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Synthesis of transition metal isocyanide complexes containing hydrogen bonding sites in peripheral locations

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Dedicated to Professor Dr. W. Beck on the occasion of his 65th birthday.

Abstract

The isocyanides $CNC_6H_2R_2$-2,6-CHO-4 (**1a–b**) (**a**: R = Me; **b**: R = $CHMe_2$), react with hydroxylamine, 2-pyridylhydrazine, and formylhydrazide to form $CNC_6H_2R_2$-2,6-CHNOH-4 (**2a–b**), $CNC_6H_2R_2$-2,6-CHNNH(2-C_5H_4N)-4 (**3a–b**), and $CNC_6H_2R_2$-2,6-CHNNHCHO-4 (**4b**), respectively. The oxime and hydrazone derivatives **2–4** were chosen because of their potential for self-association via hydrogen bonding. Reaction of the isocyanides **1–4** (L) with FeI_2, PdI_2, and PtI_2 affords complexes of the types *trans*-[$FeI_2(L_4)$], *trans*-[$PdI_2(L)_2$], and *trans*-[$PtI_2(L_2)$]. The molecular structures of the complexes *trans*-[$FeI_2(L_4)$] (L = **1b**, **2a** and **2b**) and *trans*-[$PdI_2(L)_2$] (L = **2b**) were determined by X-ray crystallography. The oxime derivatives form extended hydrogen bonded networks.

Keywords: Isocyanides; Oximes; Hydrazones; Isocyanide metal complexes; Iron complexes; Palladium complexes; Platinum complexes

1. Introduction

Isocyanide metal complexes [1–9] are attractive as building blocks for molecular materials [10–25]. Due to their unique bonding capabilities and slender shapes, isocyanide ligands are capable of forming metal complexes with regular, yet open molecular structures based on all major coordination geometries. Furthermore, because of the presence of partial metal–carbon multiple bonds, significant electronic interactions between the metal centers and unsaturated organic systems are possible [26–29]. By introducing suitable weak interaction sites in peripheral locations, the isocyanide metal complexes can be induced to undergo molecular self-assembly, whereby the geometric and electronic information stored in them can be exploited to control the physical properties of the self-assembled molecular materials [30–36]. The choice of the weak interaction sites is important, since they represent the primary means to control the relative orientations of the building blocks in the assembled structures. We have recently developed isocyanide metal complexes carrying nitrogen donor groups and have demonstrated the formation of coordination polymers in combination with unsaturated metal complexes or metal ions [37,38]. In view of their proven versatility in molecular self-assembly processes, it appeared desirable to include hydrogen-bonding groups in the design of the isocyanide metal complex building blocks [39–60]. However, isocyanides containing hydrogen-bonding groups are not easily accessible, since the presence of such groups is largely incompatible with the conditions of the major isocyanide syntheses [61,62]. Thus there is a need for methods to generate hydrogen bonding groups after the preparation of the isocyanide functionality. It would furthermore appear desirable to have the option to introduce the hydrogen-bonding groups either before [63–79] or after [80–93] coordination of the isocyanides to metal centers [94]. This way, the possible interference of the hydrogen-bonding groups with the formation of the isocyanide metal complexes could be avoided as well. In order to satisfy these demands, we considered the grafting of entire hydrogen-bonding fragments onto isocyanides. The procedure described here is based on the reactivity of formyl-substituted arylisocyanides.

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2. Experimental

4-Amino-3,5-dimethylbenzaldehyde was prepared as described in the literature [97]. 2,6-Diisopropylaniline, trifluoroacetic acid, 2-hydrazinopyridine, hydroxylamine, hydrazine hydrate, FeI_2, PdI_2, and PtI_2 were purchased from commercial sources. 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. Formylhydrazide was prepared by treatment of ethylformate with hydrazine monohydrate. 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 Butterworth Laboratories.

2.1. Syntheses

2.1.1. 4-Formyl-2,6-dimethylphenylisocyanide (**1a**)

A mixture of acetic anhydride (0.734 g, 7.187 mmol) and formic acid (0.330 g, 7.187 mmol) is heated with stirring for 2 h at 50–60°C in a flask fitted with a drying tube. The solution is cooled to room temperature. 4-Amino-3,5-dimethylbenzaldehyde (0.51 g, 3.423 mmol) is added gradually over a 10 min period using a water bath to maintain the temperature below 39°C. The mixture is allowed to cool to 30°C, and diethyl ether is added to the suspension. The mixture is stirred for 24 h at room temperature. The resulting 4-formylamino-3,5-dimethylbenzaldehyde is filtered off and washed with ether. Toluene is used to recrystallize the crude product to give white needle-shaped crystals. Yield: 0.375 g, 62%. ^1H NMR ($CDCl_3$), two isomers: δ 9.95, 9.93 (s, 1H, CHO), 8.43, 8.20 (s, 1H, NHCHO), 7.65, 7.60 (s, 2H, C_6H_2), 7.43, 7.14 (br, 1H, NHCHO), 2.33, 2.40 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 193.7 (CHO), 162.0 (NHCHO), 131.0, 130.4, 126.9 (C_6H_2), 18.7 (CH_3). IR (KBr, cm^{-1}): ν = 1700 (s), 1662 (s).

Triphosgene (1.028 g, 3.465 mmol) is first dissolved in dry CH_2Cl_2 and then added dropwise over a 30 min period into a mixture containing 4-formylamino-3,5-dimethylbenzaldehyde (1.736 g, 9.804 mmol) and triethylamine (1.39 ml, 9.804 mmol) in CH_2Cl_2 (30 ml) at −78°C under nitrogen. The reaction mixture is allowed to warm up to room temperature and is stirred for 8 h at room temperature. The product is isolated by column chromatography on silica gel using *n*-hexane/EtOAc (2:1) as the eluent (R_f = 0.65). A white solid is obtained. Yield: 0.775 g, 50%, m.p. 89–90°C. ^1H NMR ($CDCl_3$): δ 9.97 (s, 1H, CHO), 7.64 (s, 2H, C_6H_2), 2.51 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 191.1 (CHO), 171.2 (CN), 136.1, 135.6, 128.9 (C_6H_2), 19.0 (CH_3). IR (KBr, cm^{-1}): ν = 2115 (s, CN), 1700 (s, CHO). HRMS (M^+) *m/e* Calc. for $C_{10}H_9NO$: MW = 159.0684. Found: 159.0683. *Anal.* Calc. for $C_{10}H_9NO$ (MW = 159.188) with 0.25 mol H_2O: C, 73.38; H, 5.85; N, 8.56. Found: C, 74.05; H, 5.68; N, 8.73%.

