

Reactivity of ferrocenylalkyl isocyanides. Formation of potential antibiotics and of gold(I) complexes

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Abstract

Reactions of the ferrocenylalkyl isocyanides $C\equiv NCH(R)Fc$ ($Fc = Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)$, $R = cHex$, tBu) with imines and carboxylic acids lead to derivatives of valine or of antibiotics (β -lactams and penicillins) containing the ferrocenyl group which could not be cleaved from the molecules under acidic conditions. The formation of the penicillin derivatives is stereoselective. The isocyanides $C\equiv NCH(R)Fc$ ($R = H$, iPr , $cHex$) and $C\equiv N(EtO_2C)C=CHFc$ react with $[AuCl(PPh_3)]$ to give the corresponding gold(I) complexes $[AuL(PPh_3)]A$ ($L =$ ferrocenyl alkyl isocyanide, $A = Cl$ or BPh_4 when the reaction is carried out in the presence of $Na[BPh_4]$). Cyclic voltammetry in aprotic medium shows that these complexes undergo a reversible single electron oxidation at the iron(II) site at a platinum electrode at a potential which is similar to that observed for the corresponding uncoordinated isocyanides. © 1998 Elsevier Science S.A.

Keywords: Ferrocenylalkyl isocyanides; Gold(I) complexes; Electrochemistry; Four-component reactions; β -Lactams

1. Introduction

The combination of ferrocene with an isocyanide functional group in one molecule is of potential interest for the construction of bimetallic compounds with the possibility of electronic communication between the two metal centres, since the isocyanide group is known as a good ligand for transition metals. We have prepared such compounds and tested their reactivity in the formation of chromium carbonyl complexes [1] and studied their electrochemistry [2]. We found that reactions involving the isocyanide group performed well, while reactions based on the formation of carbanions by deprotonation of the position α to the isocyanide were not successful. We now wish to report on the reactivity of ferrocenylalkyl isocyanides in typical inorganic and organic reactions, namely with a gold(I) phosphine centre or with imines and carboxylic acids, to form products with potential biological activity.

2. Results and discussion

2.1. Reactions with imines and carboxylic acids (four-component reactions)

A typical organic reaction of isocyanides is the four-component reaction, consisting in the combination of an isocyanide, an amine, a carbonyl compound, and an acid to form a single product (possibly as a mixture of diastereoisomers) [3]. Interesting compounds thus obtained are peptide derivatives [4,5] and antibiotics [6]. The four-component reactions performed in this study with ferrocenylalkyl isocyanides are shown in Fig. 1. The products (1)–(3) have been fully characterised by 1H and ^{13}C NMR spectroscopy, chromatography, and elemental analysis (see Section 4).

In the reaction leading to the valine derivative (1), the carbonyl compound (2-methylpropanal) and the amine (benzylamine) were precondensed to the imine prior to treatment with the isocyanide and benzoic acid. A mixture of two diastereoisomers (each as a racemic mixture) in the ratio 1:1 was obtained, showing that the stereogenic centre present in the ferrocene derivative

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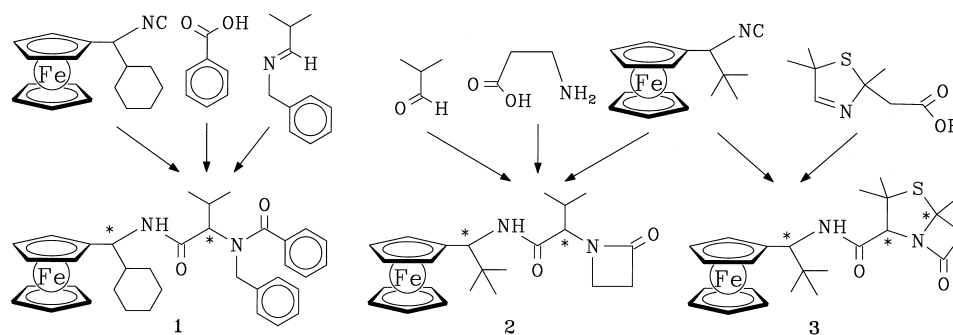


