.44–1.68 (br, 12H)	2.31 (s, 12H, CH_3) 6.67–6.72 (m, 1H) 6.90–6.93 (m, 2H) 7.17–7.30 (m, 3H)	7.8 (s, J_{Pt-C} = 21), 14.8 (t, *J* = 17), 19.1, 20.8, 120.1, 127.7, 129.1, 129.3, 131.0, 135.4, 135.7, 143.4, 144.3, 165.7 (br, CN_4)	14.1 (J_{Pt-P} = 2460)	2134
13	1.19, 1.28 (dt, 12H, *J* = 8)	1.75–1.91 (m, 8H, $-CH_2$) 2.01–2.17 (m, 4H, $-CH_2$) 2.32 (s, 12H, $-CH_3$) 6.61–6.72 (m, 2H) 6.81–6.87 (m, 4H)	8.91 (d, *J* = 2), 18.9 (d, *J* = 30), 19.4, 23.8 (dd, *J* = 12, 32), 119.9, 127.8, 130.6 (s, NCN) 143.7	80.9	2109
14[e]	1.67 (m, 2H) 2.69 (m, 4H)	1.88 (m, 12H, CH_3) 6.46–6.51 (m, 2H) 6.66–6.69 (m, 4H) 7.36–7.49 (m, 12H) 7.74–7.80 (m, 8H)	18.8, 23.0, 25.0 118.8, 127.2, 128.0, 128.5 (t, *J* = 6), 128.8 130.0, 131.2, 133.0 (t, *J* = 6), 143.4	12.0	2100
15	2.16 (m, 4H)	2.01 (s, 12H, CH_3) 6.56–6.61 (m, 2H) 6.73–6.75 (m, 4H) 7.43–7.57 (m, 12H) 7.86–7.93 (m, 8H)	19.2, 27.0 (t, *J* = 24) 119.6, 126.6, 127.3, 127.5, 129.2, 129.3, 129.5, 129.5(s, NCN), 131.6, 132.3,133.1, 133.3, 133.6 (d, *J* = 11), 143.6	57.9	2131

[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; brs, broad singlet; q, quartet; m, multiplet. [d] KBr. [e] Spectral data for **13** were obtained in DMSO at 25 °C.

isocyanide at 80 °C for 24 h also produce the same bis(carbodiimido) complexes. In contrast, the analogous reactions with alkyl isocyanides (*tert*-butyl and cyclohexyl isocyanides) do not produce any desired mono(carbodiimido) or bis(carbodiimido) complexes and give only bis(tetrazolato)–platinum(II) complexes.[10] These results suggest that the steric bulk of 2,6-dimethylphenyl on the tetrazolato ring might exert an influence facilitating N_2 elimination from the tetrazolato ring forcing the formation of the carbodiimido group.

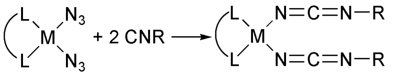
We have also prepared bis(carbodiimido) complexes possessing chelating phosphine ligands (eqn. (2)). Treating bis(azido)–nickel(II) and –palladium(II) complexes, which contain chelating phosphine ligands {depe (1,2-bis(diethylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), or dppe

Table 3 A comparison of bonding parameters for the terminal η^1-carbodiimido fragment

Complex	M–N/Å	M–N_α=C=N_β			Ref.
		N_α=C/Å	C=N_β/Å	N=C=N/°	
Pd(N=C=N–R)$_2$(PMe$_3$)$_2$, **1**	2.080(6)	1.162(9)	1.265(10)	174.8(9)	This work
	2.089(6)	1.144(9)	1.272(9)	172.2(8)	
Pd(N=C=N–R)$_2$(PEt$_3$)$_2$, **2**	2.021(4)	1.191(6)	1.261(7)	170.4(6)	This work
Pd(N=C=N–2,6-Et$_2$C$_6$H$_3$)$_2$(PMe$_3$)$_2$, **4**	2.087(5)	1.165(8)	1.270(9)	173.2(7)	This work
	2.089(5)	1.172(8)	1.258(8)	168.7(7)	
Ni(N=C=N–R)$_2$(PEt$_3$)$_2$, **6**	1.841(4)	1.177(5)	1.266(5)	171.1(5)	This work
Pt(N=C=N–R)$_2$(PEt$_3$)$_2$, **8**	2.018(5)	1.178(7)	1.250(8)	170.3(8)	This work
Pt[CN$_4$(R)](N=C=N–R)(PMe$_3$)$_2$, **11**	2.031(8)	1.17(1)	1.23(1)	168.0(10)	This work
Pd(Ph)(N=C=N–R)(PMe$_3$)$_2$	2.087(3)	1.172(4)	1.270(4)	172.8(3)	11
Pd[CN$_4$(R)](N=C=N–R)(PMe$_3$)$_2$	2.030(5)	1.156(7)	1.235(8)	169.7(6)	10
Pd[CN$_4$(R)](N=C=N–R)(PMe$_2$Ph)$_2$	1.988(8)	1.150(11)	1.274(11)	171.4(10)	10
Ni(L)(2-Clpcyd)	1.874(10)	1.154(16)	1.306(16)	171.4(13)	7
[Pd(terpy)(2,6-Cl$_2$pcyd)]	2.018(4)	1.162(7)	1.231(7)	170.3(6)	7
Cp$_2$Ti(N=C=N–Ph)$_2$	2.002(4)	1.187(7)	1.260(7)	173.8(6)	1
	1.985(5)	1.177(6)	1.247(7)	171.3(5)	
[Ru(py)$_4$(2-Cl-pcyd)$_2$]	2.041(6)	1.170(8)	1.297(9)	174.1(7)	7
	2.060(6)	1.165(8)	1.287(9)	172.0(7)	
[(bpy)Cu(2,3-Cl$_2$pcyd)$_2$]	1.928(7)	1.150(11)	1.274(11)	170.3(9)	7
	1.950(6)	1.158(11)	1.255(11)	173.8(10)	
	1.951(7)	1.158(12)	1.281(11)	172.6(11)	
	1.933(7)	1.135(12)	1.272(12)	173.1(10)	
[Mn(bpy)$_2$(ocn)$_2$]	2.131(4)	1.175(5)	1.278(6)	172.3(4)	12
	2.107(4)	1.171(6)	1.281(5)	174.0(5)	

