ELSEVIER

Inorganica Chimica Acta 284 (1999) 205–214

Inorganica Chimica Acta

Synthesis and formation of metal complexes of 4-alkynyl and 4-cyano-2,6-diisopropylphenylisocyanides

Zhong-lin Lu[a], Andreas Mayr[b,*], Kung-Kai Cheung[a]

[a]*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China*
[b]*Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, USA*

Received 2 February 1998; accepted 6 May 1998
Dedicated to Professor Warren R. Roper on the occasion of his 60th birthday

Abstract

The 4-halo-2,6-diisopropyl-*N*-formylanilides HC(O)NH-C_6H_2-i-Pr_2-2,6-X-4, (**2a**) (X = Br) and **2b** (X = I), serve as precursors for the bromo-, iodo-, alkynyl- and cyano-substituted diisopropylphenylisocyanides CN-C_6H_2-i-Pr_2-2,6-X-4, (**3a**) (X = Br) and **3b** (X = I), CN-C_6H_2-i-Pr_2-2,6-R-4, (**6**) (R = C≡CSiMe_3), (**7**) (R = C≡CH), (**9**) (R = C≡C-C_6H_4-C≡CSiMe_3-4), **10** (R = C≡C-C_6H_4-C≡CH-4) and **12** (R = CN). The new isocyanides readily form complexes with several metal iodides: CoI_2L_4, **13** (L = **7**), MI_2L_2, **14–23** (M = Pd and Pt, L = **3a**, **3b**, **7**, **10**, **12**), and AuIL, **24** and **25** (L = **10** and **12**). The crystal structures of the complexes **13**, **15** (M = Pt, L = **3a**), and **22** (M = Pd, L = **12**) have been determined by X-ray crystallography.

Keywords: Isocyanide complexes; Alkyne complexes; Nitrile complexes; Crystal structures; Transition metal

1. Introduction

On account of their favorable steric and electronic properties, isocyanide metal complexes [1–10] are promising as building blocks for organometallic molecular materials. The most important structural and electronic element of metal isocyanides in this context is the presence of partial metal–carbon multiple bonds. Metal–carbon π interactions contribute towards the stability of metal–isocyanide linkages and they provide a mechanism for the electronic communication between the metal center and unsaturated isocyanide ligands [11–14]. Thus the metal center, as a single atom not only controls the overall geometry, but also exerts a dominant influence on the electronic properties of the building blocks. By connecting such isocyanide metal complexes in a stereochemically controlled and electronically coupled manner, one can expect to gain access to a variety of molecular materials with novel properties [15–31]. The type of molecular components most needed at present for the development of this type of materials chemistry are suitably functionalized isocyanides. We have recently demonstrated that metal complexes of isocyanides carrying nitrogen donor groups [32,33] or hydrogen-bonding groups [34] can serve as building blocks for the self-assembly of coordination polymers. The strategy for the synthesis of isocyanide metal complexes bearing hydrogen-bonding sites was based on the attachment of entire hydrogen-bonding groups to formyl-substituted arylisocyanides [34]. The significance of this procedure lies in its wide range of applicability. Due to the selective reactivity of aldehyde functionality, the procedure is suitable for the introduction of many types of functional groups into isocyanide metal complexes, before or after the establishment of the isocyanide metal complex core. In the course of this work, we found functionalized derivatives of 2,6-diisopropylphenylisocyanide to be particularly useful because of the relatively good solubility of metal complexes of this type of ligand. In an effort to further broaden the synthetic basis for the design of isocyanide metal complexes as building blocks for molecular materials, we present here several procedures for the introduction of functional groups into 2,6-diisopropylphenyl-isocyanides based on well-established transformations of bromo- and iodo-aryl compounds [35–39]. These types of transformations are particularly well suited to complement the previously developed method as far as the extension of the length and variation of the shapes of functionalized isocyanides is concerned.

2. Experimental

2,6-Diisopropylaniline, Me_3SiCCH, ICl, CoI_2, CuI, CuCN, PdI_2, $Pd(dba)_2$, $PdCl_2(PPh_3)_2$, PtI_2, and AuI were

*Corresponding author. Tel.: +1-516-632-7951; fax: +1-516-632-7960.

0020-1693/99/$ – see front matter
PII: S0020-1693(98)00288-6

purchased from commercial sources. 4-Iodo-1-trimethylsilylethynylbenzene was prepared as described in the literature [40]. 2,6-Diisopropylaniline was distilled prior to use. The metal halides were dried under vacuum for 1 h prior to use. THF, ether, CH_2Cl_2, and *n*-hexane were distilled under N_2 from appropriate drying agents. All other solvents and reagents were of analytical grade and were used as received, unless otherwise noted. The syntheses of the transition metal complexes were performed under an atmosphere of N_2. The NMR spectra were recorded at 300 MHz for ^1H NMR and 75.4 MHz for ^{13}C NMR. The elemental analyses were performed by the Analytical Laboratory of Peking University.

2.1. Syntheses

2.1.1. 2,6-Diisopropyl-4-bromo-1-formamidobenzene (**2a**)

To a stirred solution of 2,6-diisopropylaniline (20 ml, 106 mmol) in dichloromethane/methanol (1:1, v/v, 100 ml) is added a solution of bromine (5.5 ml, 108 mmol) in dichloromethane/methanol (1:1, v/v, 50 ml) dropwise via a pressure funnel at room temperature. After stirring for 12 h (reaction monitored by TLC), the solvent is evaporated. The solid is recrystallized with dichloromethane/*n*-hexane (2:1, v/v). 2,6-Diisopropyl-4-bromo-aniline hydrobromide is obtained as a white crystalline solid (28.7 g). Yield 80.3%. ^1H NMR ($CDCl_3$): δ 10.06 (br, 2H), 7.36 (s, 2H), 6.95 (br, 1H), 3.69 (m, 2H), 1.30 (d, 12H). 2,6-Diisopropyl-4-bromo-aniline hydrobromide (5.0 g, 15.0 mmol) is neutralized with 20% aqueous sodium hydroxide (25 ml) at room temperature for 1 h. The mixture is extracted with diethyl ether (3×60 ml). The combined extracts are dried over magnesium sulfate. After filtration and evaporation of the solvent, 2,6-diisopropyl-4-bromoaniline (**1a**) is obtained as a yellow oil (3.5 g). Yield 91.5%. ^1H NMR ($CDCl_3$): δ 7.11 (s, 2H), 3.68 (br, s, 2H), 2.89 (h, 2H), 1.25 (d, 12H).

A mixture of acetic anhydride (10.5 ml) and formic acid (10.5 ml) is heated for 2 h under 50–60°C with stirring. Then the solution is cooled to room temperature. 2,6-Diisopropyl-4-bromoaniline (13.9 g, 54.3 mmol) is dropped into this solution within a few minutes. Then diethyl ether (150 ml) is added. The resulting solution is stirred at room temperature for 24 h and neutralized to pH 7 with 10% aqueous sodium carbonate. The organic phase is dried over magnesium sulfate. After filtration and evaporation of the solvent, the product is obtained as a white solid which can be recrystallized from diethyl ether (13.5 g). Yield: 87.5%. ^1H NMR ($CDCl_3$), two isomers: δ 8.46 (d, $J = 1.32$ Hz) and 7.98 (d, $J = 11.79$ Hz) (CHO), 7.31 (s) and 7.30 (s) (2H, C_6H_2), 7.07 (d, $J = 11.85$ Hz) and 6.72 (s) (1H, NH), 3.17 (h) and 3.09 (h) (2H, CH); 1.20 (d, $J = 6.84$ Hz) and 1.19 (d, $J = 6.91$ Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$), two isomers: δ 164.7, 160.4, 149.2, 148.6, 129.0, 128.6, 127.9, 127.3, 127.1, 123.9, 123.3, 29.0, 28.6, 23.8, 23.4. IR (CH_2Cl_2, cm^{-1}): 1701, 1687 (NHCH=O). MS (EI): 283/285 (100%, M^+).