Fig. 1.

does not have sufficient chiral-inducing capability to influence the stereochemistry at the newly-formed stereogenic centre in the valine moiety of (**1**). The total lack of stereocontrol contrasts sharply with the well-known high-inducing ability of ferrocenylalkylamines [7]. A rationale for the difference is that the stereogenic centre in an isocyanide does not come as close to the imine carbon in the transition state and in the intermediates of the reaction as the stereogenic centre in the amine does. A better result, however, was obtained in the formation of the β -lactam (**2**) from 2-methylpropanal and β -alanine. Here, the diastereoisomers formed in a 3:1 ratio. In 2,5,5-trimethyl-2,5-dihydrothiazole-2-acetic acid, finally, three of the four functional groups are preorganised, and the stereogenic centre present in this starting material should lead to four diastereomeric penicillin derivatives (**3**) (each as racemic mixture). Interestingly, only two of them are formed. This selectivity can be explained by the mechanism of the four-component reaction which starts with a nucleophilic attack of the carboxylate to the isocyanide group. This enforces a *cis*-arrangement of the amido substituent (formed by the reaction of this intermediate with the protonated imine) and the β -lactam ring. The configurations of the two diastereoisomers are therefore R_{Fc}^*, R^*, R^* and R_{Fc}^*, S^*, S^* , where the subscript Fc denotes the stereogenic centre in the position α to ferrocene.

For practical applications, it would be necessary to cleave the ferrocenylalkyl substituent from the potential antibiotic under mild conditions. From the products of four-component reactions with ferrocenylalkyl amines, this can be achieved with trifluoroacetic acid which leads to the formation of highly stable α -ferrocenylalkyl carbocations [8]. Surprisingly, this failed completely in the case of the products (**1**)–(**3**) obtained from ferrocenylalkyl isocyanides. No reaction occurred. The only obvious difference is that the ferrocenylalkyl moiety is bound to a secondary nitrogen atom in the compounds (**1**)–(**3**) while it is bound to a tertiary nitrogen atom in the products from ferrocenylalkyl amines. This difference prevents the use of the ferrocenylalkyl isocyanides as reagents for the synthesis of β -lactam antibiotics.

2.2. Reactions with the gold(I) centre

The isocyanide group is able to coordinate to a variety of transition metal sites (for reviews, see Refs. [9–11]), and we have reported previously the coordination to the chromium pentacarbonyl centre to form the corresponding dinuclear complexes $[(CO)_5Cr\{CNCH(R)Fc\}]$ ($R = H$ or organic substituent) [1,2]. We have now chosen the gold(I) centre of $[AuCl(PPh_3)]$ as target since gold(I) phosphine complexes are known to catalyse aldol type reactions of isocyanides with potential industrial applications [12]. Such complexes are also known to act as chemotherapeutic agents with antitumor and antiarthritic activities [13]. For this purpose, we have already prepared a few gold(I) complexes with bulky thiolates, in particular $[Au(SC_6H_2R_3-2,4,6)(PPh_3)]$ ($R = Me, iPr$), either by addition of PPh_3 to $[Au(SC_6H_2R_3-2,4,6)]_6$ or by reaction of $[AuCl(PPh_3)]$ in THF with the appropriate thiol in the presence of $KOH/EtOH$ [14]. Such thiolate complexes and their crystal structure analysis have been obtained earlier also by Schmidbaur et al. [15] by the reaction of $[AuCl(PPh_3)]$ with the corresponding thiols in the presence of triethylamine.

In the present study, we have observed that refluxing a THF solution of $[AuCl(PPh_3)]$ with $CNCH_2Fc$ for two days leads to the formation of the expected complex $[Au(CNCH_2Fc)(PPh_3)]Cl$ (**4**). When the reaction is carried out in the presence of $Na[BPh_4]$, heating is not required and the complexes $[Au(CNCH(R)Fc)(PPh_3)][BPh_4]$ ($R = iPr$ (**5**) or *c*Hex (**6**)) and $[Au\{CN(EtO_2C)C=CHFc\}(PPh_3)][BPh_4]$ (**7**) are isolated from the reaction with the appropriate ferrocenyl isocyanide at room temperature.

