Reactivity of alkynyl Pd(II) azido complexes toward organic isocyanides, isothiocyanates, and nitriles

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Abstract

Alkynyl Pd(II) azido complexes of the type [Pd(N3)(C=C-R)L2] (1–3) were obtained by reactions of aqueous NaN3 with [Pd(Cl)(C=C-R)L2] (R = Ph or C(O)OMe). Treating compounds 1–3 with organic isocyanides (R–NC) afforded novel complexes, trans-[Pd(C=C-Ph)(N=S)(C6F5)2](14) and [Pd(C=C-R)(CN)2(PEt3)2](15), respectively. Bis(phosphine) bis(cyano) complexes of Pd and Ni, [M(CN)2L2] (L = PEt3, PMe3; L2 = DEPE), could be obtained independently by the reactions of [M(N3)2L2] with excess Me3SiCN in organic solvents.

Keywords: Azido; Cycloaddition; Alkynyl; Carbodiimide; Palladium

1. Introduction

Dipolar cycloaddition of unsaturated organic compounds such as isocyanide, nitrile, and alkyne to an azido ligand, which gives metal complexes containing C- or N-coordinated heterocycles, has been an interesting subject for many decades [1–18]. We recently reported several late transition-metal complexes containing such heterocycles (C-coordinated), which were prepared by treating bis(phosphine) metal complexes of bis(azido) [M(N3)2(PR3)2] and mono(azido) methyl or phenyl [M(N3)(R)(PR3)2] (R = Me or Ph) with organic isocyanides [19]. Although many derivatives of late transition-metal mono- or bis(azido) complexes have been employed to study on the formation of metal complexes containing the heterocycles mentioned above, azido metal–alkynyl complexes have been relatively unexplored. The alkylnyl ligand exhibits interesting properties such as cluster formation involving the bridging alkylnyl ligand and in multinuclear complexes [20–22], its conversion...
to the corresponding vinylidene species [23], and its potential optical or liquid crystalline properties as a molecular wire having linear –C≡C– units [24]. We here wish to report the preparation of alkynyl palladium(II)-azido complexes and their reactivity toward organic isocyanides and organic pseudo-halides (isothiocyanates and nitriles).

2. Results and discussion

Alkynyl palladium(II) azido complexes 1–3 have been prepared by usual coupling reactions and then subsequent metathetical substitution with NaN₃ as shown in Eqs. (1) and (2). These complexes have been obtained as white crystalline solids in high yields and characterized by IR, NMR, and elemental analyses. Formation of those complexes can be readily confirmed by monitoring the strong absorption bands in the range of 2050–2100 cm⁻¹ due to the N₃ and C≡C stretching bands.

\[
PdCl₂L₂ \xrightarrow{CuBr, Et₂NH} R≡Pd\_Cl \quad (1)
\]

\[
R≡Pd\_Cl \xrightarrow{NaN₃} R≡Pd\_N₃ \quad (2)
\]

2.1. Reactions with isocyanides

As mentioned in Section 1, we recently reported that bis(phosphine) group 10 metal complexes, [M(N₃)₂(PR₃)₂] and [M(N₃)(R)PR₃] (R = Me or Ph), reacted with various isocyanides to give complexes containing carbodiimido or tetrazolato groups through cycloaddition of isocyanides to the metal–azido bond [19]. On the basis of these results, we have examined the reactivity of alkynyl palladium(II) azido complexes toward isocyanides as shown in Eq. (3). Treatment of the isocyanide with the azido complex caused immediate evolution of nitrogen gas, and their reaction was monitored by the appearance of new strong bands at ca. 2170 cm⁻¹ due to the N₃ and C≡C stretching bands.

\[
R = \text{Ph}, \quad L = \text{PMe₃, PEt₃; } \quad R = \text{MeO(CO), L = PMe₃, (3)}
\]

No other products (for example, an imino-bonded complex formed by the isocyanide insertion into the Pd–C bond) were observed. The formation of carbodiimido Pd(II) complexes appears to involve an initial formation of a C-coordinated tetrazolato ring by the cycloaddition of isocyanide into the palladium-azido bond and then the subsequent ring conversion to an end-on NCN group with the elimination of N₂ to give a final product. In a recent work, we reported that the formation of the carbodiimido or C-coordinated tetrazolato group was dependent not only on the type of an attacking isocyanide and but also on the steric bulk of alkyl substituents on the aryl ring that might facilitate N₂ elimination from the tetrazolato ring to give the corresponding carbodiimido group [19a,19b].