2.1.2. 2,6-Diisopropyl-4-iodo-1-formamidobenzene (**2b**)

First, 2,6-diisopropyl-4-iodoaniline (**1b**) is prepared following the procedure described for compound **1a**, using iodine monochloride instead of bromine: 2,6-diisopropylaniline (10 ml, 53 mmol), iodine monochloride (3 ml). The product is obtained as a light brown oil (14.0 g). Yield: 87.5%. ^1H NMR ($CDCl_3$): δ 7.28 (s, 2H, C_6H_2), 3.73 (br, s, 2H, NH_2), 2.84 (m, $J = 6.8$ Hz, 2H, CH), 1.24 (d, $J = 6.8$ Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$), 140.1, 135.0, 131.7, 81.1, 27.9, 22.2. Compound **2b** is then obtained following the procedure described for **2a**: **1b** (5.2 g, 17.2 mmol), acetic anhydride (3 ml) and formic acid (3 ml). The product is obtained as white crystalline solid (4.8 g). Yield: 84.5%. ^1H NMR ($CDCl_3$), two isomers: δ 8.43 (s) and 7.98 (d) (1H), 7.50 (s) and 7.49 (s) (2H), 7.27 (d) and 6.77 (s) (1H), 3.19–2.98 (m, 2H), 1.19 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 164.7 and 160.4 (NHCHO), 149.1, 148.6, 133.3, 133.1, 95.4, 28.8, 28.4, 23.4. IR (CH_2Cl_2, cm^{-1}): 1697 (C=O). MS (EI): 331 (100%, M^+).

2.1.3. 2,6-Diisopropyl-4-bromo-1-isocyanobenzene (**3a**)

To a stirred mixture of **2a** (1.0 g, 3.52 mmol) and Et_3N (0.6 ml) in THF (70 ml) is added a solution of triphosgene (0.349 g, 1.18 mmol) in THF (15 ml) at −78°C. The mixture is allowed to warm slowly to room temperature and is continued to be stirred for 20 h. Then aqueous sodium carbonate (10%, 25 ml) is added and the mixture is stirred for another hour. The mixture is evaporated under reduced pressure to remove THF. After adding more water, the mixture is extracted with chloroform (3 × 100 ml). The organic layers are combined, washed with water (2 × 50 ml), dried over magnesium sulfate, and the solvent is removed under vacuum. The compound is purified by chromatography on silica gel using *n*-hexane/dichloromethane (v/v, 100:5) as the eluent to afford a white crystalline solid (0.51 g, yield: 54%). ^1H NMR ($CDCl_3$): δ 7.29 (s, 2H, C_6H_2), 3.34 (h, $J = 6.9$ Hz, 2H, CH), 1.27 (d, $J = 6.9$ Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.0, 147.0, 126.8, 123.9, 29.9, 22.4. IR (CH_2Cl_2, cm^{-1}): 2120 (s, NC). *Anal*. Calc. for $C_{13}H_{16}BrN$: C, 58.66; H, 6.06; N, 5.26. Found: C, 58.57; H, 5.88; N, 5.26%.

2.1.4. 2,6-Diisopropyl-4-iodo-1-isocyanobenzene (**3b**)

3b is obtained following the procedure described for **3a**. **2b**, triphosgene (0.74 g, 2.49 mmol), Et_3N (1.4 ml), reaction time: 12 h, sodium carbonate (10%, 50 ml). The compound is purified by chromatography on silica gel using *n*-hexane/dichloromethane (v/v, 9:1) as the eluent to afford a white to very light yellow waxy or oily product (1.66 g, yield: 87.7%). ^1H NMR ($CDCl_3$): δ 7.48 (s, 2H, C_6H_2), 3.54–3.24 (h, $J = 6.9$ Hz, 2H, CH), 1.26 (d, $J = 6.9$ Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.2 (CN), 146.9, 132.8, 123.3, 96.1, 29.8, 22.5. IR (CH_2Cl_2, cm^{-1}): 2120 (NC). FAB-MS: 314 (100%, $(M+1)^+$). *Anal*. Calc. for $C_{13}H_{16}IN$: C, 49.86; H, 5.15; N, 4.47. Found: C, 50.04; H, 5.15; N, 4.37%.

2.1.5. 3,5-Diisopropyl-4-formamido-1-trimethylsilylethynylbenzene (**4**)

A flask containing **2a** (5.0 g, 17.6 mmol), bis(dibenzylideneacetone)palladium(0) (0.206 g), triphenylphosphine (0.472 g) and CuI (0.078 g) is evacuated and back-filled with nitrogen several times. Then triethylamine (60 ml) and trimethylsilylacetylene (3.0 ml) are added via a syringe. The mixture is stirred at 60–70°C for about 24 h under nitrogen. After the reaction is complete (monitored by TLC), the resulting mixture is cooled to room temperature, filtered through a plug of silica gel, and washed with diethyl ether (120 ml). The combined filtrates are washed with water and dried over magnesium sulfate. After evaporation of the solvent, the crude product is recrystallized from *n*-hexane to give an off-white crystalline solid, 4.12 g. Yield: 77.8%. The product can also be obtained in higher yields by using **2b** as the starting material. ^{1}H NMR ($CDCl_3$), two isomers: δ 8.47 (s) and 7.99 (d) (1H), 7.30 (s) and 7.29 (s) (2H), 6.85 (d) and 6.66 (s) (1H), 3.2–3.0 (m, 2H), 1.21 (d, 12H), 0.27 (s, 9H). ^{13}C NMR: δ 163.5, 147.3, 145.9, 128.1, 125.4, 104.7, 95.5, 29.0, 23.8, −0.1. IR (CH_2Cl_2, cm^{-1}): 2154 (C≡C), 1697 (C=O). MS (EI): 301 (75%, M^+), 329 (100%, $(M+28)^+$).

2.1.6. 3,5-Diisopropyl-4-formamido-1-ethynylbenzene (**5**)

A methanol solution (15 ml) of **4** (1.63 g, 5.42 mmol) is treated with potassium hydroxide (0.38 g/8 ml H_2O) for 2 h at room temperature. After hydrolysis is complete (monitored by TLC), methanol is removed under reduced pressure. Then more water is added, and the mixture is extracted with diethyl ether (2×50 ml). The combined extracts are washed with water and dried over magnesium sulfate. After evaporation of the solvent under reduced pressure, the product is obtained as a white or very light yellow solid (1.19 g, yield: 96%). ^{1}H NMR ($CDCl_3$), two isomers: δ 8.48 (s) and 8.01 (d, $J = 11.81$ Hz) (1H, 7.33 (s, 2H, C_6H_2), 7.13 (d, $J = 11.6$ Hz) and 6.77 (s) (1H), 3.23–3.00 (m, 3H, CH, CCH), 1.21 (d, $J = 6.9$ Hz, 12H, CH3). ^{13}C NMR ($CDCl_3$): δ 165.1, 160.5 (NHCHO), 146.9, 146.5, 130.7, 129.3, 127.8, 127.6, 122.6, 122.4, 83.8, 83.4, 28.8, 28.4, 23.47. FAB-MS: 230 (100%, $(M+1)^+$).

2.1.7. 3,5-Diisopropyl-4-isocyano-1-trimethylsilylethynylbenzene (**6**)

The compound is obtained following the procedure described for **3a**. Compound **4** (1.200 g, 3.98 mmol), triphosgene (0.45 g, 1.52 mmol), Et_3N (1.0 ml), reaction time: 17 h, potassium carbonate (10%, 30 ml). The compound is purified by chromatography on silica gel using *n*-hexane as the eluent (white solid, 0.906 g, yield: 80.3%). ^{1}H NMR ($CDCl_3$): δ 7.25 (s, 2H, C_6H_2), 3.33 (m, $J = 6.9$ Hz, 2H, CH), 1.26 (d, $J = 6.9$ Hz, 12H, CH_3), 0.28 (s, 9H, Si-CH_3). ^{13}C NMR ($CDCl_3$): δ 170.0 (CN), 145.2, 127.2, 124.2, 104.4, 96.2, 29.9, 22.55, 0.1. IR (CH_2Cl_2, cm^{-1}): 2147 (w, CC), 2118 (s, NC). FAB-MS: 284 (100%, $(M+1)^+$).