2.1.2. 4-Formyl-2,6-diisopropylphenylisocyanide (**1b**)

Following an established literature procedure [98], a mixture of 2,6-diisopropylaniline (3.545 g, 20 mmol), previously distilled trifluoroacetic acid (30 ml) and hexamethylenetetramine (2.804 g, 20 mmol) is refluxed for 12 h at 85–90°C. Cold water (60 ml) is added, and the mixture is made basic by addition of sodium carbonate (about 5 g). The resulting crude 4-amino-3,5-diisopropylbenzaldehyde is extracted with ether and purified by column chromatography on silica gel using *n*-hexane/EtOAc (3:1) as the eluent (R_f = 0.26) and thin-layer chromatography on silica using acetone/diethyl ether/*n*-hexane (1:1:4) as the eluent. A light yellow solid is obtained. Yield: 1.46 g, 35%. ^1H NMR ($CDCl_3$): δ 9.74 (s, 1H, CHO), 7.55 (s, 2H, C_6H_2), 4.43 (br, 2H, NH_2), 2.90 (septet, 2H, CH), 1.29 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 191.4 (CHO), 146.8, 131.6, 127.2, 125.8 (C_6H_2), 27.9 (CH), 22.1 (CH_3). IR (KBr, cm^{-1}): ν = 3470–3250 (m, NH_2), 1707 (m), 1629 (s), 1583 (s), 1560 (s).

A mixture of acetic anhydride (6.338 g, 51.7 mmol) and formic acid (2.858 g, 51.7 mmol) is heated with stirring for 2 h at 50–60°C in a flask fitted with a drying tube. The solution is cooled to room temperature. 4-Amino-3,5-diisopropylbenzaldehyde (5.31 g, 25.86 mmol) is added gradually over a 10 min period using a water bath to maintain the temperature below 39°C. The mixture is allowed to cool to 30°C, and diethyl ether is added. The mixture is stirred for 24 h at room temperature. A 10% solution of aqueous sodium carbonate (150 ml) is used to neutralize the reaction mixture. The resulting 4-formylamino-3,5-diisopropylbenzaldehyde is isolated by column chromatography on silica gel using *n*-hexane/EtOAc (3:2) as the eluent (R_f = 0.27). A pale yellow crystalline solid is obtained. Yield: 4.34 g, 72%, m.p. 91–92°C. ^1H NMR ($CDCl_3$), two isomers: δ 10.04 (s), 10.02 (s) (1H, CHO), 8.49 (d, J = 1.39 Hz), 8.07 (d, J = 11.63 Hz) (1H, NCHO), 7.74 (s), 7.73 (s) (2H, C_6H_2), 7.50 (d, J = 11.61 Hz), 7.02 (s) (1H, NH), 3.26 (m, 2H, CH), 1.26 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 192.2, 191.9 (CHO), 164.9, 160.3 (NHCHO), 147.5, 136.3, 136.2, 135.7, 135.4, 125.4, 125.2 (C_6H_2), 30.0, 28.6 (CH), 23.5, 23.4 (CH_3). IR (KBr, cm^{-1}): ν = 3200 (s, NH), 1697 (s), 1674 (s), 1657 (s). HRMS (M^+) *m/e* Calc. for $C_{14}H_{19}NO_2$: MW = 233.1416. Found: 233.1414.

Triphosgene (1.034 g, 3.48 mmol) is first dissolved in dry CH_2Cl_2 (15 ml) and is added dropwise over a 30 min period into a mixture containing 4-formylamino-3,5-diisopropylbenzaldehyde (2.44 g, 10.45 mmol) and triethylamine (1.06 g, 10.45 mmol) in CH_2Cl_2 (20 ml) at −78°C under nitrogen. The reaction mixture is allowed to warm up to room temperature and is stirred for 8 h at room temperature. The methylene chloride solution is washed several times with 10% aqueous Na_2CO_3. The solvent is removed, and the product is purified by column chromatography on silica gel using *n*-hexane/EtOAc (6:1) as the eluent (R_f = 0.45). A

pale yellow crystalline solid is obtained. Yield: 1.48 g, 66%, m.p. 55–56°C. ^{1}H NMR ($CDCl_3$): δ 9.95 (s, 1H, CHO), 7.63 (s, 2H, C_6H_2), 3.36 (septet, 2H, CH), 1.26 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 190.4 (CHO), 171.8 (CN), 145.2, 135.2, 123.7, (C_6H_2), 28.9 (CH), 21.4 (CH_3). IR (KBr, cm^{-1}): $\nu = 2114$ (s, CN), 1698 (s, CHO). HRMS (M^+) *m/e* Calc. for $C_{14}H_{17}NO$: MW = 215.1310. Found: 215.1311. *Anal.* Calc. for $C_{14}H_{17}NO$ (MW = 215.296): C, 78.10; H, 7.96; N, 6.51. Found: C, 78.05; H, 7.86; N, 6.69%.

2.1.3. $CNC_6H_2Me_2$-2,6-(CH=NOH)-4 (**2a**)

To a suspension of hydroxylamine hydrochloride (0.093 g, 1.33 mmol) in pyridine (0.105 g, 1.33 mmol), a solution of **1a** (0.2 g, 1.257 mmol) in methylene chloride/methanol (10:1, 30 ml) is added. The mixture is stirred for 24 h. The reaction mixture is washed with 10% aqueous sodium carbonate solution (20 ml). After removal of the solvent, a yellow solid is obtained. The solid is extracted with hot *n*-hexane and any insoluble impurities are filtered off. After removal of the solvent, a white powder is obtained. Yield: 0.175 g, 80%, m.p. 130–131°C. ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 1H, CH=N), 8.06 (br, 1H, OH), 7.32 (s, 2H, C_6H_2), 2.44 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.0 (CN), 149.1 (C=N), 135.5, 132.2, 126.2, (CH), 18.9 (CH_3). IR (KBr, cm^{-1}): ν = 3390–3080 (br, OH), 2113 (s, CN). HRMS (M^+) *m/e* Calc. for $C_{10}H_{10}N_2O$: MW = 174.0793. Found: 174.0792.

2.1.4. CNC_6H_2-i-Pr_2-2,6-(CH=NOH)-4 (**2b**)

A mixture of **1b** (0.289 g, 1.35 mmol) and hydroxyamine hydrochloride (0.098 g, 1.41 mmol) is stirred in THF (30 ml). Pyridine (0.12 ml, 1.41 mmol) is added. The mixture is stirred at room temperature for 20 h. The solvent is removed, and the product is isolated by column chromatography using *n*-hexane/EtOAc (3:1) as the eluent ($R_f = 0.5$). A white solid is obtained. Yield: 0.253 g, 81%, m.p. 143–144°C. ^{1}H NMR ($CDCl_3$): δ 8.40 (s, 1H, CH=N), 8.14 (s, 1H, OH), 7.38 (s, 2H, C_6H_2), 3.39 (septet, 2H, CH), 1.30 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.8 (CN), 149.7 (C=N), 145.7, 132.8, 122.1 (C_6H_2), 29.8 (CH), 22.5 (CH_3). IR (KBr, cm^{-1}): ν = 3640–3100 (br, O–H), 2114 (s, CN). HRMS (M^+) *m/e* Calc. for $C_{14}H_{18}N_2O$: MW = 230.1419. Found: 230.1414.