These reactions involve the displacement of the *chloride* ligand by the isocyanide and lead to ionic species. This is clearly different from the reported [16] formation of neutral isocyanide complexes $[AuCl(CNC_6H_4F-3 \text{ or } -4)]$ by displacement of *dimethylsulfide* from $[AuCl(SMe_2)]$ by the isocyanide. As no further nucleophiles are present in the reaction mixture, the isocyanide complexes do not react further to form imino derivatives, as was observed in the reaction of

[AuCl(PPh₃)] with aromatic isocyanides in KOH/methanol [17]. Here, chloride is displaced by the isocyanide first, and the coordinated isocyanide is then attacked nucleophilically by the methoxide ion to form, e.g., [Au{C(OMe)=NC₆H₅}(PPh₃)].

The complexes (5)–(7) were isolated as yellow solids and characterised by IR, ¹H NMR and ³¹P NMR spectroscopy, cyclic voltammetry and elemental analysis. Their IR spectra exhibit bands typical for triphenylphosphine and the $\nu(\text{CN})$ vibration of the isocyanide ligands (the latter falling in the range of 2100–2180 cm⁻¹ in KBr discs), whereas the strong $\nu(\text{Au–Cl})$ band at 325 cm⁻¹ [18,19] of the parent complex [AuCl(PPh₃)] is not observed, confirming the replacement of chloride by the isocyanide ligand. The shift of the $\nu(\text{CN})$ vibration upon coordination to the gold(I) centre is quite low ($|\Delta\nu| \leq 40 \text{ cm}^{-1}$), indicating that only a modest activation of the isocyanide group can be expected. By cyclic voltammetry in 0.2 M [NBu₄][BF₄] in CH₂Cl₂, THF or acetonitrile, the ferrocenylalkyl isocyanide complexes exhibit a single-electron reversible anodic wave at a half-wave oxidation potential which is very close to that of the free ligands [1,2,20] ($|\Delta E_{1/2}| \leq 0.06 \text{ V}$). This wave is assigned to the Fe(II)/Fe(III) transition. Therefore, the coordination of the isocyano group to the gold(I) centre does not have an appreciable effect on the energy of the HOMO as compared to the free ligand. A similar behaviour was observed upon coordination of ferrocenylalkyl isocyanides to the Cr(CO)₅ centre [1,2]. The main reason for this observation is probably the separation of the isocyanide from the ferrocene moiety by a tetracoordinated carbon atom in (4)–(6) or two carbon atoms (although unsaturated) in (7) which leads to an attenuation of the electronic effects.

3. Conclusion

In this study, the potential of ferrocenylalkyl isocyanides to the synthesis of compounds with pharmaceutical applications was explored. They undergo readily four-component reactions to form peptide and antibiotic derivatives. The chiral inducing power of ferrocenylalkyl isocyanides with a stereogenic centre α to the isocyanide group is, however, not very high, and mixtures of diastereoisomers are always obtained. To achieve stereoselectivity requires a suitable preorganization of the other functional groups prior to reaction with the isocyanide, as is the case with the dihydrothiazole derivative which leads to only four of the expected eight stereoisomers of the penicillin derivative (3). From the experience with ferrocenylalkyl amines as chiral inducing agents in four-component reactions, it was expected that the ferrocenylalkyl group should be easily cleaved from the reaction products under acidic conditions to leave the active antibiotic. However, this was not the

case, a fact which prevents the use of the ferrocenylalkyl isocyanides as auxiliaries for the synthesis of antibiotics.

The coordination ability of the isocyano group towards a transition metal can be used for the preparation of bimetallic complexes with potential use as chemotherapeutics, such as the gold(I) complexes described here. Electronic effects of such a coordination on the redox properties of the iron(II) site are not sufficiently intense to allow for a definite interpretation, nor does the shift of the $\nu(\text{CN})$ vibration upon coordination. The attenuation of the electronic effects by saturated carbon bridges between the two metal centres may account for the lack of electronic communication between iron and gold.