R is 2,6-Me$_2$C$_6$H$_3$, unless otherwise stated. L = 1,3-bis(2′-pyridylimino)isoindolinato; 2-Clpcyd = 2-chlorophenylcyanamido; terpy = terpyridine; ocn = *o*-nitrophenylcyanamido-*N*.

(1,2-bis(diphenylphosphino)ethane)}, with 2,6-dimethylphenyl isocyanide at 60 °C for 5 h produces the corresponding bis(carbodiimido) complexes in high yields. These reactions proceed even at room temperature but require longer reaction times. Complexes **13**–**15** are less soluble in common organic solvents and display poorer crystallinity, compared with the monodentate tertiary phosphine analogues.



M = Pd: R = 2,6-$Me_2C_6H_3$, L-L = depe, **13**
R = 2,6-$Me_2C_6H_3$, L-L = dppp, **14**
M = Ni: R = 2,6-$Me_2C_6H_3$, L-L = dppe, **15**

(2)

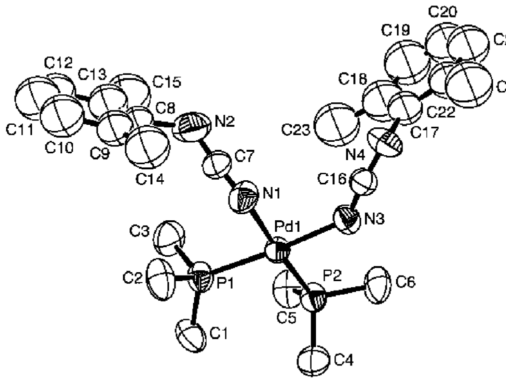


Fig. 1 ORTEP drawing[26] of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–P1 2.256(2), Pd1–P2 2.269(2), N2–C8 1.438(10), N4–C17 1.425(11); N1–Pd1–N3 88.2(2), N1–Pd1–P1 86.4(2), N3–Pd1–P1 174.6(2), N1–Pd1–P2 172.8(2), N3–Pd1–P2 90.4(2), P1–Pd1–P2 94.97(7), C7–N1–Pd1 136.9(6), C7–N2–C8 124.3(7), C16–N3–Pd1 138.1(6), C16–N4–C17 126.6(7).

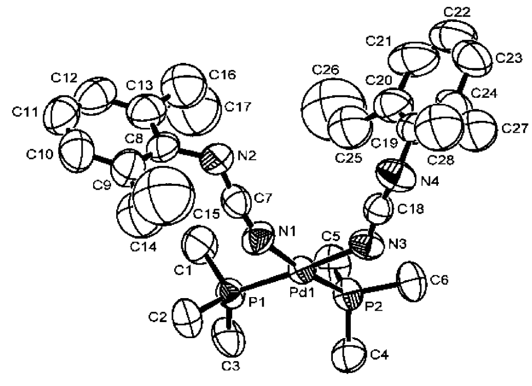


Fig. 2 ORTEP drawing of **4**. Selected bond lengths (Å) and angles (°): Pd1–P1 2.257(2), Pd1–P2 2.268(2), N2–C8 1.435(8), N4–C19 1.426(9); N1–Pd1–N3 88.6(2), N1–Pd1–P1 86.5(2), N3–Pd1–P1 175.0(2), N1–Pd1–P2 173.4(2), N3–Pd1–P2 89.6(2), P1–Pd1–P2 95.37(7), C7–N1–Pd1 135.0(5), C7–N2–C8 126.4(6), C18–N3–Pd1 135.4(5), C18–N4–C19 126.4(6).

Structures

Molecular structures of **1**, **2**, **4**, **6**, **8** and **11** have been determined by X-ray diffraction. Bonding parameters for the terminal η^1-carbodiimido ligand of Group 10 metal complexes containing a carbodiimido or bis(carbodiimido) ligand as well as bis(carbodiimido) complexes of other transition metals are summarized in Table 3. The crystal data and intensity data are given in Table 4. Figs. 1 and 2 show the ORTEP drawings of complexes **1** and **4**, which have a slightly distorted square-planar coordination, containing two *cis* phosphines and two *cis* carbodiimido groups. These ORTEP drawings clearly show that the nitrogen atom of the carbodiimido ligand (N=C=N) is bonded to the Pd center. As shown in Table 3, the Pd–N distances (2.080(6) and 2.089(6) Å for **1**; 2.087(5) and 2.089(5) Å for **4**) of the carbodiimido ligand in both compounds are very close to that (2.087(3) Å) found in *trans*-PdPh(N=C=N–2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$.[11] However, these bonds are somewhat longer than those (2.030(5) and 1.988(8) Å) found in the carbodiimido complexes, *trans*-Pd[CN$_4$(R)](N=C=N–R)L$_2$ (R = 2,6-Me$_2$C$_6$H$_3$; L = PMe$_3$ or PMe$_2$Ph),[10] suggesting a stronger *trans* influence of PMe$_3$ compared with the tetrazolato ring (CN$_4$(R)). The proximal nitrogen–carbon bond (N_α=C) distances are observed to range from 1.144(9)–1.191(6) Å and are very close to the C≡N bond distance (1.16 Å).[13] On the other hand, the distal nitrogen–carbon bond distances (C=N_β) are in the range of 1.23(1)–1.297(9) Å, indicating some double bond