2.1.5. $CNC_6H_2Me_2$-2,6-[CH=NNH(C_5H_4N-2)]-4 (**3a**)

A solution of 2-hydrazinopyridine hydrochloride (0.30 g, 1.647 mmol) in water (10 ml) is treated with a solution of sodium carbonate (0.34 g, 3.21 mmol) in water (10 ml). The mixture is extracted with ether (three times, 20 ml each time). The ether extracts are pooled, dried over magnesium sulphate, and the solvent is removed. The residue is added to a solution of **1a** (0.135 g, 0.852 mmol) in THF (50 ml). The mixture is stirred for 20 h at room temperature. The solvent is removed, and the product is purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (1:1) as the eluent ($R_f = 0.33$). A yellow solid is obtained. Yield: 0.113 g, 53%, m.p. 199–200°C. ^{1}H NMR ($CDCl_3$): δ 9.10 (s, 1H, NH), 8.16 (m, 1H), 7.66 (m, 2H), 7.39 (3H), 6.82 (m, 1H) (CH=N, C_6H_2, C_5H_4N), 2.45 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.9 (CN), 156.5, 147.5, 138.3, 137.3, 135.3, 135.2, 125.5, 124.6, 116.1, 107.7 (C=N, C_6H_2, C_5H_4N), 19.0 (CH_3). IR (KBr, cm^{-1}): $\nu = 2114$ (s, CN), 1597 (s), 1582 (s). HRMS (M^+) *m/e* Calc. for $C_{15}H_{14}N_4$: MW = 250.1218. Found: 250.1213.

2.1.6. CNC_6H_2-i-Pr_2-2,6-[CH=NNH(C_5H_4N-2)]-4 (**3b**)

The procedure described for **3a** is followed. The product is purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (3:2) as the eluent ($R_f = 0.29$). A yellow solid is obtained. Yield: 74%, m.p. 196–198°C. ^{1}H NMR ($CDCl_3$): δ 8.80 (s, 1H, NH), 6.81–8.17 (5H, C_5H_4N), 7.45 (s, 2H, C_6H_2), 7.73 (s, 1H, CH=N), 3.39 (septet, 2H, CH), 1.33 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.9 (CN), 156.4, 147.6, 145.4, 138.2, 137.9, 135.7, 121.2, 116.2, 107.6 (C=N, C_6H_2, C_5H_4N), 29.9 (CH), 22.5(CH_3). IR (KBr, cm^{-1}): $\nu = 2112$ (s, CN), 1607 (s), 1583 (s). HRMS (M^+) *m/e* Calc. for $C_{19}H_{22}N_4$: MW = 306.1844. Found: 306.1841. *Anal.* Calc. for $C_{19}H_{22}N_4$ (MW = 306.413): C, 74.48; H, 7.24; N, 18.29. Found: C, 74.67; H, 7.30; N, 18.07%.

2.1.7. CNC_6H_2-i-Pr_2-2,6-(CH=NNHCHO)-4 (**4b**)

To a mixture of formyl hydrazide (0.07 g, 1.161 mmol) in THF (30 ml), **1b** (0.25 g, 1.161 mmol) is added. The mixture is stirred for 48 h at room temperature. The solvent is removed, and the product is purified by column chromatography using ethyl acetate/*n*-hexane (1:1) as the eluent ($R_f = 0.50$). Yield: 0.215 g, 72%, m.p. 175–177°C. ^{1}H NMR (DMSO-d_6), two isomers: δ 11.92 (d), 11.61 (s) (1H, NH), 8.73 (d), 8.24 (s) (1H, CHO), 8.13(s), 8.07 (s) (1H, CH=N), 7.58 (s), 7.62 (s) (2H, C_6H_2), 2.51 (septet, 2H, CH), 1.26 (d, 12H, CH_3). ^{13}C NMR (DMSO-d_6), two isomers: δ 170.1 (CN), 165.1, 157.2 (CHO), 146.5, 144.8, 143.8, 135.0, 124.0, 122.2, 121.8 (C=N, C_6H_2), 29.4 (CH), 22.1 (CH_3). IR (KBr, cm^{-1}): $\nu = 2114$ (s, CN), 1699 (s, CHO), 1601 (w, C=N). HRMS (M^+) *m/e* Calc. for $C_{15}H_{19}N_3O$: MW = 257.1528. Found: 257.1526.

2.1.8. Trans-[FeI_2(CNC_6H_2-i-Pr_2-2,6-CHO-4)$_4$] (**5b**)

To a suspension of FeI_2 (0.072 g, 0.232 mmol) in THF (15 ml) under N_2, **1b** (0.198 g, 0.919 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns brownish yellow first. The mixture is kept stirring overnight. The solvent is removed under reduced pressure to afford a green solid. Dark green sheet-like crystals are obtained from CH_2Cl_2/*n*-hexane. Yield: 0.211 g, 79%, m.p. 257–258°C (dec.). ^{1}H NMR (CD_2Cl_2): δ 10.00 (s, 4H, CHO), 7.73 (s, 8H, C_6H_2), 3.81 (septet, 8H, CH), 1.29 (d, 48H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 191.7 (CHO), 177.6 (CN), 147.9, 136.5, 130.3, 125.3 (C_6H_2), 29.9 (CH), 23.1 (CH_3). IR (KBr, cm^{-1}): $\nu = 2116$ (s, CN), 1699 (s, C=O).

*2.1.9. Trans-[$FeI_2(CNC_6H_2Me_2$-2,6-(CH=NOH)-4)$_4$] (**6a**)*

To a suspension of iron(II) iodide (0.078 g, 0.252 mmol) in THF under N_2, **2a** (0.154 g, 0.887 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns green. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure to afford a green solid. The solid is reprecipitated from THF/*n*-hexane and recrystallized from THF/*n*-hexane to give dark green crystals. Yield: 0.152 g, 68%, m.p. 199–200°C (dec.). ^{1}H NMR (CD_3OD): δ 8.03 (s, 4H, CH=N), 7.43 (s, 8H, C_6H_2), 2.60 (s, 24H, CH_3). ^{13}C NMR (CD_3OD): δ 146.3, 135.0, 132.5, 126.9, 124.9 (C=N, C_6H_2), 16.8 (CH_3). IR (KBr, cm^{-1}): ν = 3400–3300 (br, OH), 2120 (s, CN). *Anal.* Calc. for $C_{40}H_{40}N_8O_4I_2Fe$ (MW = 1006.469) with 2 mol THF: C, 50.10; H, 4.91; N, 9.74. Found: C, 50.67; H, 4.97; N, 10.15%.