4. Experimental

4.1. General

The ferrocenylisocyanides were prepared as described [1,21]. [AuCl(PPh₃)] was obtained from H[AuCl₄] by a published method [22]. The reactions were carried out in the absence of air using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures. NMR spectra were recorded in CDCl₃ with Bruker AM 360 and Varian Unity 300 instruments. Internal SiMe₄ (¹H and ¹³C) and external 85% H₃PO₄ (³¹P) were used as standards; δ values are quoted. IR measurements were carried out with a Perkin-Elmer 683 spectrophotometer. Microanalyses were performed at Centro de Química Estrutural, Lisboa, and Institut für Organische Chemie der TU München, Garching. The electrochemical experiments were performed on an EG&G PARC 173 potentiostat and an EG&G PARC 175 universal programmer. A two-compartment three-electrode cell, with a platinum-wire working electrode, probed by a Luggin capillary connected to a silver wire pseudoreference electrode and a platinum auxiliary electrode, was employed. The potentials were measured in 0.2 M [NBu₄][BF₄] in CH₂Cl₂, acetonitrile, or THF, using the *trans*-[ReCl(N₂)(Ph₂PCH₂CH₂PPh₂)₂]^{0/+} redox couple ($E_{1/2}^{\text{ox}} = 0.28 \text{ V vs. SCE}$) as internal reference.

4.2. Four-component reactions

4.2.1. Compound (1)

To a solution of *N*-(2-methylpropylidene)benzylamine (10 mmol, 1.61 g) in 35 ml of dry methanol was added under nitrogen benzoic acid (10 mmol, 1.22 g) and 1-cyclohexyl-1-isocyano-methylferrocene (10 mmol, 3.05 g). The mixture was stirred for 20 h at room temperature. Volatile components were stripped off in vacuum, and the residue was treated with diethyl ether

(200 ml). The ethereal solution was washed successively with water (50 ml), 2% aqueous tartaric acid (100 ml), 1 N aqueous NaOH (100 ml) and water (50 ml). After drying with Na₂SO₄ and evaporation of the solvent, the residue was recrystallised from hexane to give a 1:1 mixture of diastereoisomers (4.10 g, 70%). They could be separated by chromatography (silica gel, hexane/ethyl acetate 2:1).

Isomer I (*R_f* 0.60), m.p. 195°C. ¹H NMR (CDCl₃, 360 MHz): 0.80–1.80 (m, 11 H, cyclohexane), 1.08 and 1.04 (2 × d, 3H each, *J* = 6.4 Hz, Me₂CH), 2.88 (m, 1H, Me₂CH), 4.10 (d, 1H, *J* = 10.3 Hz, *i*PrCH), 4.18 (s, 5H, cp), 4.13 (m, 4H, cp(subst.)), 4.58 and 4.69 (2 × d, 1H each, *J* = 15.5 Hz, CH₂Ph), 4.85 (dd, 1H, *J*₁ = 2.3 Hz, *J*₂ = 9.0 Hz, Fc–CH), 7.90 (d, br, 1H, *J* = 9.0 Hz, NH), 6.96 (m, 2H, Ph), 7.13 (m, 3H, Ph), 7.40 (m, 5H, Ph). ¹³C NMR (CDCl₃, 90.55 MHz): 19.9, 20.3 (Me₂CH), 28.9 (Me₂CH), 26.2, 26.4, 27.9, 28.4 (CH₂, cyclohexane), 43.6 (CH, cyclohexane), 53.4 (CH₂Ph), 56.0 (Fc–CH), 73.5 (CH–*i*Pr), 68.7 (cp(unsust.)), 66.0, 67.0, 67.2, 67.4 (CH, cp(subst.)), 88.0 (C_q, cp(subst.)), 126.3–136.7 (8 signals, Ph), 169.8, 173.7 (C=O). Found: C, 73.0; H, 7.4; N, 4.6%; C₃₆H₄₂FeN₂O₂ requires C, 73.2; H, 7.2; N, 4.7%.