Table 4 X-Ray data collection and structure refinement for **1**, **2**, **4**, **6**, **8** and **11**

	1	**2**	**4**	**6**	**8**	**11**
Formula	$C_{24}H_{36}N_4P_2Pd$	$C_{30}H_{48}N_4P_2Pd$	$C_{28}H_{44}N_4P_2Pd$	$C_{30}H_{48}N_4P_2Ni$	$C_{30}H_{48}N_4P_2Pt$	$C_{24}H_{36}N_6P_2Pt$
M	548.91	633.06	605.01	585.37	721.75	665.62
T/ K	295(2)	295(2)	296(2)	296(2)	295(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$Pbca$	$Pbca$	$P2_1$
a/Å	12.790(3)	9.525(4)	12.191(2)	9.385(2)	9.455(1)	9.066(2)
b/Å	13.920(3)	14.396(5)	16.580(4)	14.465(2)	14.344(2)	11.766(2)
c/Å	17.037(3)	24.183(8)	16.660(5)	24.050(3)	24.230(2)	13.601(3)
β/°	110.279(6)		109.93(2)	–		108.92(2)
V/Å^3	2845(1)	3316(2)	3166(1)	3264.7(9)	3286.0(5)	1373.8(5)
Z	4	4	4	4	4	2
$D_{calc.}$/g cm^{-3}	1.281	1.268	1.269	1.191	1.459	1.609
μ/mm^{-1}	0.781	0.680	0.709	0.716	4.391	5.246
F(000)	1136	1328	1264	1265	1456	660
No. of reflns Measured	5154	2922	5765	2862	2839	2702
No. of reflns Unique	4920	2922	5490	2862	2839	2538
No. of reflns with $I > 2\sigma(I)$	3841	1514	3711	1609	1750	2352
No. of params Refined	200	170	278	170	170	299
$\Delta\rho$ max, min/e Å^{-3}	1.043. −0.544	0.307, −0.338	0.858, −0.466	0.345, −0.273	0.791, −0.986	0.466, −0.413
GOF on F^2	1.029	0.990	1.006	1.001	1.045	1.046
R	0.0669	0.0464	0.0559	0.0543	0.0357	0.0238
$wR_2{}^a$	0.1776	0.0921	0.1371	0.1198	0.0897	0.0547
R (all data)	0.0835	0.1180	0.0906	0.1170	0.0609	0.0283
$wR_2{}^a$ (all data)	0.1937	0.1179	0.1596	0.1469	0.1088	0.0566

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

character. These asymmetric NCN linkages are common for cabodiimido complexes as shown in Table 3.

The molecular structures of complexes **2**, **6**, and **8** are shown in Figs. 3–5 and provide the first examples of bis(carbodiimido) complexes of a Group 10 triad of the type *trans*-M(N=C=N–R)$_2$(PEt$_3$)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$; M = Ni, Pd, Pt). These complexes are isostructural with one another. The central metals lie on the crystallographic center of symmetry, which explains why these crystals have a Z value of 4 instead of 8. The coordination sphere of each metal can be described as a square plane, which contains two *trans*-PEt$_3$ ligands and two *trans*-carbodiimido (N=C=N–R) ligands. The metal–nitrogen bond lengths are observed in the order Pd > Pt > Ni.

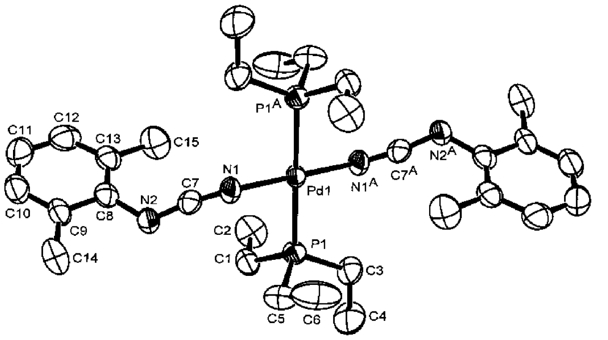


Fig. 3 ORTEP drawing of **2**. Symmetry equivalent atoms (denoted by an A) are generated by the crystallographic inversion center located at the Pd1 atom. Selected bond lengths (Å) and angles (°): Pd1–P1 2.328(2), N2–C8 1.406(7); N1–Pd1–P1 87.8(1), N1A–Pd1–P1 92.2(1), N1–Pd1–P1A 92.2(1), N1–Pd1–N1A 180.0(3), N1A–Pd1–P1A 87.8(1), P1–Pd1–P1A 180.00(8), C7–N1–Pd1 136.8(4), C7–N2–C8 125.1(5).