Figs. 1 and 2 show the molecular structures of trans-[Pd(C≡CPh)(N=C=N)–CN₄–Bu(PR₃)₂] (5) and trans-[Pd(C≡CPh)(CN₄–t-Bu)(PMMe₃)₂] (6), respectively. Crystal data are summarized in Table 1. Fig. 1 clearly shows the square-planar geometry of complex 5, which contains two PMe₃, one alkynyl, and one end-on carbodiimido (NCN–C₆H₃-2,6-Et₂) ligands. The linear phenylenethynyl group is located trans to the carbodiimido group. A triplet in ¹³C{¹H} NMR, which is coupled with two phosphine ligands and corresponds to the alkynyl carbon (C≡C or C≡Cₖ) directly bonded to the Pd metal, supports the trans-geometry of the complexes. Furthermore, a singlet at −12.3 ppm in ³¹P{¹H} NMR also supports the trans-structure. The phenyl ring in the carbodiimido ligand is nearly perpendicular to the
equatorial plane with the dihedral angle of 84.58(9)/C176.

The Pd–N bond length of 5 is close to the previously reported one in \textit{trans}-[Pd(CN₄–R)(N₂C₆H₃)] (2.030(5) Å) [19b], but it is slightly shorter than that in \textit{trans}-[Pd(Ph)(N≡C=N=C₆H₅–2,6-Me₂)](PMe₃)₂ (2.087(3) Å) [19c], suggesting a weaker \textit{trans}-influence of the phenylethynyl group than the phenyl ring. The asymmetric nitrogen–carbon bonds (1.156(4) and 1.252(4) Å) in the carbodiimido (NₑCₑN) group of 5 have also been observed for those in other carbodiimido complexes [19a]. Fig. 2 shows the structure of 6 possessing the C-coordinated tetrazolato ring. A triplet signal at 164 ppm in \textit{13}C{¹\textit{H}} NMR due to the carbon of the tetrazolato ring strongly supports the C-coordination of the ring to the Pd metal.