*2.1.10. Trans-[$FeI_2(CNC_6H_2$-*i*-Pr_2-2,6-(CH=NOH)-4)$_4$] (**6b**)*

To a green solution of $FeI_2(CNC_6H_2$-*i*-Pr_2-2,6-CHO-4)$_4$, (**5b**), (9.5 mg, 0.01 mmol) in THF (20 ml), hydroxylamine hydrochloride (2.92 mg, 0.042 mmol) and a few drops of pyridine are added at room temperature, followed by a few drops of methanol. Initially, the solution is deep green. Upon stirring overnight at room temperature, the reaction mixture turns pale green. Any solid is filtered off. The solvent is removed under reduced pressure to afford a green solid. The green solid is recrystallized from THF/*n*-pentane to give dark green crystals. Yield: 8 mg, 77%, m.p. 209–211°C (dec.). In an alternative procedure, analogous to the synthesis of **6a**, compound **6b** has been prepared by reaction of FeI_2 with **2b**. ^{1}H NMR (DMSO-d_6): δ 10.19 (br, 4H, NOH), 8.20 (s, 4H, CH=N), 7.54 (s, 8H, C_6H_2), 3.66 (septet, 8H, CH), 1.20 (d, 48H, CH_3). ^{13}C NMR (DMSO-d_6): δ 145.7, 134.0 127, 125, 121.6 (C=N, C_6H_2). IR (KBr, cm^{-1}) ν = 3500–3300 (br, O–H), 2122 (s, CN). *Anal.* Calc. for $C_{56}H_{72}N_8O_4I_2Fe$ (MW = 1230.901) with 2 mol THF: C, 56.56; H, 6.38; N, 8.24. Found: C, 56.09; H, 6.49; N, 8.22%.

*2.1.11. Trans-[$FeI_2(CNC_6H_2$-*i*-Pr_2-2,6-(CH=NNHCHO)-4)$_4$] (**7b**)*

To a suspension of FeI_2 (0.045 g, 0.145 mmol) in THF (15 ml) under N_2, **4b** (0.15 g, 0.583 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns green. The mixture is kept stirring overnight. The solvent is removed under reduced pressure to afford a green solid, which is recrystallized from THF/*n*-hexane. Yield: 0.14 g, 72%. ^{1}H NMR (DMSO-d_6): δ 11.90 (d, 4H, CHO), 8.72 (d, 4H, NH), 8.08 (s, 4H, CH=N), 7.60 (s, 8H, C_6H_2), 3.66 (septet, 8H, CH), 1.21 (d, 48H, CH_3). ^{13}C NMR (DMSO-d_6): δ 174.9 (CN), 165.1 (CHO), 145.8, 143.8, 134.7, 125.3, 122.0 (C=N, C_6H_2), 29.0 (CH), 22.4 (CH_3). IR (KBr, cm^{-1}): ν = 2122 (s, CN), 1697 (s, C=O), 1614 (w, C=N).

*2.1.12. Trans-[$PdI_2(CNC_6H_2Me_2$-2,6-CHO-4)$_2$] (**8a**)*

To a suspension of PdI_2 (0.10 g, 0.278 mmol) in THF (15 ml) under N_2, **1a** (0.09 g, 0.566 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns green first. On further stirring, a yellow precipitate forms. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure. Hot CH_2Cl_2 and benzene are added to extract the complex. A yellow–orange solid is obtained after cooling. Yield: 0.144 g, 76%, m.p. 269–271°C (dec.). ^{1}H NMR (CD_2Cl_2): δ 9.99 (s, 2H, CHO), 7.68 (s, 4H, C_6H_2), 2.66 (s, 12H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 191.3 (CHO), 138.5, 129.4, 115.7 (C_6H_2), 19.4 (CH_3). IR (KBr, cm^{-1}): ν = 2197 (s, CN), 1700 (s, C=O).

*2.1.13. Trans-[$PdI_2(CNC_6H_2$-*i*-Pr_2-2,6-CHO-4)$_2$] (**8b**)*

To a suspension of PdI_2 (0.151 g, 0.418 mmol) in THF (15 ml) under N_2, **1b** (0.179 g, 0.832 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns yellow first. On further stirring, an orange solution forms. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure to afford an orange–yellow solid. Yellow–orange crystals are obtained from methylene chloride/*n*-hexane. Yield: 0.226 g, 69%, m.p. 257.5–258°C (dec.). ^{1}H NMR (CD_2Cl_2): δ 10.05 (s, 2H, CHO), 7.77 (s, 4H, C_6H_2), 3.63 (septet, 4H, CH), 1.39 (d, 24H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 191.6 (CHO), 148.6, 138.1, 125.4 (C_6H_2), 30.3 (CH), 23.0 (CH_3). IR (KBr, cm^{-1}): ν = 2193 (s, CN), 1703 (s, C=O). *Anal.* Calc. for $C_{28}H_{34}N_2O_2I_2Pd$ (MW = 790.802): C, 42.53; H, 4.33; N, 3.54. Found: C, 42.68; H, 4.41; N, 3.68%.

*2.1.14. Trans-[$PdI_2(CNC_6H_2$-*i*-Pr_2-2,6-(CH=NOH)-4)$_2$] (**9b**)*

PdI_2 (0.1163 g, 0.323 mmol) is suspended in THF (15 ml). **2b** (0.116 g, 0.646 mmol) in THF (15 ml) is added dropwise at room temperature. Upon addition, the solution turns orange. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure to afford an orange solid. The orange product is recrystallized from THF/petroleum ether (40–60°C) to give orange crystals. Yield: 0.152 g, 57%, m.p. 203–204°C. ^{1}H NMR (acetone-d_6): δ 10.76 (s, 2H, OH), 8.25 (s, 2H, CH=N), 7.67 (s, 4H, C_6H_2), 3.61 (septet, 4H, CH), 1.37 (d, 24H, CH_3). ^{13}C NMR (acetone-d_6): δ 148.5, 148.1, 137.4, 123.1 (C=N, C_6H_2), 23.1 (CH_3). IR (KBr, cm^{-1}): ν = 2187 (s, CN). *Anal.* Calc. for $C_{28}H_{36}N_4O_2I_2Pd$ (MW = 820.832) with 0.25 mol THF: C, 41.62; H, 4.81; N, 6.69. Found: C, 41.34; H, 4.50; N, 6.66%.

*2.1.15. Trans-[$PdI_2(CNC_6H_2$-*i*-Pr_2-2,6-(CH=NNHC$_5H_4$N-2)-4)$_2$] (**10b**)*

PdI_2 (0.041 g, 0.114 mmol) is suspended in THF (10 ml). **3b** (0.07 g, 0.228 mmol) in THF (20 ml) is added dropwise at room temperature. On further stirring, an orange solution forms. The mixture is kept stirring for 3.5 h at room temperature. The solution is filtered, and the solvent is removed under reduced pressure to afford an orange solid which is recrystallized from THF/*n*-hexane. Yield: 95 mg, 86%, m.p. 275–276°C. ^{1}H NMR ($CDCl_3$): δ 8.60 (s, 2H,

NH), 6.82–8.17 (10H, C_5H_4N), 7.16 (s, 4H, C_6H_2), 7.51 (s, 2H, CH=N), 3.59 (septet, 4H, CH, 1.39 (d, 24H, CH_3). ^{13}C NMR ($CDCl_3$): δ 161.9 (CN), 156.0, 147.7, 147.4, 138.3, 137.4, 129.4, 121.5, 116.5, 107.6 (C=N, C_6H_2, C_5H_4N), 29.7 (CH), 22.9 (CH_3). IR (KBr, cm^{-1}): $\nu = 2189$ (s, CN), 1595 (m), 1578 (s). *Anal.* Calc. for $C_{38}H_{44}N_8I_2Pd$ (MW = 973.036) with 2 mol H_2O: C, 45.23; H, 4.79; N, 11.10. Found: C, 45.5; H, 4.2; N, 10.5%.