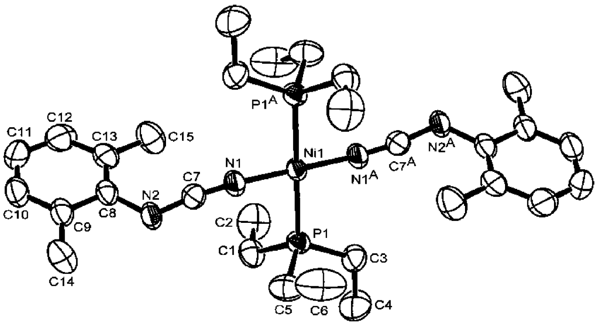


Fig. 4 ORTEP drawing of **6**. Symmetry-equivalent atoms (denoted by an A) are generated by the crystallographic inversion center. Selected bond lengths (Å) and angles(°): Ni1–P1 2.226(1), N2–C8 1.404(5); N1A–Ni1–N1 180.0(2), N1A–Ni1–P1A 87.5(1), N1–Ni1–P1A 92.5(1), N1A–Ni1–P1 92.5(1), N1–Ni1–P1 87.5(1), P1A–Ni1–P1 180.00(6), C7–N1–Ni1 148.0(4), C7–N2–C8 126.9(4).

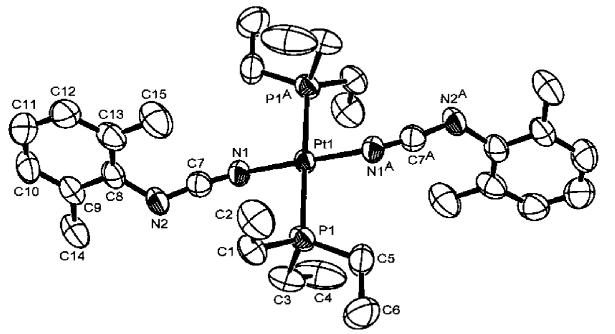


Fig. 5 ORTEP drawing of **8**. Selected bond lengths (Å) and angles (°): Pt1–P1 2.309(2), N2–C8 1.435(8); N1–Pt1–P1 87.9(2), C7–N1–Pt1 139.8(5), C7–N2–C8 125.6(6).

The molecular structure of complex **11** is shown in Fig. 6. The coordination sphere of Pt can be described as a square plane, with two *trans*-PMe$_3$ ligands, one tetrazolato ligand (CN$_4$–2,6-Me$_2$C$_6$H$_3$), and one carbodiimido ligand (NCN–2,6-Me$_2$C$_6$H$_3$). The equatorial plane, defined by Pt1, P1, P2, N1, and C7, is roughly planar with an average atomic displacement of 0.0893 Å. The tetrazolato ring and its phenyl ring are twisted from each other with a dihedral angle of 64.5(3)°.

Reactivity toward acyl halide derivatives

We have investigated the reactions of organic electrophiles with **1** to gain insight into the chemical properties of the complexes and their relationship to several synthetic organic reactions catalyzed by Group 10 metal complexes. Compound **1** rapidly reacts with two equivalents of benzoyl chloride (PhCOCl), phenyl chloroformate (PhOCOCl), and 2-thiophenecarbonyl chloride (C$_4$H$_3$SCOCl) at room temperature to give organic cyanamides such as PhCON(CN)-2,6-Me$_2$C$_6$H$_3$

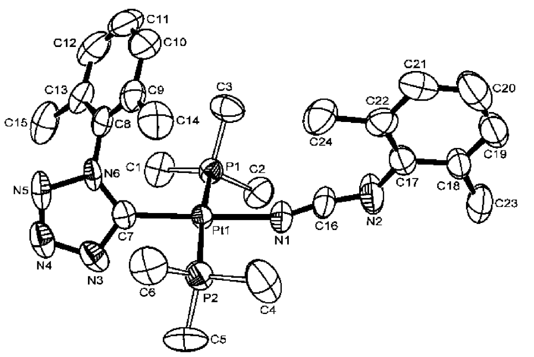
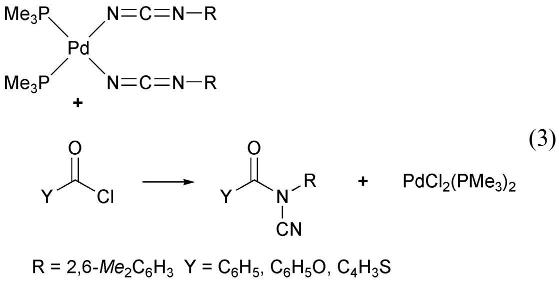


Fig. 6 ORTEP drawing of **11**. Selected bond lengths (Å) and angles (°): Pt1–C7 2.005(11), Pt1–N1 2.031(8), Pt1–P1 2.307(2), Pt1–P2 2.316(3), N1–C16 1.17(1), N2–C16 1.23(1), N2–C17 1.39(1), N3–C7 1.34(1), N3–N4 1.40(1), N4–N5 1.30(1), N5–N6 1.38(1), N6–C7 1.35(1), N6–C8 1.43(1); C7–Pt1–N1 175.3(4), C7–Pt1–P1 96.5 (3), N1–Pt1–P1 86.5 (3), C7–Pt1–P2 87.8(3), N1–Pt1–P2 89.6(3), P1–Pt1–P2 172.3(1), C16–N1–Pt1 157.5(8), C16–N2–C17 131.0(9), C7–N3–N4 105.7(9), N5–N4–N3 110.7(7), N4–N5–N6 106.2(8), C7–N6–N5 109.2(8), N3–C7–N6 108.2(9), N3–C7–Pt1 123.0(8), N6–C7–Pt1 128.3(7), N1–C16–N2 168.0(10).