2.2. Reactions with organic pseudo-halides

In order to examine the scope of the reactivity of the alkynyl Pd(II) azido complexes, we have treated them with R₁NₑCₑS (R = 2,6-Me₂C₆H₃ or CH₂CH₃) and 1,4-phenylene disisothiocyanate (C₆H₄(NₑCₑS)₂). These reactions as shown in Eq. (5), dipolar cycloaddition of an organic R₁NₑCₑS into the Pd–azido bond, proceeded smoothly at room temperature to give tetrazol–thiolato complexes, \textit{trans}-[Pd(C≡CPh)(SCN₄–R)L₂] (L = PE₃, R = 2,6-Me₂C₆H₃ (9); L = PMe₃, R = Et (10) or 2,6-Me₂C₆H₃ (11)). As shown in Eq. (6), the same reaction with 1,4-phenylene disisothiocyanate (2:1 ratio) also produced a phenylene-bridged dinuclear Pd(II) tetrazolo–thiolato complex, [(PE₃)₂(C≡CPh)(SCN₄)(l–C₆H₄)–SCN₄]Pd(C≡CPh)(PE₃)₂ (12). Complexes 9–12 were characterized by spectroscopic and analytical methods. Formulation of 12 was also confirmed by FAB(+) mass spectra. The reaction completion can be readily confirmed by monitoring the disappearance of ν(N₃) band at 2030 cm⁻¹, which results from the dipolar cycloaddition of the isothiocyanate into the Pd–azido bond. Integration ratios in each of the \textit{1H} NMR spectra of 9–12 are consistent with the proposed structures. A signal at 161–164 ppm in \textit{13}C{¹\textit{H}} NMR corresponds to the carbon atom of the tetrazolato ring, [S–(C₄N₄–R)]. A singlet in \textit{31}P{¹\textit{H}} NMR also supports the proposed \textit{trans}-structure. These spectral data strongly indicate the absence of N-bonded tetrazoline compounds M[N₄(R)(C≡S)], which can adopt an N₁- or an N₂-bonded form. Fig. 3 shows an \textbf{ORTEP} drawing of \textit{trans}-[Pd(C≡CPh)SCN₄–C₆H₅–2,6-Me₂]PMe₃ (11). The molecular structure of 11 clearly shows an S-coordinated tetrazolato ring.
Recently, we reported that reactions of bis(azido)–Pd(II) complexes with organic isothiocyanates gave tetrazole–thiolato complexes [25]. Our present work (Eqs. (5) and (6)) also gave tetrazole–thiolato Pd(II) complexes having alkynyl ligands. Although several studies [5f,6,10,14,26] on the cycloaddition of organic isothiocyanates into the transition-metal azido complexes to give N-bonded tetrazoline-5-thione, (M[N4(C=S)]) complexes have been reported, the case of tetrazole–thiolato complex formation did not appear in the literature until our recent work. It is worth noting that Beck et al. [27] previously prepared anionic tetrazole–thiolato Pd(II) and Pt(II) complexes in a way different from ours: (a) by the metathesis of metal halides with alkali metal salts of tetrazole mercaptan or (b) by the reactions of metal halides with alkyl mercaptan in the presence of amine.

![Figure 3. ORTEP drawing of 11. Selected bond lengths (Å) and angles (°): Pd1–C8 1.966(5), Pd1–P1 2.306(2), Pd1–P2 2.316(2), Pd1–S1 2.35(2), S1–C15 1.716(5), N1–C15 1.324(6), N1–S1 1.231(1), N2–N3 1.289(6), N3–N4 1.359(6), N4–C15 1.363(6), C7–C8 1.209(7); C8–Pd1–P1 85.1(2), C8–Pd1–P2 85.9(2), P1–Pd1–P2 178.0(6), C8–Pd1–S1 178.0(2), P1–Pd1–S1 95.99(6), P2–Pd1–S1 93.18(6), C15–S1–Pd1 106.3(2), C15–N1–N2 111.6(4), N3–N2–N1 105.8(4), N2–N3–N4 108.5(4).]

Table 1
X-ray data collection and structure refinement for 5, 6, 11, and 18

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<sup>a</sup> wR² = Σ[|w(Fo)² − Fc²|²]/Σ[w(Fo)²]²/1/2.
We have also examined dipolar cycloaddition reactions between alkynyl Pd(II) azido complexes and organic nitriles such as C₆F₅CN and Me₃SiCN. Treatment of 1 with excess C₆F₅CN at room temperature gave an N-coordinated tetrazolato compound, trans-[Pd(C≡CPh)(N₄C–C₆F₅)(PMe₃)₂] (13), as shown in Eq. (7). ¹H and ³¹P{¹H} NMR spectra of the crude product, which show two virtual triplets (integration ratio of 8:92) due to PMe₃ ligands in the ¹H NMR and two singlets in the ³¹P{¹H} NMR, suggest the presence of a mixture of N₁ or N₂-coordinated tetrazolato isomers. By fractional recrystallization of the crude reaction product, a pure tetrazolato complex 13 could be isolated as white solids in 37% yield.