2.1.8. 3,5-Diisopropyl-4-isocyano-1-ethynylbenzene (**7**)

To a methanol (15 ml) solution of **6** (2.5 g, 10.1 mmol) potassium hydroxide (1 M, 15 ml) is added. The mixture is stirred for 2 h. Then the solvent is removed under vacuum, and the residue is extracted with diethyl ether (3 × 50 ml). The combined extracts are washed three times with water and dried over magnesium sulfate. After filtration, the solvent is evaporated to afford 2.0 g of the product. Yield: 93%. ^{1}H NMR ($CDCl_3$): δ 7.29 (s, 2H), 3.35 (h, $J = 6.9$ Hz, 2H), 3.16 (s, 1H), 1.27 (d, $J = 6.9$ Hz, 12H). ^{13}C NMR: δ 170.1, 145.2, 127.3, 123.2, 83.0, 78.8, 29.8, 22.4. IR (CH_2Cl_2, cm^{-1}): 3299 (CC–H), 2158 (CC), 2118 (–NC). FAB-MS: 212 (38%, $(M+1)^+$).

2.1.9. 4-(3,5-Diisopropyl-4-formamidophenyl)ethynyl-1-trimethylsilylethynylbenzene (**8**)

To a mixture of **5** (0.43 g, 1.88 mmol) and 4-iodo-1-trimethylsilylethynylbenzene (0.565 g, 1.99 mmol) in triethylamine (20 ml) are added bis(triphenylphosphine)-palladium dichloride (0.026 g, 0.038 mmol) and copper(I) iodide (0.007 g, 0.038 mmol). The reaction mixture is stirred at room temperature for 6 h under nitrogen. Then the solvent is removed under reduced pressure. The residue is extracted with diethyl ether (150 ml) and purified by chromatography on silica gel using ethyl acetate/*n*-hexane (1:2, v/v) as the eluent to afford 0.61 g of product. Yield: 81%. ^{1}H NMR ($CDCl_3$), two isomers: δ 8.48 (s) and 8.3 (d) (1H), 7.50–7.43 (m, 4H), 7.35 (s, 2H), 6.80 (d) and 6.68 (s) (1H), 3.24–3.06 (m, 2H), 1.23 (d, 12H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.8, 160.4, 146.9, 146.5, 137.6, 133.1, 131.9, 131.4, 130.2, 129.9, 127.3, 127.1, 123.5, 123.4, 123.3, 123.1, 123.0, 122.5, 104.6, 96.5, 94.4, 91.4, 91.0, 90.4, 89.4, 89.0, 28.8, 28.4, 23.5. IR (CH_2Cl_2, cm^{-1}): 3408 (N–H), 2156 (CC), 1697 (C=O). FAB-MS: 402 (100%, $(M+1)^+$).

2.1.10. 4-(3,5-Diisopropyl-4-isocyanophenyl)ethynyl-1-trimethylsilylethynyl benzene (**9**)

To a stirred mixture of **8** (0.71 g, 1.77 mmol) and Et_3N (0.84 ml) in dichloromethane (30 ml) is added triphosgene (0.200 g, 0.67 mmol) in dichloromethane (10 ml) at −198°C. The mixture is gradually warmed to room temperature and stirred for 6 h. Then 10% aqueous sodium carbonate (25 ml) is added and stirring is continued for another hour. The organic phase is separated and the aqueous layer is extracted with diethyl ether (3 × 50 ml). The combined organic layers are washed with water (2 × 40 ml), dried over magnesium sulfate, and evaporated. The residue is purified on a silica gel column using *n*-hexane/ethylacetate (1:4, v/v) as the eluent to give 0.61 g of product. Yield: 90%. ^{1}H NMR ($CDCl_3$): δ 7.46 (m, 4H), 7.31 (s, 2H), 3.41–3.32 (m, 2H), 1.30 (d, 12H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.1, 145.3, 132.0, 131.5, 126.7, 124.1, 123.4, 122.8, 104.5, 96.6, 90.6, 29.8, 22.5, 0.3. IR (CH_2Cl_2, cm^{-1}): 2152 (CC), 2116 (NC). FAB-MS: 384 (30%, $(M+1)^+$).

*2.1.11. 4-(3,5-Diisopropyl-4-isocyanophenyl)ethynyl-1-ethynylbenzene (**10**)*

The compound is prepared according to the procedure described for **7**. Thus **9** (0.61 g, 1.57 mmol) and 5 ml 1 M potassium hydroxide aqueous solution afford 0.45 g of product as a yellow solid. Yield: 91%. ^{1}H NMR ($CDCl_3$): δ 7.49 (m, 4H), 7.32 (s, 2H), 3.47–3.32 (m, 2H), 3.19 (s, 1H), 1.30 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 170.0, 145.3, 132.1, 131.5, 126.7, 124.0, 123.2, 122.3, 90.7, 90.4, 83.1, 79.2, 29.8, 22.5. IR (CH_2Cl_2, cm^{-1}): 3300 (C–H), 2117 (NC). FAB-MS: 312 (100%, $(M+1)^+$).

*2.1.12. 2,6-Diisopropyl-4-cyano-1-formamidobenzene (**11**)*

A stirred mixture of **2a** (4.05 g, 17.6 mmol), cuprous cyanide (1.81 g, 20.2 mmol) and dimethylformamide (50.0 ml) is refluxed for 6 h. The resulting brown mixture is poured (residues are transferred with hot dimethylformamide) into a solution of hydrated ferric chloride (12.0 g) and concentrated hydrochloric acid (20 ml) in water (120 ml), whereby the mixture is maintained at 60–70°C for 20 min. After cooling to room temperature, the mixture is extracted with diethyl ether (3 × 100 ml). The combined extracts are washed with dilute hydrochloric acid, water, and 10% aqueous sodium hydroxide. The organic layer is dried, filtered, and the solvent is removed under reduced pressure. The crude product is purified on a silica gel column using *n*-hexane/ethyl acetate (2:1, v/v) as the eluent to afford 2.74 g of white solid product. Yield: 84%. ^{1}H NMR ($CDCl_3$), two isomers: δ 8.49 (d) and 8.04 (d, $J = 11.47$ Hz) (1H, CHO), 7.49 and 7.48 (2H, C_6H_2); 7.28 (d, $J = 12.67$ Hz) and 6.92 (s) (1H, NH), 3.27–3.08 (m, 2H), 1.22–1.19 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 146.5, 127.5, 118.2, 113.3, 30.0, 22.3. IR (CH_2Cl_2, cm^{-1}): 3408 (N–H), 2233 (CN), 1699 (C = O). MS (EI): 230 (100%, M^+).

*2.1.13. 3,5-Diisopropyl-4-isocyanobenzonitrile(**12**)*

To a solution of **11** (2.0 g, 8.8 mmol) and diisopropylamine (3.3 ml, 23.2 mmol) in CH_2Cl_2 (100 ml), phosphoryl oxychloride (0.85 ml, 9.1 mmol) in CH_2Cl_2 (10 ml) is added dropwise with stirring at −5–0°C and stirred for another 1 h. Then a solution of sodium carbonate (3.0 g) in water (30 ml) is added at a slow rate to ensure that the temperature of the mixture does not rise above 30°C. After stirring for 1 h at room temperature, more water (50 ml) and CH_2Cl_2 (100 ml) are added. The organic layer is separated and washed with water (3 × 50 ml). The solvent is removed under reduced pressure and the residue is purified by column chromatography on silica gel, using *n*-hexane/CH_2Cl_2 (1:1, v/v) as the eluent (1.37 g, yield: 74%). The product can also be obtained in a similar yield by dehydration of **11** with triphosgene/NEt_3. ^{1}H NMR ($CDCl_3$): δ 7.47 (s, 2H), 3.40 (h, 2H), 1.30 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 146.5, 127.5, 118.2, 113.3, 30.0, 22.3. IR (CH_2Cl_2, cm^{-1}): 2233 (w, –CN), 2115 (s, –NC). MS (EI): 212 (34%, M^+), 197 (100%, $(M-15)^+$).