(92%), PhO(CO)N(CN)-2,6-$Me_2C_6H_3$ (85%), and C_4H_3SCON-(CN)-2,6-$Me_2C_6H_3$ (91%), respectively (eqn. (3)). However, those reactions of **1** carried out with excess CO (1 atm) or iodobenzene did not occur and only resulted in the recovery of the starting compound.



(3)

The pure organic cyanamides are isolated as white crystalline solids without requiring column chromatography and have been identified by IR and NMR spectroscopy, and elemental analysis. Their IR spectra display strong absorption bands at 2228–2242 cm^{-1} and 1665–1758 cm^{-1}, due to the characteristic C≡N and CO groups, respectively. The ^{13}C NMR spectra also confirm the corresponding carbon atoms. Interestingly, we could not observe isomeric linear carbodiimides of the type Y(CO)N=C=N–R, which has been further confirmed by X-ray diffraction. Two of the molecular structures of these cyanamides, PhCON(CN)-2,6-$Me_2C_6H_3$ and C_4H_3SCON(CN)-2,6-$Me_2C_6H_3$, demonstrate the formation of bent cyanamides (Fig. 7 and 8). Although we could not provide conclusive information about the formation of organic cyanamides, we speculate the reaction proceeds by one of two pathways. The first pathway is direct electrophilic abstraction, which begins with the attack of the electrophile (YCOCl) at the distal nitrogen of the carbodiimido ligand. This pathway seems to be sterically favorable and can avoid the uncommon oxidation state of +4 arising from the oxidative addition of the electrophile. A second pathway involves equilibrium to give a palladium cyanamide species that subsequently undergoes electrophilic attack at its proximal nitrogen to lead to the product (Scheme 3). Recently, Yamamoto and co-workers reported the palladium-catalyzed couplings of isocyanides, allyl carbonate, and trimethylsilyl azide to give allyl cyanmides and also proposed the equilibrium between a π-allyl-supported palladium–carbodiimide and a palladium–cyanamide as the intermediate.[2] By the way, our reaction is rapid at room temperature and does not show any spectroscopically identifiable linear carbodiimide, Y(CO)N=C=N–R in the reaction mixture. Therefore, the first pathway seems to be more plausible than the second in our case. The above reactions suggest that our palladium–carbodiimido complexes might act as important intermediates or precursors in the transition-metal-catalyzed organic cyanamide formation and might be utilized in preparing various organic cyanamides.

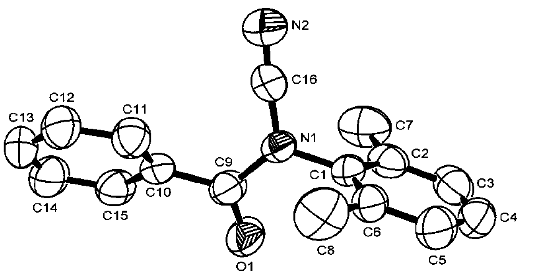


Fig. 7 ORTEP drawing of PhCON(CN)-2,6-$Me_2C_6H_3$. Selected bond lengths (Å) and angles (°): O1–C9 1.203(4), N1–C16 1.350(6), N1–C9 1.417(5), N1–C1 1.464(5), N2–C16 1.146(5); N1–C9–C10 118.4(4), N2–C16–N1 175.6(5).

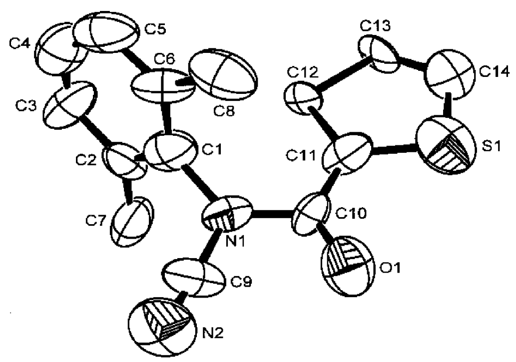
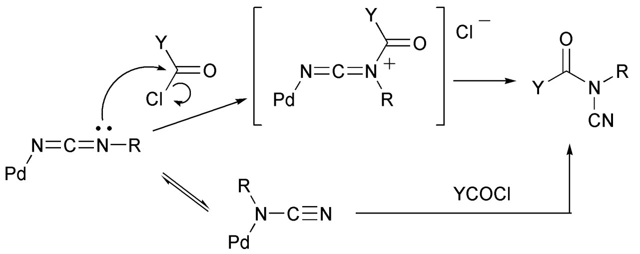


Fig. 8 ORTEP drawing of C_4H_3SCON(CN)-2,6-$Me_2C_6H_3$. Selected bond lengths (Å) and angles (°): O1–C10 1.174(15), N1–C9 1.338(18), N1–C10 1.413(16), N1–C1 1.484(19), N2–C9 1.103(18); N1–C10–C11 121.0(11), N2–C9–N1 173.0(17).



Scheme 3

Although several η^2 (or η^1)-carbodiimido complexes are known,[14–21] useful synthetic routes to bis(carbodiimido) compounds of Group 10 metals with a linear N=C=N fragment (η^1-coordinated) are limited. In this work, we have shown that various bis(carbodiimido) complexes of Group 10 metals can be readily prepared by the reactions of Group 10 metal–bis(azido)–phosphine complexes with isocyanides (2,6-dimethylphenyl or 2,6-diethylphenyl isocyanide). Our synthetic strategy is expected to be utilized in preparing other transition-metal–bis(carbodiimido) complexes with a linear N=C=N fragment. In addition, we have first demonstrated a set of crystal structures of bis(carbodiimido) complexes of a Group 10 triad. These complexes are expected to act as carbodiimido-transfer agents in preparing various organic cyanamides.