Isomer II (*R_f* 0.48), m.p. 208°C. ¹H NMR (CDCl₃, 360 MHz): 0.80–1.75 (m, 11H, cyclohexane), 1.08 and 1.14 (2 × d, 3H each, *J* = 6.4 Hz, Me₂CH), 3.15 (m, 1H, Me₂CH), 3.67 (d, 1H, *J* = 11.1 Hz, *i*PrCH), 4.19 (s, 5H, cp), 4.12 (m, 4H, cp(subst.)), 4.51, 4.69 (2 × d, 1H each, *J* = 15.5 Hz, CH₂Ph), 4.79 (dd, 1H, *J*₁ = 3.0 Hz, *J*₂ = 8.5 Hz, Fc–CH), 8.40 (d, br, 1H, *J* = 8.5 Hz, NH), 7.19 (m, 2H, Ph), 7.30 (m, 3H, Ph), 7.43 (m, 5H, Ph). ¹³C NMR (CDCl₃, 90.55 MHz): 19.2, 20.0 (Me₂CH), 28.5 (Me₂CH), 25.8, 25.9, 28.0, 28.1 (CH₂, cyclohexane), 43.6 (CH, cyclohexane), 52.6 (CH₂Ph), 54.4 (Fc–CH), 76.8 (CH–*i*Pr), 68.4 (cp(unsust.)), 65.6, 66.6, 67.0, 67.2 (CH, cp(subst.)), 88.3 (C_q, cp(subst.)), 126.3–136.3 (8 signals, Ph), 168.7, 173.7 (C=O). Found: C, 73.3; H, 7.0; N, 4.7%; C₃₆H₄₂FeN₂O₂ requires C, 73.2; H, 7.2; N, 4.7%.

4.2.2. Compound (2)

2-Methylpropanal (0.72 g, 10 mmol), β-alanine (0.89 g, 10 mmol), and 1-isocyano-2,2-dimethyl-propylferrocene (2.81 g, 10 mmol) were dissolved in dry methanol (20 ml) and stirred for 5 h at room temperature. The precipitated product (3.71 g, 90%) was dissolved in chloroform (50 ml) and filtered over silica gel (20 g). After evaporation of the solvent, the residue consisted of a 3:1 mixture of diastereoisomers. The main isomer was isolated in pure form by recrystallization from acetone. Yield 2.26 g (60%), m.p. 212°C. ¹H NMR (CDCl₃, 360 MHz): 0.82 (s, 9H, Me₃C), 1.06, 1.08 (2 × d, 3H each, *J* = 6.6 Hz, Me₂CH), 2.38 (m, 1H, Me₂CH), 2.92 (t, 2H, *J* = 4.0 Hz, CH₂–N), 3.47, 3.59 (2 × m, 1H each, CH₂–CO), 4.18 (s, 5H, cp(unsust.)),

4.10 (m, 5H, cp(subst.) + Fc–CH), 4.68 (d, 1H, *J* = 10.3 Hz, CO–CH–N). ¹³C NMR (CDCl₃, 90.55 MHz): 19.4 (Me₂CH), 26.6 (Me₃C), 28.2 (Me₂CH), 35.9, 38.7 (2 × CH₂), 36.1 (Me₃C), 56.9 (Fc–CH), 62.8 (CO–CH–N), 68.6 (cp(unsust.)), 65.7, 66.7, 67.4, 69.7 (CH, cp(subst.)), 87.8 (C_q, cp(subst.)), 167.8, 168.0 (C=O). Found: C, 64.9; H, 7.79; N, 6.88%; C₂₃H₃₂FeN₂O₂ requires C, 65.09; H, 7.60; N, 6.60%.