*2.1.14. trans-[CoI_2(4-CN-3,5-diisopropyl-$C_6H_2CCH)_4$] (**13**)*

CoI_2 (18.0 mg, 0.058 mmol) is dissolved in absolute ethanol to give a blue solution. Upon addition of **7** (50.0 mg, 0.237 mmol), the solution turns dark brown immediately. After the mixture is stirred for 12 h, the solvent is removed under reduced pressure, and the residue is washed with *n*-hexane/diethyl ether. A dark brown solid is isolated by filtration (48.0 mg, yield: 71%). Brown crystals are obtained from CH_2Cl_2/hexane. ^{1}H NMR ($CDCl_3$): δ 3.5. (br), 1.4 (br). IR (CH_2Cl_2, cm^{-1}): 3300 (C–H), 2170 (NC).

*2.1.15. trans-[PdI_2(CN-C_6H_2-3,5-diisopropyl-4-Br)$_2$] (**14**)*

A 50 ml flask is charged with **3a** (48.3 mg, 0.18 mmol) and PdI_2 (33 mg, 0.09 mmol). The flask is evacuated and back-filled with nitrogen three times, and CH_2Cl_2 (20 ml) is added. The mixture is stirred at room temperature for 12 h. The solution is filtered, and the solvent is removed under vacuum. The brown residue is washed with *n*-hexane and collected by filtration (65 mg). Yield: 70%. ^{1}H NMR ($CDCl_3$): δ 7.35 (s, 2H, C_6H_2), 3.52 (h, 2H, CH), 1.32 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 148.9, 127.3, 126.2, 29.8. IR (CH_2Cl_2, cm^{-1}): 2197 (s, –NC). *Anal*. Calc. for $C_{26}H_{32}Br_2I_2N_2Pd$: C, 34.96; H, 3.59; N, 3.14. Found: C, 35.22; H, 3.50; N, 2.97%.

*2.1.16. trans-[PtI_2(CN-C_6H_2-2,6-diisopropyl-4-Br)$_2$] (**15**)*

The procedure for the synthesis of **14** is followed. Thus, reaction of PtI_2 (30.0 mg, 0.067 mmol) and **3a** (35.6 mg, 0.134 mmol) in 20 ml methylene chloride gives an orange solid (32 mg). Yield: 49%. ^{1}H NMR ($CDCl_3$): δ 7.35, 3.52, 1.32. ^{13}C NMR ($CDCl_3$): δ 149.3, 127.2, 126.2, 30.0, 22.7. IR (CH_2Cl_2, cm^{-1}): 2191 (s, –NC). *Anal*. Calc. for $C_{26}H_{32}Br_2I_2N_2Pt$: C, 31.80; H, 3.26; N, 2.85. Found: C, 31.86; H, 3.10; N, 2.66%.

*2.1.17. trans-[PdI_2(CN-C_6H_2-2,6-diisopropyl-4-I)$_2$] (**16**)*

The procedure for the synthesis of **14** is followed. ^{1}H NMR ($CDCl_3$): δ 7.35, 3.48, 1.32. ^{13}C NMR ($CDCl_3$): δ 148.6, 133.4, 98.7, 29.6, 22.8. IR (CH_2Cl_2, cm^{-1}): 2195 (s, –NC). *Anal*. Calc. for $C_{26}H_{32}I_4N_2Pd$: C, 31.63; H, 3.24; N, 2.84. Found: C, 31.77; H, 3.18; N, 2.49%.

*2.1.18. trans-[PtI_2(CN-C_6H_2-2,6-diisopropyl-4-I)$_2$] (**17**)*

The procedure for the synthesis of **14** is followed. ^{1}H NMR ($CDCl_3$): δ 7.55, 3.48, 1.31. ^{13}C NMR ($CDCl_3$): δ 148.6, 133.4, 98.5, 29.6, 22.8. IR (CH_2Cl_2, cm^{-1}): 2189 (s, –NC). *Anal*. Calc. for $C_{26}H_{32}I_4N_2Pt$: C, 29.02; H, 2.98; N, 2.60. Found: C, 29.26; H, 2.95; N, 2.23%.

*2.1.19. trans-[PdI_2(4-CN-3,5-diisopropyl-$C_6H_2CCH)_2$](**18**)*

The procedure for the synthesis of **14** is followed. Thus, reaction of PdI_2 (45.0 mg, 0.125 mmol) and **7** (55.0 mg, 0.260 mmol) in 20 ml methylene chloride gives an orange

solid (60.0 mg). Yield: 61%. ^{1}H NMR ($CDCl_3$): δ 7.34 (s, 2H), 3.53 (h, 2H), 3.23 (s, 1H), 1.33 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 147.2, 127.6, 125.1, 123.4, 82.7, 80.0, 29.6, 22.8. IR (CH_2Cl_2, cm^{-1}): 3300 (C–H), 2196 (NC). *Anal*. Calc. for $C_{30}H_{34}I_2N_2Pd$: C, 46.01; H, 4.35; N, 3.59. Found: C, 46.08; H, 4.34; N, 3.47%.

2.1.20. *trans-[PtI$_2$(4-CN-3,5-diisopropyl-C$_6$H$_2$CCH)$_2$] (**19**)*

The procedure for the synthesis of **14** is followed. Thus PtI_2 (33.0 mg, 0.074 mmol) and **7** (31.5 mg, 0.260 mmol) in 20 ml methylene chloride afford an orange solid (40.0 mg). Yield: 62%. ^{1}H NMR ($CDCl_3$): δ 7.37 (s, 2H), 3.53 (h, 2H), 3.30 (s, 1H), 1.32 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 147.6, 128.1, 125.3, 83.0, 80.1, 30.0, 22.9. IR (CH_2Cl_2, cm^{-1}): 3300 (C–H), 2189 (NC). *Anal*. Calc. for $C_{30}H_{34}I_2N_2Pt$: C, 41.33; H, 3.90; N, 3.21. Found: C, 41.55; H, 3.91; N, 2.62%.

2.1.21. *trans-[PdI$_2$(4-(4-CN-3,5-diisopropyl-C$_6$H$_2$CC)-C$_6$H$_4$-CCH)$_2$] (**20**)*

The procedure for the synthesis of **14** is followed. Reaction of PdI_2 (20.0 mg, 0.055 mmol) and **10** (34.6 mg, 0.111 mmol) affords a yellow product (32.0 mg). Yield: 51%. $C_{46}H_{42}PdI_2N_2$, FW: ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 4H), 7.37 (s, 2H), 3.54 (m, 2H), 3.20 (s, 1H), 1.27 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 147.2, 132.2, 131.6, 127.1, 126.0, 122.9, 122.6, 91.6, 90.4, 83.1, 79.3, 29.7, 22.9. IR (CH_2Cl_2, cm^{-1}): 2193 (–NC), 3290 (CC–H). *Anal*. Calc. for $C_{46}H_{42}Br_2I_2N_2Pd{\cdot}0.5\ C_6H_4$: C, 57.33; H, 4.78; N, 2.73. Found: C, 57.75; H, 4.75; N, 2.22%.