Experimental

General, materials and measurements

All manipulations of air-sensitive compounds were performed under N_2 or argon with the use of standard Schlenk techniques. Solvents were distilled from Na–benzophenone. The analytical laboratories at Basic Science Institute of Korea and at Kangnung National University carried out the elemental analyses. IR spectra were recorded on a Perkin-Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectra were obtained on JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si and to external 85% H_3PO_4. $Pd(N_3)_2L_2$ (L = PMe_3, PEt_3, PMe_2Ph; L_2 = depe, dppp) and $Pt(N_3)_2L_2$ (L = PMe_3 or PEt_3) were prepared by ligand-exchange reactions of $Pd(N_3)_2$(tmeda)[22] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) and $Pt(N_3)_2$(COD)[22] (COD = cycloocta-1,5-diene) with corresponding tertiary or chelating phosphine ligands. $Ni(N_3)_2L_2$ (L = PMe_3, PEt_3; L_2 = dppe) were prepared by the literature method.[23] 2,6-Diethylphenyl isocyanide was prepared as described in the literature.[24]

Preparations

Complexes 3–6. To a Schlenk flask containing $Pd(N_3)_2(PMe_2Ph)_2$ (0.321 g, 0.688 mmol) was added THF/CH_2Cl_2 (10 cm^3, 3 : 2 v/v ratio) and 2,6-dimethylphenyl isocyanide (0.181 g, 1.38 mmol) in that order. The mixture was heated at 60 °C for 5 h, and the initial yellow solution slowly turned a reddish orange. After stirring, the solvent was removed completely, and the resulting residue was solidified with CH_2Cl_2 and diethyl ether to give yellow solids. Recrystallization from CH_2Cl_2/hexane gave yellow crystals of $Pd(N{=}C{=}N{-}R)_2(PMe_2Ph)_2$ (R = 2,6-$Me_2C_6H_3$), **3** (0.360 g).

Complexes **4**–**6** were prepared in a similar way to compound **3**.

Complexes 7 and 8. To a Schlenk flask containing $Pt(N_3)_2(PMe_3)_2$ (0.430 g, 0.996 mmol) was added toluene (10 cm^3) and 2,6-dimethylphenyl isocyanide (0.262 g, 1.99 mmol) in that order. The mixture was heated at 80 °C for 24 h, during which time the reaction mixture slowly turned to a colorless solution. After stirring, the solvent was removed completely, and the resulting residue was solidified with diethyl ether and hexane to give a white powder. Recrystallization from CH_2Cl_2/hexane gave white crystals of *trans*-$Pt(N{=}C{=}N{-}R)_2(PMe_3)_2$ (R = 2,6-$Me_2C_6H_3$), **7** (0.338 g).

Complex **8** was analogously prepared.

Similar reactions of $Pt(N_3)_2(PMe_3)_2$ with *tert*-butyl (or cyclohexyl) isocyanide under the conditions described above gave white solids. The isolated solids were identified as *trans*-$Pt[CN_4(R)]_2(PMe_3)_2$ (R = *tert*-butyl, cyclohexyl) by comparing their spectral data with those of a sample of the genuine compound.[10]

Complexes 9. To a Schlenk flask containing $Ni(N_3)_2(PMe_3)_2$ (0.309 g, 1.048 mmol) was added CH_2Cl_2 (9 cm^3) and 2,6-dimethylphenyl isocyanide (0.275 g, 2.096 mmol) in that order. The initial dark red solution immediately turned dark yellow with the evolution of nitrogen. After stirring for 24 h at room temperature, the solvent was completely evaporated under vacuum, and then the resulting residue was solidified with diethyl ether. The solids were filtered off and washed with diethyl ether (2 × 2 cm^3). Recrystallization from CH_2Cl_2/diethyl ether gave brown crystals of *trans*-$Ni[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$ (R = 2,6-$Me_2C_6H_3$), **9** (0.240 g). Thermal treatment of **9** in THF/CH_2Cl_2 (3 : 2 v/v ratio) at 60 °C for 5 h converted to the bis(carbodiimido) complex, $Ni(N{=}C{=}N{-}R)_2(PMe_3)_2$ (R = 2,6-$Me_2C_6H_3$), **5** in 96% yield.

Complexes 10–12. To a Schlenk flask containing $Pt(N_3)_2(PMe_3)_2$ (0.430 g, 0.996 mmol) was added CH_2Cl_2 (4 cm^3) and 2,6-dimethylphenyl isocyanide (0.106 g, 0.811 mmol) in that order. The mixture was stirred at room temperature for 3 h, and the solvent was removed. The resulting residue was solidified with diethyl ether and hexane to give a white powder, which was recrystallized from CH_2Cl_2/hexane to produce white crystals of *trans*-$Pt[CN_4(R)]_2(PMe_3)_2$ (R = 2,6-$Me_2C_6H_3$), **10** (0.213 g).

Thermal treatment of **10** in THF/CH_2Cl_2 (3 : 2 v/v ratio) at 60 °C for 5 h gave the carbodiimido complex, $Pt[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$ (**11**) in 60% yield. Direct reactions of $Pt(N_3)_2L_2$ (L = PMe_3 or PEt_3) with 2,6-dimethylphenyl isocyanide at 60 °C for 5 h also produce the same complexes, $Pt[CN_4(R)](N{=}C{=}N{-}R)(PMe_3)_2$ {(L = PMe_3 (**11**), PEt_3 (**12**)) in, 54 and 92% yield, respectively.