IR spectrum of 13 shows a characteristic C≡C band without the N₃ band of the starting material. Earlier works by Beck and co-workers [5c,6] and several other research groups [14b,14c,28,29] demonstrated the similar N¹- or N²-coordination modes in the tetrazolato Pd(II) or Pt(II) complexes. In particular, Paul and Nag [14a] observed that both N¹ and N²-bound tetrazolato isomers were formed by the reactions of Ni(II) azido complexes with benzonitrile derivatives with the relative abundances dependent on the reaction stoichiometry and that the N²-bound isomer was a sole product in the case of p-NO₂C₆H₅CN.

Interestingly, similar reactions of 2 with excess Me₃SiCN at room temperature led to the formation of unusual metal cyano complexes, trans-[Pd(C≡CPh)-(CN)(PMe₃)₂] (14, 85%) and [Pd(CN)₂(PMe₃)₂] (15, trace), as a mixture (Eq. (8)).

Complex 14 is soluble in diethyl ether and so can be readily extracted from the mixture. IR spectrum of 14 shows a strong absorption band at 2108 cm⁻¹ due to ν(CN), which is overlapped with a weak ν(C≡C) band. In the ¹³C{¹H} NMR spectrum of 14, a triplet at 136.0 (J = 13 Hz) ppm due to the C≡N and two triplets at 105.0 (J = 17 Hz) and 110.9 (J = 4 Hz) ppm, corresponding to the C=C and C≡C, respectively, strongly support the presence of a cyano group and an alkynyl group coordinated to the Pd center. The same reaction with 1 also produced a mixture of [Pd(C≡CPh)(CN)(PMe₃)₂] (16) and [Pd(CN)₂(PMe₃)₂] (17), but quite similar solubility of these complexes prohibited the isolation of a pure alkynyl Pd(II) cyano complex (16).

Bis(cyano) palladium(II) complexes 15 and 17 could be independently prepared from [Pd(N₃)₂L₂] (L = PEt₃, PMe₃, or DEPE) and two equivalent or excess Me₃SiCN as shown in Eq. (9). Furthermore, this synthetic method could successfully apply to the preparation of a nickel(l) analog Ni(CN)₂(PEt₃)₂. Fig. 4 shows the molecular structure of 18. Considering the structures of cyano pal-
ladium and nickel complexes 14–19, an order of trans-effect strengths among ligands appears to be azido < alky- 

\[
M(N_3)_2L_2 + 2 \text{Me}_3\text{SiCN} \rightarrow M(\text{CN})_2L_2 
\]

(9)

The formation of cyano complexes 14 and 15 (Eq. (8)) indicates that Pd–C (alkynyl) and Pd–N bonds are cleaved by the relatively weak nucleophile (CN−) to give metal cyano complexes. However, we could not observe that other types of organic nitriles (R–CN) gave such cyano complexes. There are a couple of examples demonstrating the replacement of carbon-donor ligands by the CN− agent (in the form of Me3SiCN). For example, Tsuji et al. [30] reported palladium-catalyzed cyaniation in reactions between Me3SiCN and allylic acetate or carbonates. In this study, Me3SiCN converted a π-allyl palladium acetate complex to a dicyano Co(III) ethane complex to a dicyano Co(III) complex by the oxidative addition of Me3SiCN [31]. Generally, transition-metal cyano complexes are prepared from transition-metal halides and alkali metal cyanoide by metathesis in alcohol or aqueous media. Therefore, the formation of the cyano complexes with Me3SiCN and allylic acetate or carbonates. Moreover, Butenschoen and co-workers recently reported the transformation of a cyclopentadienyl Co(I) complex to a dicyano Co(III) complex by the oxidative addition of Me3SiCN [31]. Generally, transition-metal cyano complexes are prepared from transition-metal halides and alkali metal cyanide by metathesis in alcohol or aqueous media. Therefore, the formation of the cyano complexes with Me3SiCN (Eqs. (8) and (9)) can be an efficient way of introducing the cyano group to metal–azido complexes in organic solvents, and this type of cyaniation may be expanded to prepare other pseudo-halogen compounds of transition metals.