2.1.22. *trans-[PtI$_2$(4-(4-CN-3,5-diisopropyl-C$_6$H$_2$CC)-C$_6$H$_4$-CCH)$_2$] (**21**)*

The procedure for the synthesis of **14** is followed. ^{1}H NMR (CD_2Cl_2): δ 7.43 (m, 4H), 7.34 (s, 2H), 3.48 (m, 2H), 3.19 (s, 1H), 1.27 (d, 12H). ^{13}C NMR (CD_2Cl_2): δ 147.6, 132.6, 132.1, 127.6, 126.2, 123.4, 122.9, 110.1, 91.7, 90.8, 83.3, 79.6, 30.0, 23.0. IR (CH_2Cl_2, cm^{-1}): 3292, (w, CC–H), 2189 (NC). *Anal*. Calc. for $C_{46}H_{42}Br_2I_2N_2Pt{\cdot}0.5\ C_6H_4$: C, 52.78; H, 4.39; N, 2.51. Found: C, 52.35; H, 4.32; N, 1.93%.

2.1.23. *trans-[PdI$_2$(4-CN-3,5-diisopropyl-C$_6$H$_2$CN)$_2$] (**22**)*

The procedure for the synthesis of **14** is followed. Reaction of PdI_2 (33.9 mg, 0.094 mmol) and **12** (42 mg, 0.197 mmol) in dichloromethane to give 53.0 mg orange–yellow solid. Yield: 72%. ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 2H), 3.58 (h, 2H), 1.36 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 148.5, 127.9, 117.7, 115.2, 29.9, 22.7. IR (CH_2Cl_2, cm^{-1}): 2196 (–NC), 2233 (CN). *Anal*. Calc. for $C_{28}H_{32}I_2N_4Pd$: C, 42.83; H, 4.08; N, 7.14. Found: C, 42.64; H, 3.91; N, 7.03%.

2.1.24. *trans-[PtI$_2$(4-CN-3,5-diisopropyl-C$_6$H$_2$CN)$_2$] (**23**)*

The procedure for the synthesis of **14** is followed. Reaction of PtI_2 (33.3 mg, 0.074 mmol) and **12** (32.0 mg, 0.150 mmol) in dichloromethane to give 36 mg green–yellow solid. Yield: 56%. ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 2H), 3.58 (h, 2H), 1.36 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 148.4, 127.9, 117.8. 115.0, 29.8, 22.7. IR (CH_2Cl_2, cm^{-1}): 2187 (–NC), 2234 (CN). *Anal*. Calc. for $C_{28}H_{32}I_2N_4Pt$: C, 38.48; H, 3.67; N, 6.41. Found: C, 38.31; H, 3.53; N, 6.30%.

2.1.25. *[AuI(4-(4-CN-3,5-diisopropyl-C$_6$H$_2$CC)-C$_6$H$_4$-CCH)] (**24**)*

A 50 ml flask is charged with **10** (21.0 mg, 0.067 mmol) and AuI (20 mg, 0.062 mmol). The flask is evacuated and back-filled with nitrogen three times, and THF (20 ml) is added. The mixture is stirred at room temperature for 4 h. The solution is filtered, and the solvent is removed under vacuum. The off-white residue is washed with *n*-hexane and collected by filtration (30.5 mg). Yield: 78%. ^{1}H NMR ($CDCl_3$): δ 7.50 (s, 4H), 7.37 (s, 2H), 3.28–3.18 (m, 2H), 3.20 (s, 1H), 1.34–1.32 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 146.6, 132.2, 131.6, 127.3, 126.7, 122.8, 122.7, 92.3, 83.0, 79.5, 30.1, 22.5. IR (CH_2Cl_2, cm^{-1}): 3300 (w, CH), 2197 (s, NC).

2.1.26. *[AuI(4-CN-3,5-diisopropyl-C$_6$H$_2$CN)] (**25**)*

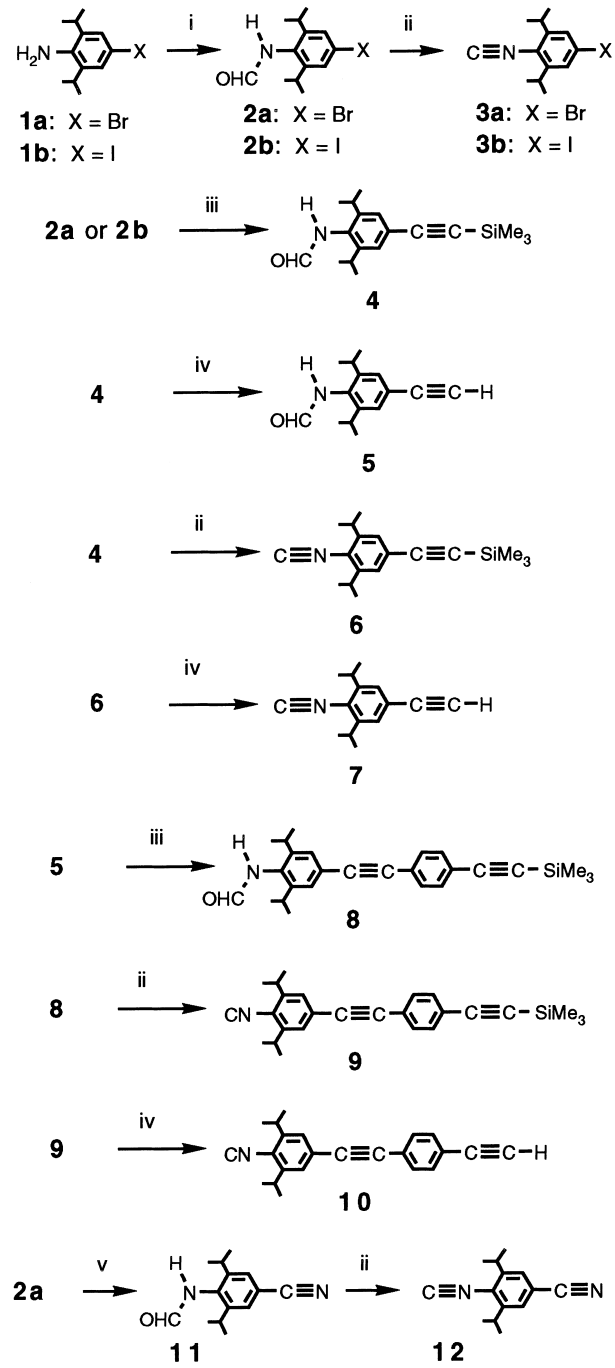
The complex is synthesized according to the method for **24**. Thus AuI (34.6 mg, 0.107 mmol) and **12** (25.6 mg, 0.120 mmol) in 50 ml THF afford 34.0 mg of product. Yield: 60%. ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 2H), 3.32–3.23 (m, 2H), 1.35–1.32 (d, 12H). IR (CH_2Cl_2, cm^{-1}): 2200 (–NC), 2233 (CN).

2.2. Crystal structure determinations

The diffraction data for compound **22** were collected on an MAR Imaging Plate Detector System using X-ray radiation from a MAR generator (sealed tube 50 kV and 50 mA), and processed by DENZO [41]. The diffraction data for compound **13** were collected on a Rigaku AFC7R four-circle diffractometer using X-ray radiation from a Rigaku RU-200 rotating-anode generator at 50 kV and 160 mA and processed by the MSC/RIGAKU diffractometer control software. The diffraction data for compound **15** were collected on a Enraf-Nonius CAD4 four-circle diffractometer using X-ray radiation from a sealed tube (50 kV and 26 mA) and processed by the CAD4 software (PC version). The X-ray radiation from all three generators was graphite-monochromatized Mo Kα X-ray radiation ($\lambda = 0.71073$Å). Empirical absorption corrections from ψ-scans were applied to the data for compounds **13** and **15** and no absorption correction was made on compound **22**. All structure determinations and numerical calculations were made using the MSC crystal structure analysis package-TeXsan [42] using a Silicon Graphic Computer, and the full-matrix least–squares refinements were on F using reflections with $I > 3\sigma(I)$. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculations, but not refined.