2.1.16. Trans-[PdI_2(CNC_6H_2-i-Pr_2-2,6-(CH=NNHCHO)-4)$_2$] (**11b**)

PdI_2 (0.043 g, 0.120 mmol) is suspended in THF (10 ml). **4b** (0.062 g, 0.241 mmol) in THF (20 ml) is added dropwise at room temperature. On further stirring, a yellow solution is obtained. The mixture is stirred overnight to afford an orange solution. The solution is filtered and the solvent is removed under reduced pressure and an orange solid is obtained. Recrystallization from THF/petroleum ether (40–60°C). Yield: 80 mg, 76%. ^1H NMR (DMSO-d_6): δ 12.00 (d, 2H), 8.75 (d, 2H) (CHO, NH), 8.10 (s, 2H, CH=N), 7.67 (s, 4H, C_6H_2), 3.46 (septet, 4H, CH), 1.31 (d, 24H, CH_3). ^{13}C NMR (DMSO-d_6): δ 165.2 (CHO), 146.7, 143.4, 136.9, 130.4, 122.6, 122.2 (CN, C_6H_2), 29.3 (CH), 22.4 (CH_3). IR (KBr, cm^{-1}): $\nu = 2189$ (s, CN), 1699 (s, C=O). *Anal.* Calc. for $C_{30}H_{38}N_6O_2I_2Pd$ (MW = 874.884) with 0.5 mol THF: C, 42.38; H, 4.67; N, 9.23. Found: C, 42.38; H, 4.69; N, 9.15%.

2.1.17. Trans-[PtI_2(CNC_6H_2-i-Pr_2-2,6-CHO-4)$_2$] (**12b**)

PtI_2 (0.156 g, 0.348 mmol) is suspended in THF (15 ml). **1b** (0.15 g, 0.696 mmol) in THF (15 ml) is added dropwise at room temperature. The solution turns yellowish brown first. On stirring, a yellow solution forms. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure to afford a yellow solid. The yellow product is recrystallized from THF/*n*-hexane. Yield: 0.225 g, 83%, m.p. 237–238°C. ^1H NMR (CD_2Cl_2): δ 10.04 (s, 2H, CHO), 7.77 (s, 4H, C_6H_2), 3.63 (septet, 4H, CH), 1.39 (d, 24H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 191.6 (CHO), 148.6, 137.9, 125.4 (C_6H_2), 30.2 (CH), 23.0 (CH_3). IR (KBr, cm^{-1}): $\nu = 2185$ (s, CN), 1705 (s, C=O). *Anal.* Calc. for $C_{28}H_{34}N_2O_2I_2Pt$ (MW = 1059.078): C, 38.24; H, 3.89; N, 3.19. Found: C, 38.30; H, 3.94; N, 3.19%.

2.1.18. Trans-[PtI_2(CNC_6H_2-i-Pr_2-2,6-(CH=NOH)-4)$_2$] (**13b**)

Black solid PtI_2 (0.067 g, 0.151 mmol) is dried under reduced pressure for 1 h at room temperature and suspended in THF (15 ml). **2b** (0.07 g, 0.301 mmol) in THF (15 ml) is added dropwise at room temperature. Upon addition, the solution turns yellow. The mixture is kept stirring overnight at room temperature. The solvent is removed under reduced pressure to afford a yellow solid. The yellow product is recrystallized from THF/petroleum ether (40–60°C). Yield: 0.063 g, 47%, m.p. 234–235°C (dec.). ^1H NMR (acetone-d_6): δ 10.80 (s, 2H, OH), 8.24 (s, 2H, CH=N), 7.66 (s, 4H, C_6H_2), 3.60 (septet, 4H, CH), 1.37 (d, 24H, CH_3). ^{13}C NMR (acetone-d_6): δ 148.6, 148.0, 137.2, 123.1 (C=N, C_6H_2), 29 (CH), 23.1 (CH_3). IR (KBr, cm^{-1}): $\nu = 3300$–3150 (br, OH), 2185 (s, CN). *Anal.* Calc. for $C_{28}H_{36}N_4O_2I_2Pt$ (MW = 909.522) with 0.5 mol THF: C, 38.11; H, 4.26; N, 5.93. Found: C, 38.12; H, 3.98; N, 6.09%.

2.1.19. Trans-[PtI_2(CNC_6H_2-i-Pr_2-2,6-(CH=NNHCHO)-4)$_2$] (**14b**)

Black solid PtI_2 (0.131 g, 0.291 mmol) is dried under reduced pressure for 1 h at room temperature and suspended in THF (10 ml). **4b** (0.15 g, 0.583 mmol) in THF (20 ml) is added dropwise at room temperature. The mixture is stirred overnight at room temperature to afford a yellow solution. A yellow solid is obtained after removal of solvent. The yellow solid is recrystallized from THF/ether. Yield: 0.15 g, 71%. ^1H NMR (DMSO-d_6): δ 11.98 (d, 2H, CHO), 8.73 (d, 2H, NH), 8.07 (s, 2H, CH=N), 7.65 (s, 4H, C_6H_2), 3.43 (septet, 4H, CH), 1.29 (d, 24H, CH_3). ^{13}C NMR (DMSO-d_6): δ 165.3 (CHO), 146.6, 143.5, 136.8, 122.5, 122.3 (C=N, C_6H_2), 29.2 (CH), 22.4 (CH_3). IR (KBr, cm^{-1}): $\nu = 2185$ (s, CN), 1701 (s, C=O). *Anal.* Calc. for $C_{30}H_{38}N_6O_2I_2Pt$ (MW = 963.574) with 0.5 mol THF: C, 38.45; H, 4.24; N, 8.40. Found: C, 38.18; H, 4.12; N, 8.15%.

2.2. Crystal structure determinations

Diffraction data for compounds **5b** and **6a** were collected on a MAR Imaging Plate Detector System using graphite-monochromatized Mo Kα X-ray radiation ($\lambda = 0.71073$ Å) from a MAR generator (sealed tube 50 kV and 50 mA), and processed by DENZO [95]. The diffraction data for compounds **6b** and **9a** were collected on a Rigaku AFC7R four-circle diffractometer using graphite-monochromatized Mo Kα X-ray radiation ($\lambda = 0.71073$ Å) from a Rigaku RU-200 rotating-anode generator at 50 kV and 160 mA and processed by the MSC/RIGAKU diffractometer control software. Empirical absorption corrections from ψ-scans were applied to the data for compounds **6b** and **9a** and no absorption correction was made on compounds **5b** and **6a**. All structure determinations were done using the MSC crystal structure analysis package TeXsan [96] 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

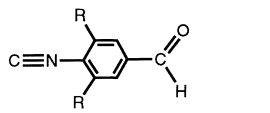
3.1. Synthesis of the isocyanides and the isocyanide metal complexes

The 4-isocyanobenzaldehydes **1a** and **1b** were prepared in the established fashion from the corresponding anilines

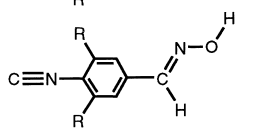
[97,98] by formylation and subsequent dehydration [99,100]. As the aldehyde group is one of the most versatile functionalities, many possibilities exist for the attachment of hydrogen bonding groups or other intermolecular interaction sites. The formation of oximes, hydrazones and related derivatives was chosen to demonstrate the new approach. Compounds **1** react with hydroxylamine and various hydrazine derivatives to afford the functionalized isocyanides **2–4**. The oxime, 2-pyridylhydrazone, and formylhydrazone functionalities contain molecular fragments capable of forming pairwise hydrogen bonds [30–36, 39–46].