4.2.3. Compound (3)

2,5,5-Trimethyl-2,5-dihydrothiazole-2-acetic acid (1.87 g, 10 mmol) and 1-isocyano-2,2-dimethyl-propylferrocene (2.81 g, 10 mmol) were dissolved in 20 ml of dry methanol and stirred for 24 h at room temperature. After removal of the solvent, the residue was dissolved in cyclohexane/ethyl acetate 5:1 (80 ml) and the solution filtered over silicagel (20 g). After evaporation of the solvent, the product (3.77 g, 82%) consisted of a 1:1 mixture of diastereoisomers which were separated by chromatography (silica gel, hexane/diethyl ether 3:1).

Isomer I (*R_f* 0.39), m.p. 145–150°C. ¹H NMR (CDCl₃, 360 MHz): 0.86 (s, 9H, Me₃C), 1.58, 1.81, 1.83 (3 × s, 3H each, CH₃), 3.39, 3.53 (2 × d, 1H each, *J* = 16.0 Hz, CH₂), 4.09 (s, 1H, CH), 4.14 (s, 5H, cp), 4.12 (m, 2H, cp(subst.)), 4.19 (m, 2H, cp(subst.)), 4.69 (d, 1H, *J* = 9.6 Hz, Fc–CH), 9.48 (m, br, 1H, *J* = 9.6 Hz, NH). ¹³C NMR (CDCl₃, 90.55 MHz): 26.7 (Me₃C), 28.6, 28.7, 29.4 (CH₃), 35.7 (Me₃C), 53.6 (CH), 58.1 (Fc–CH), 68.5 (cp(unsust.)), 66.3, 67.5 (C_q), 66.3, 70.1 (CH, cp(subst.)), 76.4 (CH–N), 89.0 (C_q, cp(subst.)), 163.3, 173.6 (C=O). Found: C, 61.3; H, 7.1; N, 5.8%; C₂₄H₃₂FeN₂O₂S requires C, 61.5; H, 6.9; N, 6.0%.

Isomer II (*R_f* 0.34), oil. ¹H NMR (CDCl₃, 360 MHz): 0.84 (s, 9H, Me₃C), 1.68, 1.83, 1.84 (3 × s, 3H each, CH₃), 3.34, 3.52 (2 × d, 1H each, *J* = 16.0 Hz, CH₂), 4.14 (s, 5H, cp), 4.13 (m, 2H, cp(subst.)), 4.19 (m, 2H, cp(subst.)), 4.24 (s, 1H, CH), 4.84 (d, 1H, *J* = 10.0 Hz, Fc–CH), 9.11 (m, br, 1H, *J* = 10.0 Hz, NH). ¹³C-NMR (CDCl₃, 90.55 MHz): 26.5 (Me₃C), 28.5, 28.7, 29.2 (CH₃), 36.9 (Me₃C), 53.6 (CH₂), 58.1 (Fc–CH), 68.7 (cp(unsust.)), 66.7, 66.8 (C_q), 66.2, 66.9 (CH, cp(subst.)), 75.9 (CH–N), 87.3 (C_q, cp(subst.)), 164.0, 173.7 (C=O). Found: C, 61.2; H, 7.0; N, 5.8%; C₂₄H₃₂FeN₂O₂S requires C, 61.5; H, 6.9; N, 6.0%.

4.3. Gold complexes

4.3.1. [Au(CNCH₂Fc)(PPh₃)]Cl (4)

To a solution of [AuCl(PPh₃)] (0.15 g, 0.30 mmol) in THF (30 ml) under nitrogen was added isocyano-methylferrocene (0.14 g, 0.60 mmol). The solution was heated to reflux for two days. After cooling, the solution was concentrated. Pentane was added dropwise until a

yellow precipitate appeared. It was filtered off and dried in a vacuum. The analytical sample contains 1/2 molecule of pentane per molecule of the complex. IR (KBr) 2140 cm^{-1} , $\nu(\text{CN})$. ^1H NMR (CDCl_3 , 300 MHz): 4.15 (s, 5H, cp(unsubst.)), 3.98, 4.33 ($2 \times$ s, 2H each, substituted cyclopentadienyl), 4.60, 4.68 (broad, $2 \times$ d, 1H each, $J = 10\text{ Hz}$, CH_2), 7.60 (m, 6H, Ph), 7.73 (m, 6H, Ph), 7.85 (m, 3H, Ph). ^{31}P NMR (CDCl_3 , 121.4 MHz): 16.4. Found: C, 52.4; H, 3.6; N, 2.3%; $\text{C}_{32.5}\text{H}_{32}\text{AuClFeNP}$ requires C, 51.6; H, 4.3; N, 1.9%.