3. Results and discussion

The 4-bromo- and 4-iodo-2,6-diisopropylanilines **1a** and **1b** were chosen as the starting materials for the present study and prepared by treatment of 2,6-diisopropylaniline with bromine and iodine monochloride [43], respectively (Scheme 1). Formylation of **1a** and **1b** with formic acetic anhydride affords the formamides **2a** and **2b**, which are dehydrated to give the isocyanides **3a** and **3b** [44,45].



Scheme 1. (i) formic acetic anhydride; (ii) triphosgene/triethylamine; (iii) 4-$IC_6H_4CCSiMe_3/PdCl_2(PPh_3)_2$/CuI; (iv) KOH; (v) CuCN.

Substitution of the halogens in **2a** and **2b** by the trimethylsilylalkynyl group to afford **4** is achieved by cross-coupling with trimethylsilyacetylene in the presence of catalytic amounts of bis(dibenzylideneacetone)palladium(0) and copper(I) iodide [39–41]. Treatment of **4** with aqueous KOH affords acetylene **5**, which is dehydrated to give the 4-isocyanophenylacetylene **7**. Compound **7** can also be obtained from **4** by reversing the hydrolysis and dehydration steps, via the 4-isocyano-1-trimethylsilylethynylbenzene **6**. The extended trimethylsilylphenylacetylene derivative **8** is obtained by reaction of **5** with 4-iodophenyl(trimethylsilyl)acetylene [40] under conditions similar to those employed in the synthesis of compound **4**. Dehydration of **8** and subsequent desilylation affords the extended isocyanophenylacetylene derivatives **9** and **10**. The 4-isocyanobenzonitrile **12** is obtained in two steps from **2a** by sequential treatment with copper(I) cyanide and dehydration with triphosgene/triethylamine.

The new isocyanides **3**, **6**, **7**, **9**, **10**, and **12** are characterized by a strong absorption in the IR near 2120 cm^{-1} [1–10]. The acetylene groups of compounds **4**–**10** give rise to weak bands near 2150 cm^{-1} [46]. The nitrile derivatives **11** and **12** exhibit weak absorptions at around 2230 cm^{-1} for the nitrile groups [47,48].

In contrast to the isocyanide ligands bearing nitrogen donor groups or hydrogen-bonding groups which we have synthesized previously, the alkynyl groups of the ligands **7** and **10** are not suitable for reversible self-assembly processes. These ligands are, however, useful for the construction of larger discrete polymetallic units or polymeric metal complexes by means of establishing metal–alkynyl links [31,49–54]. Several oligomeric and polymeric metal complexes based on the isocyanophenylacetylide ligands 4-CNC_6H_4CC and 3-Me-4-CNC_6H_3CC have recently been described by Puddephatt and co-workers [24].

Due to the presence of the bulky isopropyl substituents, metal complexes of the new isocyanides can be expected to possess both increased stability and higher solubility than complexes of isocyanides without alkyl substituents. The relatively low solubility of some metal complexes of unsubstituted isocyanobenzonitriles has previously made it difficult, in several cases, to obtain coordination polymers. It is hoped that the higher solubility of metal complexes of the bulkier isocyanide **12** will facilitate the formation of crystalline coordination polymers by molecular self-assembly.

As expected, the new isocyanides readily form transition metal complexes (Scheme 2). The isocyanide **7** combines with cobalt(II) iodide to afford complex **13**. The isocyanides **3**, **7**, **10**, and **12** combine with palladium(II) iodide and platinum(II) iodide to afford the complexes **14**–**23**. The gold complexes **24** and **25** were prepared by addition of **10** and **12** to gold(I) iodide.

Due to the *trans* arrangement of the iodide ligands in complexes **13**–**23**, the four isocyanide ligands in **13** are arranged in equatorial fashion and the two isocyanide ligands in complexes **14**–**23** are mutually *trans*. Thus the

CoI_2 + 4L ⟶ trans-$CoI_2(CNR)_4$

13: CNR = **7**

MI_2 + 2L ⟶ trans-$MI_2(CNR)_2$

M = Pd, Pt

14: M = Pd; CNR = **3a**
15: M = Pt; CNR = **3a**
16: M = Pd; CNR = **3b**
17: M = Pt; CNR = **3b**
18: M = Pd; CNR = **7**
19: M = Pt; CNR = **7**
20: M = Pd; CNR = **10**
21: M = Pt; CNR = **10**
22: M = Pd; CNR = **12**
23: M = Pt; CNR = **12**

AuI + L ⟶ AuI(CNR)

24: CNR = **10**
25: CNR = **12**

Scheme 2.

IR spectra of these compounds exhibit only single absorptions for the isocyanide ligands. Upon coordination to the metal centers, the stretching frequencies of the isocyanide ligands experience a characteristic shift to higher energies, by about 50 cm^{-1} for Co(II) and 70–80 cm^{-1} for Pd(II), Pt(II), and Au(I) [1–10]. Only single sets of NMR signals are observed for the isocyanide ligands in all complexes **13**–**25**.

The molecular structures of complexes **13**, **15**, and **22** were established by X-ray crystallography. The crystallographic data are collected in Table 1, selected bond distances and bond angles are listed in Table 2. Drawings of the molecular structures are shown in Fig. 1. The intramolecular geometric parameters of the compounds **13**, **15**, and **22** are unexceptional. All bond distances and bond angles are within the ranges established for the respective types of isocyanide metal complex [55–57]. Noteworthy is a special feature of the crystal packing of the cobalt complex **13**. As shown in Fig. 2, the molecular units are arranged in a way that the alkynyl carbon atoms C(9), C(24), and the iodide atom I(1) of three adjacent molecular units form a close triangle with intermolecular distances of I(1)···C(9) 3.845(0) Å, I(1)···C(24) 4.37(1) Å, and C(9)···C(24) 3.98(1) Å. The two shorter of these distances, namely, I(1)···C(9) and C(9)···C(24), suggest the presence of hydrogen bonds involving the C≡C–H groups. The orientations of the terminal acetylene groups indicate that C(8)≡C(9)–H serves as a hydrogen bond donor towards I(1) [I(1)–C(9)–C(8) = 158.3(7)°] and C(23)≡C(24)–H as a hydrogen bond donor towards π(C(8)≡C(9)) [C(8)–C(24)–C(23) = 165.1(9)° C(8)–C(9)–C(24) = 95.8(7)°]. Thus the acetylene group C(8)≡C(9)–H acts both as a