In summary, we prepared three novel alkynyl Pd(II) azido complexes and examined their reactivity toward organic isocyanides, isothiocyanates, and nitriles. Depending on the organic substrates, complexes containing five-membered heterocycles (C- or N-coordinated tetrazolato or tetrazole–thiolato) or carbodimido groups were formed. These results show an overall agreement with those previously found in bis(azido) group 10 metal complexes [19a]. One interesting finding in this study is that Me3SiCN can serve as an efficient agent in introducing the cyano group into the transition-metal azido complexes in organic solvents to give cyano or bis(cyano) Pd(II) and Ni(II) complexes.

3. Experimental

3.1. General

All manipulations of air-sensitive compounds were performed under N2 or Ar by standard Schlenk tech-

iques. Solvents were distilled from Na-benzophenone. The analytical laboratory at the Kangnung National University carried out elemental analyses using CE instruments EA1110. IR spectra were recorded on a Perkin–Elmer BX spectrophotometer. NMR (1H, 13C{1H}, and 31P{1H}) spectra were obtained on a JEOL Lambda 300 MHz spectrometer. Chemical shifts were referenced to internal Me4Si and to external 85% H3PO4. [PdCl(C≡C–R)L2] (R = Ph, C(O)OMe; L = PMe3, PEt3) were prepared by the literature method [32].

3.2. Preparation of trans-[Pd(N3)(C≡C–R)L2] (R = Ph, L = PMe3 (1), PEt3 (2); R = (CO)OMe, L = PMe3 (3))

To a THF solution (10 ml) of [PdCl(C≡CPh)(PMe3)2] (0.344 g, 0.87 mmol) was added an aqueous solution of NaN3 (0.113 g, 1.74 mmol) by a cannula. After stirring the reaction mixture for 24 h at room temperature, the solvent was completely evaporated. The residue was then extracted with CH2Cl2. The collected extract was reduced to 3 ml under vacuum. Addition of n-hexane (10 ml) caused separation of pale brown solids, which were freshly chromatographed from alumina (eluant, CH2Cl2) and then recrystallized from ether to give white solids (83%) of [PdCl(C≡CPh)(PMe3)2] (1). IR (KBr, cm−1): 2120 (w, C=O), 2046 (s, br, N3). 1H NMR (CDCl3, δ): 1.58 (t, 18 H, C(CH3)3), 7.17–7.31 (m, 5 H, Ph). 13C{1H} NMR (CDCl3, δ): 14.1 (t, J = 16 Hz, P(CH3)3), 93.7 (t, J = 19 Hz, C≡C≡C), 108.0 (t, J = 5.3 Hz, C≡C≡C), 126.1, 127.0, 128.1, 130.9 (t, J = 1.6 Hz). 31P{1H} NMR (CDCl3, δ): −14.8(s). Anal. Calc. for C14H23N3P2Pd: C, 49.40; H, 7.20; N, 8.21%. Found: C, 49.40; H, 7.20; N, 8.21%.

Complexes 2 and 3 were similarly prepared. Complex 2 (79 %): IR (KBr, cm−1): 2117 (w, C≡C), 2052 (s, br, N3). 1H NMR (CDCl3, δ): 1.24 (q, 18 H, J = 7.9 Hz, P(CH3CH2)2), 1.96 (m, 12 H, P(CH2CH3)2), 7.15–7.27 (m, 5 H, Ph). 13C{1H} NMR (CDCl3, δ): 8.34 (s, P(CH2CH3)2), 15.4 (t, J = 14 Hz, P(CH2CH3)2), 93.4 (br s, C≡C≡C), 108.0 (t, J = 5 Hz, C≡C≡C), 125.8, 127.6, 128.1, 130.7 (t, J = 1 Hz). 31P{1H} NMR (CDCl3, δ): −13.6(s). Anal. Calc. for C20H33N3P2Pd: C, 49.44; H, 7.26; N, 8.65. Found: C, 49.40; H, 7.20; N, 8.21%.