The new isocyanides combine with FeI_2, PdI_2, and PtI_2 to give the complexes **5–14**. The grafting procedure can also be performed on coordinated formylisocyanoarene ligands as demonstrated by the synthesis of complex **6b** from **5b** and hydroxylamine. The IR and NMR spectroscopic parameters of complexes **5–14** are consistent with a *trans* arrangement of the iodo ligands in all complexes, i.e. square planar and linear geometries of the tetrakis-isocyanide and bis-isocyanide metal cores, respectively. The formyl-substituted complexes **5**, **8**, and **12** easily dissolve in methylene chloride or THF, but the complexes **6–7**, **9–11**, and **13–14**, which all carry potential hydrogen-bonding sites, are significantly less soluble. The lower solubility of the latter complexes strongly suggests that the metal complex units are interconnected by hydrogen bonds to form extended chains and networks.

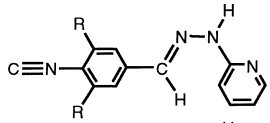
Compounds **1-14**: **a**: R = CH_3; **b**: R = $CH(CH_3)_2$



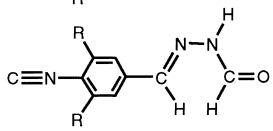
1a, **1b**



2a, **2b**



3a, **3b**



4b

trans-$[FeI_2(L)_4]$

5b: L = **1b**
6a, **6b**: L = **2a**, **2b**
7b: L = **4b**

trans-$[MI_2(L)_2]$

8a and **8b**: M = Pd; L = **1a**, **b**
9b: M = Pd; L = **2b**
10b: M = Pd; L = **3b**
11b: M = Pd; L = **4b**
12b: M = Pt; L = **1b**
13b: M = Pt; L = **2b**
14b: M = Pt; L = **4b**

Prior to this work, a number of isocyanides and isocyanide metal complexes bearing groups capable of hydrogen-bonding, e.g. hydroxy, carboxyl, and carboxamide functionalities, have been prepared [63–79]. Noteworthy in the present context is also the report by Fehlhammer et al. on the isodiazomethane complex $[PdI_2(CNNH_2)_2]$ [80]. This compound was isolated as the diethetate, indicating that the amino groups form strong hydrogen bonds. The synthetic methods used in the preparation of such isocyanides are typically only applicable to a narrow range of hydrogen-bonding groups. In contrast, the grafting procedure described here is free of the limitations dictated by the reaction conditions encountered during the synthesis of the isocyanide functionality. The attachment of entire hydrogen-bonding groups via transformations of the formyl functionality can also be applied to coordinated isocyanide ligands without affecting the metal-isocyanide core. Earlier attempts to achieve the transformation of the ester functionalities of analogous complexes of alkylisocyanobenzoate ligands proved less successful [101]. Several transformations on coordinated isocyanide and cyanide ligands resulting in the formation of hydrogen-bonding functionalities have been reported [94]. Of particular relevance is the formation of oximes and hydrazones of coordinated γ-oxoalkylisocyanides described by Beck and coworkers [88].

3.2. X-ray crystallographic studies

The molecular structures of compounds **5b**, **6a**, **6b**, and **9a** are shown in Figs. 1–4, respectively. The crystallographic data are compiled in Table 1. The crystal structure of complex **5b** reveals no specific intermolecular interactions. The shortest contact [O(1)–C(18), 3.161(6) Å] arises from the approach of the carbonyl oxygen atom O(1) towards C(18) of the arene ring C(16)–C(21), whereby the carbonyl CO vector is roughly perpendicular to the plane of the phenyl ring. There are no significant π stacking interactions between the isocyanoarene rings.

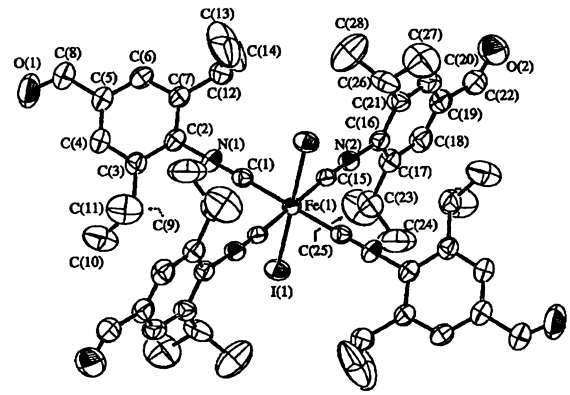


Fig. 1. Molecular structure of **5b**. The thermal ellipsoids are shown at the 35% probability level. Selected bond distances (Å) and angles (°). Fe(1)–I(1) 2.6353(3), Fe(1)–C(1) 1.871(4), N(1)–C(1) 1.145(5), N(2)–C(15) 1.160(4), O(1)–C(8) 1.183(5), O(2)–C(22) 1.153(6); I(1)–Fe(1)–C(1) 89.93(10), I(1)–Fe(1)–C(15) 89.98(9), C(1)–Fe(1)–C(15) 88.2(1).