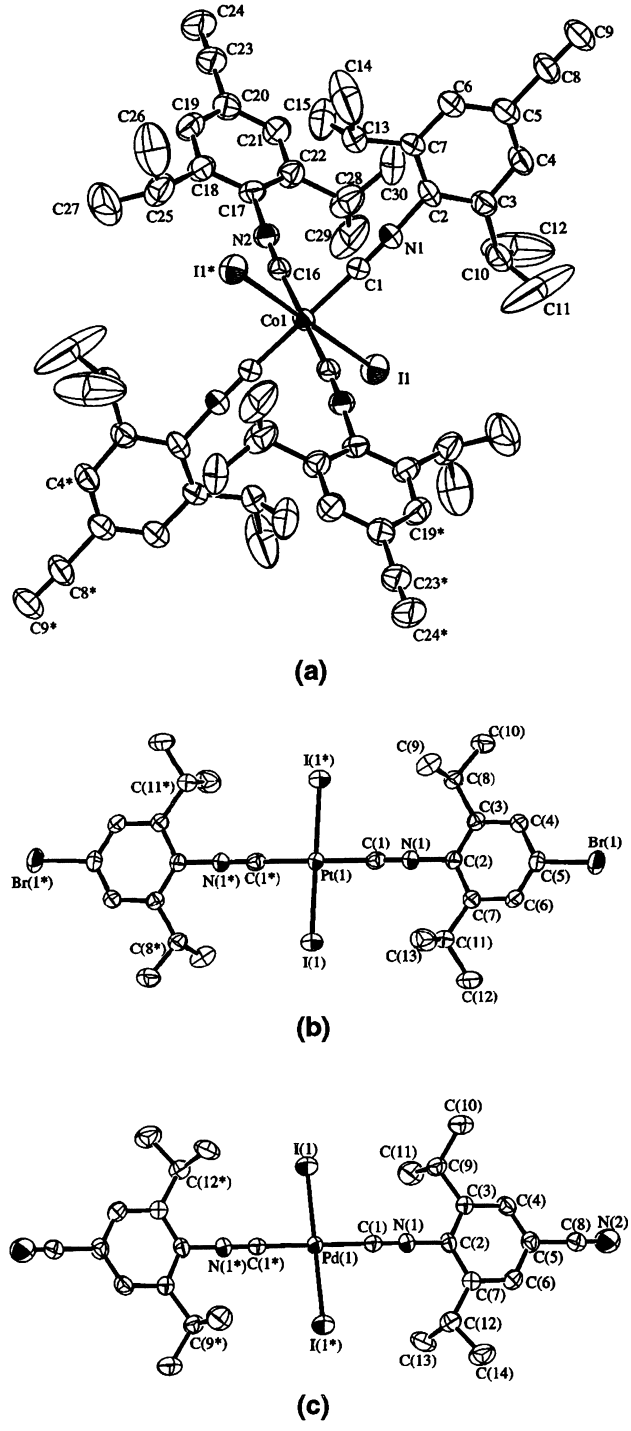


Fig. 1. (a) Molecular structure of complex **13**. (b) Molecular structure of complex **15**. (c) Molecular structure of complex **22**. The thermal ellipsoids are shown at the 50% probability level.

hydrogen bond donor and acceptor. Hydrogen bonds involving C≡C triple bonds as acceptors and CC–H groups as donors are very weak, but several examples have been well documented in recent studies [58,59]. The ability of iodide ligands in iodometal isocyanide complexes to serve as hydrogen bond acceptors has previously been found in the complex [FeI_2(CN-C_6H_3-2,6-Me_2-4-CHNOH)$_4$], where

Table 1
Crystal and data collection parameters for complexes **13**, **15**, and **22**

	13	**15**	**22**
Formula	$C_{60}H_{68}CoI_2N_4O_4{\cdot}CH_2Cl_2$	$C_{26}H_{32}Br_2N_2Pt$	$C_{28}H_{32}I_2N_4Pd$
Formula weight	1242.90	981.26	784.80
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P1$ (No. 2)
a (Å)	11.36(1)	20.015(4)	8.578(2)
b (Å)	21.351(9)	8.478(2)	9.585(2)
c (Å)	13.649(10)	18.880(2)	10.770(2)
α (°)			66.80(2)
β (°)	102.04(6)	110.32(2)	67.45(2)
γ (°)			83.06(2)
V (Å)^3	3236(3)	3004.4(9)	751.2(4)
Z	2	4	1
T (K)	301	301	301
Crystal color	reddish brown	yellow	orange
Crystal dimensions (mm)	0.20×0.10×0.40	0.20×0.05×0.35	0.15×0.05×0.30
d (calc) (g cm^{-3})	1.275	2.169	1.735
μ (cm^{-1})	13.38	93.92	26.96
Scan mode	ω-2θ	ω-2θ	ω-2θ
2θ max. (°)	50.0	49.9	51.2
Unique reflections	5869	2833	2453
Reflections ($I>3\sigma(I)$) used in least-squares refinement	3041	2056	1733
No. of variables	316	151	160
R	0.042[a]	0.028[a]	0.032[a]
R_w	0.051[b]	0.036[b]	0.040[b]
p-factor	0.021	0.016	0.019
(Δ/σ) max	0.05	0.01	0.01
Goodness-of-fit	1.72	2.24	1.62
$\Delta\rho$, e Å^{-3}	−0.55/0.77	−1.33/0.48	−0.35/0.65

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma_w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w = F_o^2/[\sigma^2(I)+(pF_o^2)^2]$.

Table 2

(a) Selected bond lengths (Å) and bond angles (°) for complex **13**			
Co(1)–I(1)	2.8448(7)	Co(1)–C(1)	1.850(6)
Co(1)–C(16)	1.849(7)	N(1)–C(1)	1.139(7)
N(1)–C(2)	1.414(8)	N(2)–C(16)	1.151(7)
N(2)–C(17)	1.410(8)	C(5)–C(8)	1.441(9)
C(8)–C(9)	1.148(9)	C(20)–C(23)	1.43(1)
C(23)–C(24)	1.137(10)		
I(1)–Co(1)–C(1)	89.7(2)	I(1)–Co(1)–C(16)	91.4(2)
C(1)–Co(1)–C(16)	92.6(3)	Co(1)–C(1)–N(1)	175.5(6)
Co(1)–C(16)–N(2)	175.6(6)		
(b) Selected bond lengths (Å) and bond angles (°) for complex **15**			
Pt(1)–I(1)	2.6054(7)	Pt(1)–C(1)	1.946(6)
Br(1)–C(5)	1.900(6)	N(1)–C(1)	1.146(8)
N(1)–C(2)	1.395(7)		
I(1)–Pt(1)–C(1)	90.7(2)	Pt(1)–C(1)–N(1)	179.2(6)
(c) Selected bond lengths (Å) and bond angles (°) for compound **22**			
Pd(1)–I(1)	2.5905(3)	Pd(1)–C(1)	1.960(5)
N(1)–C(1)	1.137(6)	N(1)–C(2)	1.406(6)
N(2)–C(8)	1.020(6)	C(5)–C(8)	1.517(7)
I(1)–Pd(1)–C(1)	89.7(1)	Pd(1)–C(1)–N(1)	179.6(4)

the oxime groups of one pair of mutually *trans* isocyanide ligands form O···I contacts of 3.59(1) Å [34]. The hydrogen bond distances found in the structure of **13** are perhaps somewhat longer than one might expect for the respective types of interactions. Also, the hydrogen bonds are probably not optimized in terms of the intermolecular distances and the direction of the approach of the C–H bonds towards the acceptor groups, that is, C(23)C(24)–H does not point towards the midpoint of the C(8)≡C(9) triple bond, and C(8)C(9)–H does not point directly towards the iodide ligand.

4. Conclusions

Several new alkynyl- and cyano-substituted diisopropylphenylisocyanides have been prepared from 4-bromo- and 4-iodo-2,6-diisopropylphenylformamide as precursors, utilizing palladium-catalyzed cross-coupling and copper-mediated substitution reactions. The 4-alkynylphenylisocyanide ligands in complexes **13** and **14**–**23** are arranged in square planar and linear arrangements, respectively. The terminal acetylene groups are oriented exactly along the extended coordination axes of the transition metal centers. Thus it should be possible, via established metal acetylide

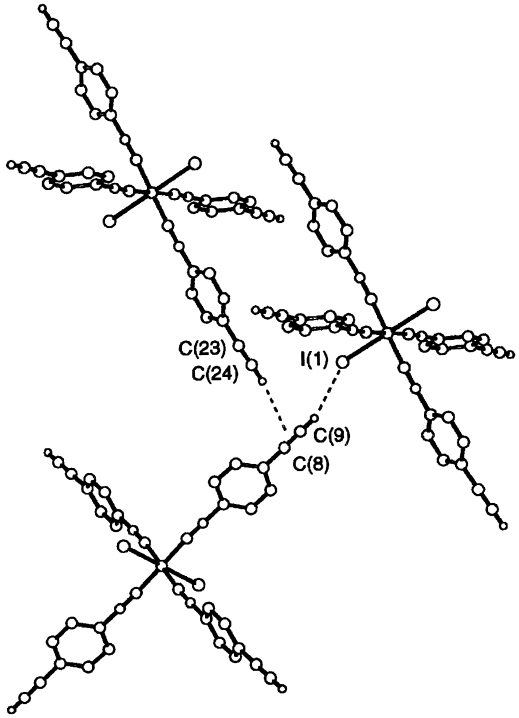


Fig. 2. Three adjacent molecular units in the solid-state structure of **13**. The intermolecular contacts involving the terminal acetylene groups are indicated by dotted lines.

chemistry, to create directional connections with additional metal complex fragments in order to create larger transition metal complex building blocks of exactly defined geometric shapes.