Complexes 13–15. To a Schlenk flask containing $Pd(N_3)_2$(depe)$_2$ (0.498 g, 1.26 mmol) was added THF/CH_2Cl_2 (10 cm^3, 3 : 2 v/v ratio) and 2,6-dimethylphenyl isocyanide (0.329 g, 2.51 mmol). The mixture was heated at 60 °C for 5 h, and the initial yellow solution gradually turned orange. After stirring, the solvent was then removed completely, and the resulting residue was solidified with diethyl ether and hexane to give a yellow powder. Recrystallization from CH_2Cl_2/hexane gave yellow crystals of $Pd[N{=}C{=}N{-}(R)]_2$(depe) (R = 2,6-$Me_2C_6H_3$), **13** (0.397 g).

Complexes **14** and **15** were analogously prepared.

Reactions of 1 with acyl chloride derivatives. At room temperature, benzoyl chloride (0.292 g, 2.07 mmol) was added to a CH_2Cl_2 solution (5 cm^3) containing complex **1** (0.542 g, 0.987 mmol). The initial orange solution instantly turned to a pale yellow suspension. After stirring for 1 h, the reaction mixture was fully evaporated *in vacuo* to give a pale yellowish residue. The residue was extracted with diethyl ether (30 cm^3), and the solvent was removed *in vacuo* to give white solids. The products were crystallized from diethyl ether, washed with hexane (2 cm^3 × 2) at 0 °C, and dried *in vacuo* to give white crystals of PhCON(CN)-2,6-$Me_2C_6H_3$ (0.432 g, 92%). Data for PhCON(CN)-2,6-$Me_2C_6H_3$: ν_{max}/cm^{-1}: 2228 (s) and 1714 (s) (Found: C, 77.05; H, 5.72, N, 11.51. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19%); δ_H (300 MHz, $CDCl_3$ at 25 °C) 2.38 (6H, s, CH_3), 7.16–7.30 (3H, m, C_6H_3), 7.53–7.61 (3H, br, C_6H_5), and 7.97 (2H, br, C_6H_5); δ_C (75 MHz in $CDCl_3$ at 25 °C) 17.7 (CH_3), 109.7, 128.7, 129.0 (1C, s, CN), 129.3, 130.2, 130.5, 133.4, 135.9, 167.4 (1C, s, CO). The residual solids were identified as $PdCl_2(PMe_3)_2$ in 96% yield by comparison of the NMR data with those of an authentic sample.

The analogous reactions with phenyl chloroformate and 2-thiophenecarbonyl chloride also gave organic cyanamides, PhO(CO)N(CN)-2,6-$Me_2C_6H_3$ (85%) and C_4H_3SCON(CN)-2,6-$Me_2C_6H_3$ (91%), respectively. Data for PhO(CO)N(CN)-2,6-$Me_2C_6H_3$: ν_{max}/cm^{-1}: 2242 (s) and 1758 (s) (Found: C, 72.47; H, 5.35, N, 10.77. $C_{16}H_{14}N_2O_2$ requires C, 72.16; H, 5.30; N, 10.52%); δ_H (300 MHz, $CDCl_3$ at 25 °C) 2.43 (6H, s, CH_3), 7.17–7.32 (6H, m, C_6H_5), 7.39–7.44 (2H, br, C_6H_5); δ_C (75 MHz in $CDCl_3$ at 25 °C) 17.7 (CH_3), 107.5, 120.8, 126.8, 129.2, 129.7, 130.1 (1C, s, CN), 130.4, 132.3, 136.1, 150.2 (1C, s, CO). Data for C_4H_3SCON(CN)-2,6-$Me_2C_6H_3$: ν_{max}/cm^{-1}: 2235 (s) and 1665 (s) (Found: C, 65.91; H, 4.79, N, 10.40. $C_{14}H_{12}N_2OS$ requires C, 65.60; H, 4.72; N, 10.93%); δ_H (300 MHz, $CDCl_3$ at −60 °C) 2.37 (6H, s, CH_3), 7.03 (1H, dd, *J* = 4, C_6H_5), 7.23–7.33 (3H, m, C_6H_5), 7.58 (2H, dd, *J* = 2, C_4H_3S); δ_C (75 MHz in $CDCl_3$ at −60 °C) 18.1 (CH_3), 108.1, 127.9, 129.7, 130.1, 131.6, 132.4, 132.9, 133.9, 136.0, 137.4, 161.3 (1C, s, CO). NMR data of C_4H_3SCON(CN)-2,6-$Me_2C_6H_3$ at low temperature displayed the presence of a minor conformer, and raising the temperature of the sample resulted in a broad signal.

X-Ray structure determination

All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator, details are summarised in Table 4. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 25–36 reflections in the range of $10.0° < 2\theta < 25.0°$. 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 with the use of the SHELX-97 programs.[25] Structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 values, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were generated in ideal positions and refined in a riding mode. The 2,6-dimethylphenyl rings of **1** and the ethyl groups on the phenyl rings of **2** were extremely disordered, and therefore the carbon atoms in these fragments were isotropically refined.