4.3.2. $[\text{Au}\{\text{CNCH}(\text{R})\text{Fc}\}(\text{PPh}_3)][\text{BPh}_4]$ ($\text{R} = i\text{Pr}$ (5), $c\text{Hex}$ (6)) and $[\text{Au}\{\text{CN}(\text{EtO}_2\text{C})\text{C} = \text{CHFc}\}(\text{PPh}_3)][\text{BPh}_4]$ (7)

To a solution of $[\text{AuCl}(\text{PPh}_3)]$ (0.15 g, 0.30 mmol) in THF (30 ml) under nitrogen was added the corresponding isocyanide (0.60 mmol), followed by $\text{Na}[\text{BPh}_4]$ (0.42 g, 1.2 mmol). The mixture was stirred for 7 days at room temperature. After concentration, the residue was dissolved in dichloromethane. After filtering, diethyl ether was added to the solution until a yellow precipitate appeared. It was filtered off and dried in a vacuum.

$\text{R} = i\text{Pr}$ (5): IR (KBr) 2180 cm^{-1} , $\nu(\text{CN})$. ^1H NMR (CDCl_3 , 300 MHz): 0.80, 0.94, 0.99, 1.03 ($4 \times$ d, 1.5H each, $J = 6.6\text{ Hz}$, CH_3), 1.30 (m, 1H, Me_2CH), 4.85 (m, 1H, $\text{CN}-\text{CH}$), 4.25 (s, 5H, cp(unsubst.)), 4.17, 4.30 ($2 \times$ m, 2H each, cp(subst.)), 7.05–7.90 (m, 35H, Ph). ^{31}P NMR (CDCl_3 , 121.4 MHz): 43.4. Found: C, 67.9; H, 5.5; N, 2.1%; $\text{C}_{57}\text{H}_{52}\text{AuBFenP}$ requires C, 65.5; H, 5.0; N, 1.3%.

$\text{R} = c\text{Hex}$ (6): IR (KBr) 2180 cm^{-1} , $\nu(\text{CN})$. ^1H NMR (CDCl_3 , 300 MHz): 0.95 (m, 4H, $c\text{Hex}$); 1.23 (m, 4H, $c\text{Hex}$); 1.70 (m, 2H, $c\text{Hex}$); 5.80 (m, 1H, $c\text{Hex}$); 4.17 (s, 5H, cp(unsubst.)); 4.08 (m, 4H, cp(subst.)); 6.95–7.80 (m, 35H, Ph). ^{31}P NMR (CDCl_3 , 121.4 MHz): 38.6. An analytically pure sample could not be obtained.

$[\text{Au}(\text{CN}(\text{EtO}_2\text{C})\text{C} = \text{CHFc})(\text{PPh}_3)][\text{BPh}_4]$ (7): IR (KBr) 2100 cm^{-1} , $\nu(\text{CN})$. ^1H NMR (CDCl_3 , 300 MHz): 1.25 (t, 3H, $J = 7.2\text{ Hz}$, CH_3), 4.19 (qua, 2H, $J = 7.2\text{ Hz}$, CH_2), 4.17 (s, 5H, cp(unsubst.)), 4.31, 4.47 ($2 \times$ t, 2H each, $J = 1.8\text{ Hz}$, cp(subst.)), 7.10–7.90 (m, 36H, Ph + = CH). ^{31}P -NMR (CDCl_3 , 121.4 MHz): 43.9. An analytically pure sample could not be obtained.

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