Acknowledgements

Support for this work by the Research Grants Council of Hong Kong (RGC) and by the Committee on Research and Conference Grants (CRCG) of The University of Hong Kong is gratefully acknowledged. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation.

References

[1] L. Malatesta, F. Bonati, Isocyanide Complexes of Transition Metals, Wiley, New York, 1969.
[2] P.M. Treichel, Adv. Organomet. Chem. 11 (1973) 21.
[3] S.J. Lippard, Prog. Inorg. Chem. 21 (1976) 91.
[4] Y. Yamamoto, Coord. Chem. Rev. 32 (1980) 193.
[5] E. Singleton, H.E. Oosthuizen, Adv. Organomet. Chem. 22 (1983) 209.
[6] W.P. Fehlhammer, M. Fritz, Chem. Rev. 93 (1993) 1243.
[7] F.E. Hahn, Angew. Chem. 105 (1993) 681.
[8] F.E. Hahn, Angew. Chem., Int. Ed. Engl. 32 (1993) 650.
[9] D. Lentz, Angew. Chem. 106 (1994) 1377.
[10] D. Lentz, Angew. Chem., Int. Ed. Engl. 33 (1994) 1315.
[11] I.S. Sigal, H.B. Gray, J. Am. Chem. Soc. 103 (1981) 2220.
[12] D.S. Grubisha, J.S. Rommel, T.M. Lane, W.T. Tysoe, D.W. Bennett, Inorg. Chem. 31 (1992) 5022.
[13] R.F. Johnston, J. Coord. Chem. 31 (1994) 57.
[14] H. Xiao, K.-K. Cheung, C.-M. Che, J. Chem. Soc., Dalton Trans. (1996) 3699.
[15] A. Efraty, I. Feinstein, F. Frolow, L. Wackerle, J. Am. Chem. Soc. 102 (1980) 6341.
[16] A. Efraty, I. Feinstein, L. Wackerle, F. Frolow, Angew. Chem., Int. Ed. Engl. 19 (1980) 633.
[17] A. Efraty, I. Feinstein, L. Wackerle, F. Frolov, Angew. Chem. 92 (1980) 649.
[18] A. Efraty, I. Feinstein, F. Frolow, A. Goldman, J. Chem. Soc., Chem. Commun. (1980) 864.
[19] U. Keppeler, O. Schneider, W. Stöffler, M. Hanack, Tetrahedron Lett. 25 (1984) 3679.
[20] I. Feinstein-Jaffe, F. Frolow, L. Wackerle, A. Goldman, A. Efraty, J. Chem. Soc., Dalton Trans. (1988) 469.
[21] U. Keppeler, M. Hanack, Chem. Ber. 119 (1986) 3363.
[22] M. Hanack, S. Deger, A. Lange, Coord. Chem. Rev. 83 (1988) 115.
[23] M.J. Irwin, L.M. Rendina, J.J. Vittal, R.J. Puddephatt, J. Chem. Soc., Chem. Commun. (1996) 1281.
[24] G. Jia, R.J. Puddephatt, J.J. Vittal, N.C. Payne, Organometallics 12 (1993) 263.
[25] R. Tannenbaum, Chem. Mater. 6 (1994) 550.
[26] T. Kaharu, T. Tanaka, M. Sawada, S. Takahashi, J. Chem. Mat. 4 (1994) 859.
[27] M. Benouazzane, S. Coco, P. Espinet, J.M. Martín-Alvarez, J. Chem. Mat. 5 (1995) 441.
[28] M.J. Irwin, G. Jia, J.J. Vittal, R.J. Puddephatt, Organometallics 15 (1996) 5321.
[29] D. Fortin, M. Drouin, M. Turcotte, P.D. Harvey, J. Am. Chem. Soc. 119 (1997) 531.
[30] C.A. Daws, C.L. Exstrom, J.R. Sowa, K.R. Mann, Chem. Mat. 9 (1997) 363.
[31] M.J. Irwin, L. Manojloć-Muir, K.W. Muir, R.J. Puddephatt, D.S.J. Yufit, Chem. Soc., Chem. Commun. 219 (1997).
[32] L.-F. Mao, A. Mayr, Inorg. Chem. 35 (1996) 3183.
[33] J. Guo, A. Mayr, Inorg. Chim. Acta 261 (1997) 141.
[34] K.Y. Lau, A. Mayr, K.-K. Cheung, Inorg. Chim. Acta 285 (1999).
[35] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. (1975).
[36] L. Cassar, J. Organomet. Chem. 93 (1975) 253.
[37] H.A. Dieck, R.F. Heck, J. Organomet. Chem. 93 (1975) 259.
[38] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis (1980) 627.
[39] J. Zhang, D.J. Pesak, J.L. Ludwick, J.S. Moore, J. Am. Chem. Soc. 116 (1994) 4227.
[40] O. Lavastre, L. Ollivier, P.H. Dixneuf, S. Sibadhit, Tetrahedron 52 (1996) 5495.
[41] DENZO, in: The HKL Manual – A Description of Programs DENZO, XDISPLAYF, and SCALEPACK, by D. Gewirth, with the cooperation of the program authors Z. Otwinowski and W. Minor, 1995.
[42] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, (1985 and 1992).
[43] E.B. Merkushev, Synthesis (1988) 923.
[44] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, K. Offermann, Angew. Chem. 77 (1965) 492.
[45] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, K. Offermann, Angew. Chem., Int. Ed. Engl. 4 (1965) 72.
[46] J. Manna, K.D. John, M. Hopkins, Adv. Organomet. Chem. 38 (1995) 79.
[47] R.A. Walton, Q. Rev. Chem. Soc. 19 (1965) 126.
[48] B.N. Storhoff, H.C. Lewis, Coord. Chem. Rev. 23 (1977) 1.
[49] J. Lewis, M.S. Khan, A.K. Khakkar, B.F.G. Johnson, T.D. Marder, H.B. Fyfe, F. Wittman, R.H. Friend, A.E. Dray, J. Organomet. Chem. 425 (1992) 165.

[50] G. Jia, R.J. Puddephatt, J.D. Scott, J.J. Vittal, Organometallics 12 (1993) 3565.
[51] S.-J. Shieh, X. Hong, S.M. Peng, C.-C. Ming, J. Chem. Soc., Dalton Trans. (1994) 3067.
[52] R. Faust, F. Diederich, V. Gramlich, P. Seiler, Chem. Eur. J. 1 (1995) 111.
[53] J.A. Whiteford, C.V. Lu, P.J. Stang, J. Am. Chem. Soc. 119 (1997) 2524.
[54] V.W.W. Yam, W.K.M. Fung, K.-K. Cheung, Angew. Chem., Int. Ed. Engl. 35 (1996) 1100.
[55] F.E. Hahn, T. Lügger, J. Organomet. Chem. 481 (1994) 189.
[56] N.A. Bailey, N.W. Walker, J.A.W. Williams, J. Organomet. Chem. 37 (1972) C49.
[57] C.-M. Che, F.H. Herbstein, W.P. Schaefer, R.E. Marsh, H.B. Gray, Inorg. Chem. 23 (1984) 2572.
[58] F.H. Allen, J.A.K. Howard, V.J. Hoy, G.R. Desiraju, D.S. Reddy, C.C. Wilson, J. Am. Chem. Soc. 118 (1996) 4081.
[59] D. Mootz, A. Deeg, J. Am. Chem. Soc. 114 (1992) 5887.