Crystal data for the organic cyanamide, PhCON(CN)-2,6-$Me_2C_6H_3$: $C_{16}H_{14}N_2O$, $M = 250.29$, orthorhombic, space group *Pbca*, $a = 7.570(2)$, $b = 15.073(6)$, $c = 24.035(6)$ Å, $V = 2743(1)$ Å^3, $Z = 8$, $T = 293$ (2) K, $\mu = 0.077$ mm^{-1}, 4034 reflections measured, 2402 unique ($R_{int} = 0.2075$), from which 909 with $I > 2\sigma(I)$ were used in refinements. Final R_1 and wR_2 values were 0.0705 and 0.1356, respectively. No absorption corrections were made. Crystal data for $C_4H_3SCON(CN)$-2,6-$Me_2C_6H_3$: $C_{14}H_{12}N_2OS$, $M = 256.32$, monoclinic, space group *Pc*, $a = 8.085(2)$, $b = 11.637(2)$, $c = 14.389(3)$ Å, $V = 1302.4(5)$ Å^3, $Z = 4$, $T = 293$ (2) K, $\mu = 0.237$ mm^{-1}, 2240 reflections measured, 2240 unique ($R_{int} = 0.0000$), from which 1275 with $I > 2\sigma(I)$ were used in refinements. Final R_1 and wR_2 values were 0.0824 and 0.2218, respectively.

CCDC reference numbers 184849–184855 and 184857.

See http://www.rsc.org/suppdata/dt/b2/b204179k/ for crystallographic data in CIF or other electronic format.

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References

1 G. Veneziani, S. Shimada and M. Tanaka, *Organometallics*, 1998, **17**, 2926 and references therein.

2 S. Kamijo, T. Jin and Y. Yamamoto, *J. Am. Chem. Soc.*, 2001, **123**, 9453.

3 G. Rajca, W. Schwarz and J. Weidlein, *Z. Naturforsch., Teil B*, 1984, **39**, 1219; G. Rajca and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1986, **538**, 36; W. Einholz and W. Haubold, *Z. Naturforsch., Teil B*, 1986, **41**, 1367.

4 W. Beck, K. Burger and W. P. Fehlhammer, *Chem. Ber.*, 1971, **104**, 1816.

5 K. Burgess, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1983, 1179.

6 E. O. Fisher, W. Kleine, U. Schubert and D. Neugebauer, *J. Organomet. Chem.*, 1978, **149**, C40; V. U. Schubert, D. Neugebauer and P. Fridrich, *Acta Crystallogr., Sect. B*, 1978, **34**, 2293.

7 R. J. Letcher, W. Zhang, C. Bensimon and R. J. Crutchley, *Inorg. Chim. Acta*, 1993, **210**, 183; W. Zhang, C. Bensimon and R. J. Crutchley, *Inorg. Chem.*, 1993, **32**, 5808; P. Desjardins, G. P. A. Yap and R. J. Crutchley, *Inorg. Chem.*, 1999, **38**, 5901; C. E. B. Evans, D. Ducharme, M. L. Naklickim and R. J. Crutchley, *Inorg. Chem.*, 1995, **34**, 1350; A. R. Rezvanni and R. J. Crutchley, *Inorg. Chem.*, 1994, **33**, 170 and references therein; R. J. Crutchley, R. Hynes and E. J. Gabe, *Inorg. Chem.*, 1990, **29**, 4921.

8 B. F. Abrahams, S. J. Egan, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1099.

9 M. Wehlan, R. Thiel, J. Fuchs, W. Beck and W. P. Fehlhammer, *J. Organomet. Chem.*, 2000, **613**, 159.

10 Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo and S.-W. Lee, *J. Chem. Soc., Dalton Trans.*, 2002, 144.

11 Y.-J. Kim, Y.-S. Kwak and S.-W. Lee, *J. Organomet. Chem.*, 2000, **603**, 152.

12 X. Shen, X. Shi, B. Kang, Y. Liu, L. Gu and X. Huang, *J. Coord. Chem.*, 1999, **47**, 1.

13 J. E. Huheey, E. A. Keitter, R. L. Keitter, *Inorgnic Chemistry*, Harper Collins, New York, 4th edn., 1993, Appendix, Table E1.

14 B. M. Bycroft and J. D. Cotton, *J. Chem. Soc., Dalton Trans.*, 1973, 1867.

15 R. A. Anderson and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, 1978, **34**, 271.

16 H. Hoberg and J. Korff, *J. Organomet. Chem.*, 1978, **150**, C20.

17 M. Pasquali, S. Gambarotta, C. Floriani, A. Chiesi-Valla and C. Guastini, *Inorg. Chem.*, 1981, **20**, 165.

18 H. L. M. v. Gaal and J. P. Verlaan, *J. Organomet. Chem.*, 1977, **133**, 93.

19 D. S. Glueck, F. J. Holland and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 2719.

20 H. Werner, G. Hörlin and N. Mahr, *J. Organomet. Chem.*, 1998, **551**, 367; G. Hörlin, N. Mahr and H. Werner, *Organometallics*, 1993, **12**, 1775.

21 E. T. Hessell and W. D. Jones, *Organometallics*, 1992, **11**, 1496.

22 Y.-J. Kim, J.-C. Choi and K.-H. Park, *Bull. Korean Chem. Soc.*, 1994, **15**, 690.

23 K. Bowman and Z. Dori, *Inorg. Chem.*, 1970, **9**, 395.

24 H. Ryu, S. Knecht, L. R. Subramanian and M. Hanack, *Synth. Met.*, 1995, **72**, 289.

25 G. M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1997.

26 L. J. Farrugia, ORTEP-3 for Windows, University of Glasgow, 1997.