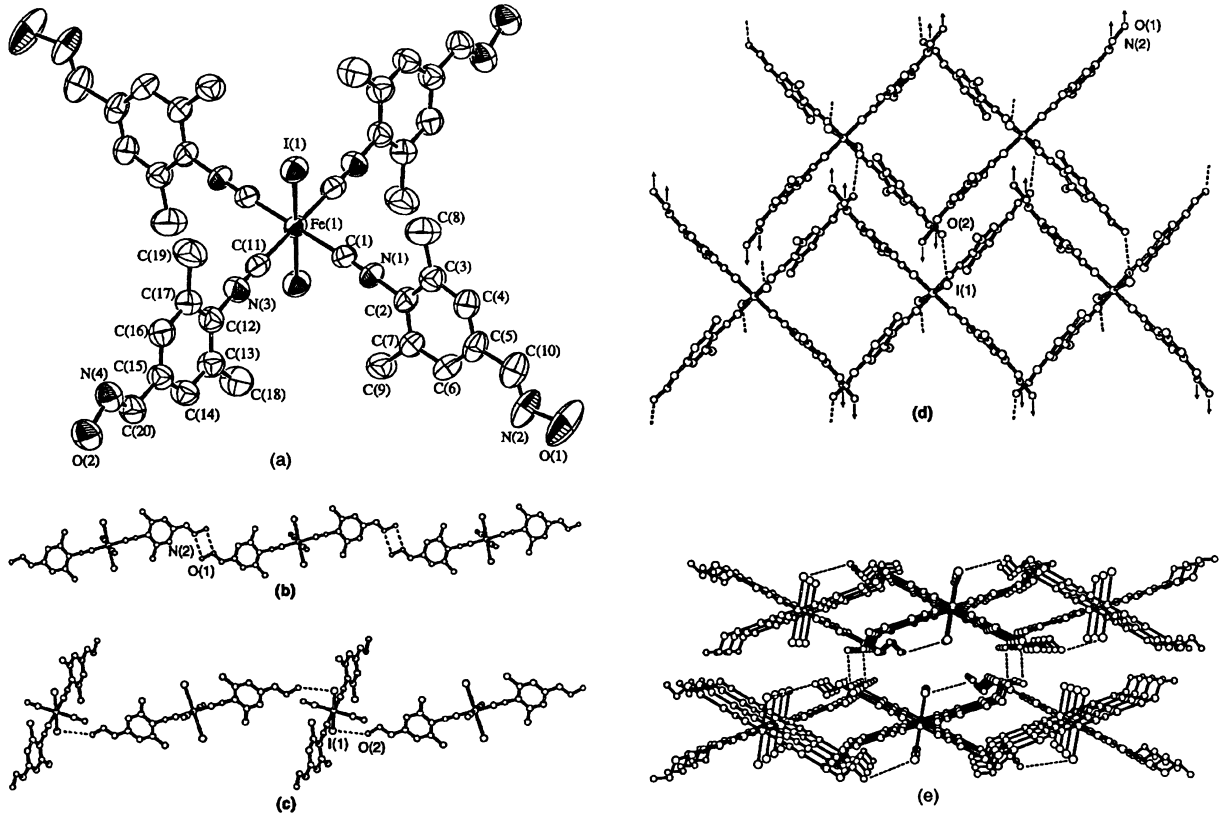


Fig. 2. (a) Molecular structure of **6a.** The thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (°). Fe(1)–I(1) 2.6343(4), Fe(1)–C(1) 1.898(6), Fe(1)–C(11) 1.884(6), N(1)–C(1) 1.120(6), N(3)–C(11) 1.142(7), N(2)–C(10) 1.277(10), N(4)–C(20) 1.269(8), N(2)–O(1) 1.385(7), N(4)–O(2) 1.430(7); I(1)–Fe(1)–C(1) 89.5(2), I(1)–Fe(1)–C(11) 89.8(2), C(1)–Fe(1)–C(11) 87.1(2). (b) Short segment of a chain formed by pairwise hydrogen-bonding of the oxime groups N(2)O(1)H (dotted lines). The isocyanide ligands not involved in these interactions are truncated to show only the NCFeCN cores. (c) Partial segment of a layer of molecular units connected by short O(2)···I(1) contacts (dotted lines). The isocyanide ligands not involved in these interactions are truncated to show only the NCFeCN cores. (d) Partial segment of a layer of complete molecular units. The O(2)···I(1) contacts are indicated by dotted lines. The pairwise hydrogen-bonding contacts of the oxime groups N(2)O(1)H (indicated by double arrows) connect to the adjacent layers above and below. (e) Partial segment of two adjacent layers. The arene groups of the isocyanide ligands are represented by single lines for clarity. The hydrogen bonds within and between the layers are indicated by dotted lines.

The molecular units of **9b**, which were designed as one-dimensional building blocks, form the expected linear chains by pairwise hydrogen-bonding of the oxime groups [O(1)–N(2), 2.824(5) Å] as shown in Fig. 4(b) [102–107]. There appear to be no other significant directional intermolecular interactions in solid **9b**.

In contrast, the intermolecular interactions in solid **6a** are more complex. Only one of the two pairs of symmetry-related mutually *trans* isocyanide ligands are joined at oxime groups via pairwise hydrogen bonding [O(1)–N(2), 2.72(1) Å] to form extended linear chains analogous to those found in solid **9b** (Fig. 2(b)). The oxime groups of the second pair of isocyanide ligands are in close contact with the iodide ligands of adjacent molecular units as shown in Fig. 2(c). The intermolecular O(2)–I(1) distance of 3.59(1) Å is close to the sum of the van der Waals radii of O and I, and relatively short compared to other intermolecular I···O contacts [108]. Even though the oxime hydrogen atoms of **6a** were not located in the X-ray structure, this distance suggests the presence of weak O(2)–H···I(1) hydrogen bonds. The arrangement of the molecular units of **6a** in the solid state is furthermore stabilized by π stacking between pairs of arene groups (Fig. 2(d)). The shortest contacts between the offset rings [109] [C(4)–C(17), C(5)–C(16), C(5)–C(17), and C(6)–C(15)] are in the range of 3.55 to 3.64 Å. The molecular units of **6a** are organized in layers. A section of a single layer is shown in Fig. 2(d). The layers are interconnected by the pairwise hydrogen bonds of the linear chains which are running in an oblique fashion through the layers (Fig. 2(e)).

The characteristic pairwise hydrogen bonds of the oxime groups are absent in the solid state structure of **6b**. The molecular units of **6b**, if pictured as square plates, overlap along opposite edges like the steps of a staircase (Fig. 3(b)). The joints between adjacent oxime groups are formed by single OH···N hydrogen bonds [O(1)–N(4), 2.790(8) Å; O(3)–N(8), 2.783(7) Å]. Each free OH group is hydrogen-bonded to a molecule of THF [O(2)–O(5), 2.654(9) Å; O(4)–O(6), 2.624(8) Å].

The hydrogen-bonding capabilities of oximes are well-documented, and hydrogen-bonded networks of polyfunctional oximes have been described [102–107]. The OH