Complex 3 (82%): IR (KBr, cm−1): 2128 (w, C≡C), 2059 (s, br, N3), 18 H, J = 3.7 Hz, PMe3), 3.68 (s, 3 H, Me). 13C{1H} NMR (CDCl3, δ): 13.9 (t, J = 16 Hz, P(CH3)2), 51.9 (s, Me), 100.0 (t, J = 5.0 Hz, C≡C≡C), 104.2 (t, J = 19 Hz, C≡C≡C), 154.2 (t, J = 1.2 Hz, CO(O)), 31P{1H} NMR (CDCl3, δ): −14.2(s). Anal. Calc. for C20H33N3P2Pd: C, 49.44; H, 7.26; N, 8.65. Found: C, 49.40; H, 7.20; N, 8.21%.
3.3. Reactions with organic isocyanides

To a Schlenk flask containing complex 1 (0.285 g, 0.71 mmol) were sequentially added CH₂Cl₂ (7 ml) and 2,6-dimethylphenyl isocyanide (0.094 g, 0.72 mmol). The initial colorless solution immediately turned to pale yellow with the evolution of nitrogen. After stirring for 2 h at room temperature, the reaction mixture was completely evaporated under vacuum, and then the resulting residue was solidified with ether. The solids were filtered and washed with hexane (5 ml). Recrystallization from ether gave yellow crystals of 4, trans-[Pd(C≡CPh)(N≡C–C₆H₄–2,6-Me₂)₂(PMe₃)₂] (0.203 g, 57%). IR (KBr, cm⁻¹): 2175 (s, br, N≡C), 1722 (w, br, C≡C). ¹H NMR (CDCl₃, δ): 1.56 (t, 18 H, J = 3.5 Hz, PMe₃), 2.35 (s, Me), 6.67–6.72 (m, 1 H, Ph), 6.90–6.93 (m, 2 H, Ph), 6.93–7.31 (m, 5 H, Ph). ¹³C{¹H} NMR (CDCl₃, δ): 14.1 (t, J = 16 Hz, P(CH₂CH₃)₂), 18.9 (s, Me), 94.6 (s, br, C₈=C), 108.6 (s, J = 5.6 Hz, C₈=C), 119.4, 125.6, 126.6, 127.3, 130.4, 130.6, 143.8 (s, Ph). The carbon atom of tetrazolato ring, CN₄ and of 9, trans-[Pd(C≡CPh)(SCN₄–C₆H₃-2,6-Me₂)(PEt₃)₂] (0.227 g, 82%). IR (KBr, cm⁻¹): 2111 (s, C≡C), 1730 (s, br, CN₄). ¹H NMR (CDCl₃, δ): 1.18 (q, 18 H, J = 7.3 Hz, P(CH₂CH₃)₂), 2.04 (s, 9 H, C(CH₃)₃), 7.17–7.33 (m, 8 H, Ph). ¹³C{¹H} NMR (CDCl₃, δ): 8.38 (s, P(CH₂CH₃)₂), 15.7 (s, P(CH₂CH₃)₂), 17.7 (s, C₈=C), 108.1 (s, C₈=C), 125.7, 127.7, 128.4, 129.9, 130.7 (s, J = 2 Hz), 133.7, 136.1, 163.7 (s, CN₄). ³¹P{¹H} NMR (CDCl₃, δ): 15.1 (s). (Anal. Calc. for C₉H₃₈N₈P₁₂: C, 53.66; H, 6.83; N, 8.63. Found: C, 53.53; H, 6.74; N, 8.39%).

3.4. Reactions with organic isothiocyanates

To a Schlenk flask containing [Pd(N₃)(C≡CPh)(PET₃)₂] (0.207 g, 0.43 mmol) were added CH₂Cl₂ (2 ml) and 2,6-dimethylphenyl isothiocyanate (0.076 g, 0.47 mmol) in sequential order. After stirring for 18 h at room temperature, the reaction mixture was completely evaporated under vacuum and then the resulting residue was solidified with hexane. The solids were filtered and washed with hexane (5 ml × 2). Recrystallization from CH₂Cl₂/ether gave pale yellow crystals of 9, trans-[Pd(C≡CPh)(SCN₄–C₆H₄–2,6-Me₂)(PEt₃)₂] (0.227 g, 82%). IR (KBr, cm⁻¹): 2111 (s, C≡C). ¹H NMR (CDCl₃, δ): 1.18 (q, 18 H, J = 8.1 Hz, P(CH₂CH₃)₂), 1.92 (s, 9 H, C(CH₃)₃), 2.04 (s, 9 H, C(CH₃)₃), 7.17–7.33 (m, 8 H, Ph). ¹³C{¹H} NMR (CDCl₃, δ): 8.38 (s, P(CH₂CH₃)₂), 15.7 (s, P(CH₂CH₃)₂), 17.7 (s, C₈=C), 108.1 (s, C₈=C), 125.7, 127.7, 128.4, 129.9, 130.7 (s, J = 2 Hz), 133.7, 136.1, 163.7 (s, CN₄). ³¹P{¹H} NMR (CDCl₃, δ): 15.1 (s). (Anal. Calc. for C₉H₃₈N₈P₁₂: C, 53.66; H, 6.83; N, 8.63. Found: C, 53.53; H, 6.74; N, 8.39%).

Complex 8, trans-[Pd(C≡C–C(OMe)C₆H₄–2,6-Me₂)(PMe₃)₂] (86%). IR (KBr, cm⁻¹): 2110 (s, C≡C), 1694 (s, br, CO). ¹H NMR (CDCl₃, δ): 1.34 (t, 18 H, J = 3.7 Hz, PMe₃), 1.76 (s, 9 H, C(CH₃)₃), 3.70 (s, 3 H, Me). ¹³C{¹H} NMR (CDCl₃, δ): 15.3 (t, J = 16 Hz, P(CH₂CH₃)₂), 31.2 (s, C(CH₃)₃), 51.8 (s, Me), 57.7 (s, C(CH₃)₃), 101.4 (t, J = 3.7 Hz, C₈=C), 117.5 (t, J = 20 Hz, C₈=C), 154.2 (s, C(O)(O)), 164.0 (t, J = 9.2 Hz, C₈=C), 31P{¹H} NMR (CDCl₃, δ): −13.7 (s). (Anal. Calc. for C₉H₃₈N₈O₂P₁₂: C, 38.60; H, 6.48; N, 12.00. Found: C, 38.22; H, 6.47; N, 11.81%).
Complex 12. [{Pd}(C≡CH)Pd(SCN)2(μ-C6F5CN)]2 (37%). IR (KBr, cm−1): 2113 (s, C≡C), 17.9 (s). 

3.5. Reactions with organic nitriles

To a Schlenk flask containing complex 1 (0.258 g, 0.64 mmol) were sequentially added CH2Cl2 (3 ml) and C6F5CN (0.372 g, 1.92 mmol). After stirring for 14 h at room temperature, the reaction mixture was completely evaporated under vacuum, and then the resulting residue was solidified with ether. The solids were filtered and washed with hexane (3 ml × 2). Repeated recrystallization from CH2Cl2/hexane gave white crystals of 13, trans-{[Pd(C≡CPh)(N≡C-C6F5CN)](PMe3)2} (0.142 g, 37%). IR (KBr, cm−1): 2123 (s, C≡C). 

Complexes 17–19 were analogously prepared. Complex 17. [Pd(SCN)(PMe3)]2 (94%). IR (KBr, cm−1): 2107 (CN). 

Complex 18. [Pd(C≡CN)(depe)] (87%). IR (KBr, cm−1): 2127 (CN). 

Complex 19. [Ni(CN)3(P(Tol)3)] (86%). IR (KBr, cm−1): 2104 (CN). 

3.6. X-ray structure determination

All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of SHELXTL programs [33]. All structures were solved by direct methods. All non-hydrogen atoms were refined.
anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 232839–232842 for compounds 5, 6, 11, and 18. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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