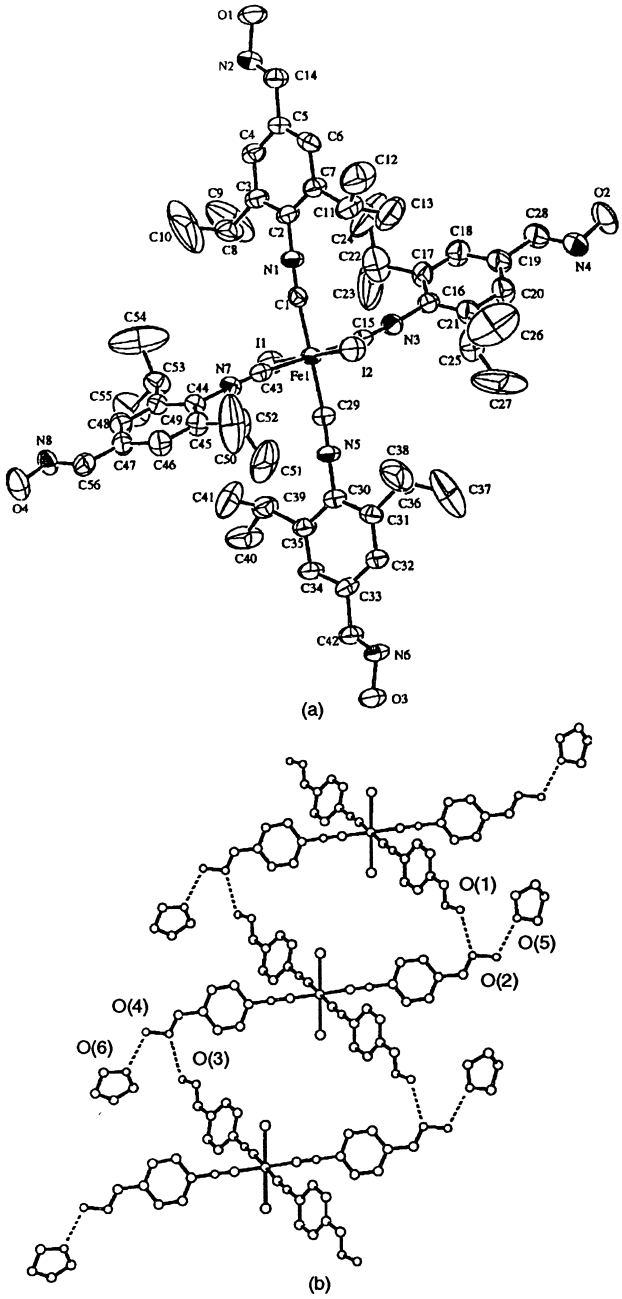


Fig. 3. (a) Molecular structure of **6b**. The thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (°). Fe(1)–I(1) 2.638(1), Fe(1)–I(2) 2.638(1), Fe(1)–C(1) 1.857(6), Fe(1)–C(15) 1.886(8), Fe(1)–C(29) 1.887(6), Fe(1)–C(43) 1.862(8), N(1)–C(1) 1.178(7), N(3)–C(15) 1.144(9), N(5)–C(29) 1.138(7), N(7)–C(43) 1.178(9), N(2)–C(14) 1.265(9), N(4)–C(28) 1.31(1), N(6)–C(42) 1.275(8), N(8)–C(56) 1.254(8), O(1)–N(2) 1.417(7), O(2)–N(4) 1.400(8), O(3)–N(6) 1.387(7), O(4)–N(8) 1.383(7); I(1)–Fe(1)–I(2) 179.16(6), I(1)–Fe(1)–C(1) 88.8(2), I(1)–Fe(1)–C(15) 91.0(2), I(1)–Fe(1)–C(29) 90.6(2), I(1)–Fe(1)–C(43) 90.8(2), C(1)–Fe(1)–C(15) 85.2(3), C(1)–Fe(1)–C(29) 179.2(4), C(1)–Fe(1)–C(43) 93.9(3). (b) Short section of the staircase of molecular units of **6b**. The isopropyl groups are omitted for clarity.

group can act as an hydrogen bond donor as well as (but rarely) an hydrogen bond acceptor. The nitrogen atom frequently serves as an hydrogen bond acceptor. The hydrogen bond distances found in this study are within the established range. In the majority of oxime structures, both the OH group and the nitrogen atom are involved simultaneously, whereby the pairwise arrangement found in the structures **6b** and **9b** is most common. However, as this study confirms, the hydrogen-bonding capability of oxime groups is flexible. In each intermolecular joint of structure **6b**, one OH group forms an hydrogen bond with an 'external' acceptor (THF), and one N atom is not engaged. In the crystal structure **6a**, one type of oxime group appears to form weak OH···I hydrogen bonds. In **6a**, the crystal packing is also stabilized by attractive π interactions between the arene rings [110]. Evidently, the hydrogen bonds of oxime groups exert a strong organizational influence on the packing of the crystals, but they are not of sufficient strength to predetermine the arrangement of the molecular units.

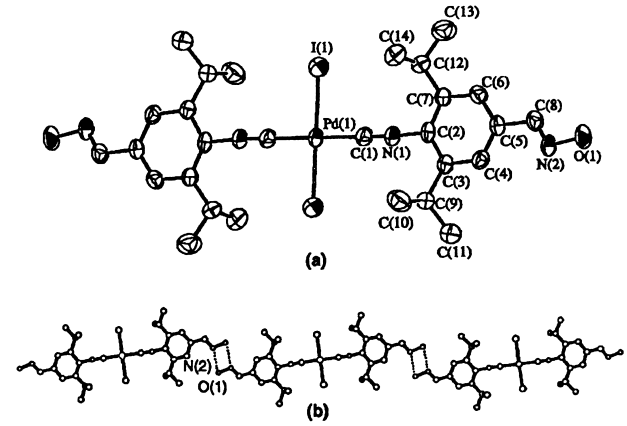


Fig. 4. (a) Molecular structure of **9b**. The thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°). Pd(1)–I(1) 2.5984(4), Pd(1)–C(1) 1.970(4), N(1)–C(1) 1.142(5), N(2)–C(8) 1.255(6), N(2)–O(1) 1.406(4); I(1)–Pd(1)–C(1) 89.1(1). (b) Short segment of a chain of hydrogen-bonded molecular units **9b**.

4. Conclusion

A versatile method for the attachment of hydrogen-bonding groups to isocyanides has been developed. The procedure is useful for the design of isocyanide metal complexes which form hydrogen-bonded networks.

5. Supplementary material

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.

Acknowledgements

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Table 1
Crystal and data collection parameters for complexes **5b**, **6a**, **6b**, and **9a**

	5b	**6a**	**6b**	**9a**
Formula	$C_{56}H_{68}FeI_2N_4O_4$	$C_{40}H_{40}FeI_2N_8O_4$	$C_{56}H_{72}FeI_2N_8O_4.2C_4H_8O$	$C_{28}H_{32}I_2N_4O_2Pd$
Formula weight	1170.83	1006.46	1375.11	816.80
Crystal habit	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P2_1/n$ (No. 14)
a (Å)	12.423(2)	12.423(3)	20.090(4)	10.066(3)
b (Å)	14.185(3)	12.864(2)	19.958(5)	17.868(5)
c (Å)	16.070(3)	16.169(3)	19.552(4)	8.943(5)
β (°)	94.55(2)	102.98(2)	115.33(1)	92.07(4)
V (Å^3)	2822.9(9)	2518.0(8)	7085(2)	1607.3(9)
Z	2	2	4	2
T (K)	301	301	301	301
Crystal color	dark green	dark green	dark green	orange
Crystal dimensions (mm)	0.20 × 0.20 × 0.30	0.20 × 0.15 × 0.30	0.20 × 0.20 × 0.30	0.15 × 0.10 × 0.25
d(calc) (g cm^{-3})	1.377	1.327	1.289	1.688
μ (cm^{-1})	14.06	15.67	11.34	25.28
Scan mode			ω–2θ	ω–2θ
2θ max (°)	51.2	51.2	45	50
Unique reflections	5463	4553	4789	2944
Reflections used in least-squares refinement ($I>3\sigma(I)$)	3809	3481	3728	2178
No. of variables	304	250	728	172
R	0.034[a]	0.049[a]	0.028[a]	0.027[a]
R_w	0.045[b]	0.076[b]	0.032[b]	0.030[b]
p-factor	0.026	0.020	0.018	0.010
(Δ/σ) max.	0.01	0.01	0.05	0.04
Goodness of fit	1.93	3.75	1.39	1.86
$\Delta\rho$ (e Å^{-3})	−0.18/0.28	−0.65/1.16	−0.34/0.62	−0.40/0.44

[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 $w = F_o^2/[\sigma^2(I) + (pF_o^2)^2]$.

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