

On Heterometallic Ferrocenyl Compounds of Gold and Platinum

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Summary. The syntheses, properties, and chemical shifts of the heterometal gold(I) complexes $FcNAu \cdot P(C_6H_4Cl-4)_3$ (**1**), $FcN'[Au \cdot PPh_3]_2$ (**2**), and $Fc'[Au \cdot PPh_3]_2$ (**3**) are reported. The electrochemical behaviour of complexes **1** and **3** is compared with that of the related platinum derivatives $(FcN)_2Pt$ (**4**) and $FcNPtCl \cdot PPh_3$ (**5**). Cyclovoltammetric measurements confirm reversible one-electron transfers.

Keywords. Gold; Platinum; Heterometallics; 2-(Dimethylaminomethyl)ferrocenyl (FcN); 2,2'-Bis-(dimethylaminomethyl)ferrocenediyl (FcN'); 1,1'-Ferrocenediyl (Fc'); Electrochemistry.

Über heterometallische Ferrocenylderivate des Golds und Platins

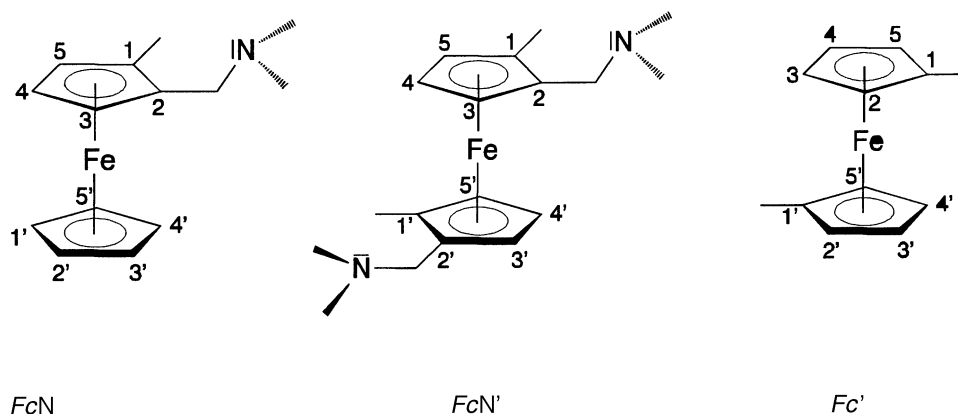
Zusammenfassung. Die Synthesen, Eigenschaften und chemischen Verschiebungen von Heterometalorganika des einwertigen Golds mit den Formeln $FcNAu \cdot P(C_6H_4Cl-4)_3$ (**1**), $FcN'[Au \cdot PPh_3]_2$ (**2**) und $Fc'[Au \cdot PPh_3]_2$ (**3**) werden mitgeteilt. Cyclovoltammetrische Messungen an **1** bzw. **3** im Vergleich mit jenen an den Organoplatinderivaten $(FcN)_2Pt$ (**4**) bzw. $FcNPtCl \cdot PPh_3$ (**5**) bestätigen reversible Einelektronenübergänge.

Introduction

We recently reported on a series of gold(I) complexes of 2-(dimethylaminomethyl)ferrocene of the formula $FcNAu \cdot PR_3$ ($R = C_6H_5$, C_6H_4F-4 , C_6H_4F-3 , C_6F_5 [1]; $C_6H_3F_2-3,4$, $C_6H_3F_2-3,5$, $C_6H_4CH_3-2$, $C_6H_4CH_3-3$, $C_6H_4CH_3-4$, C_2H_5 [2]) as well as on the related platinum complexes $(FcN)_2Pt$ and $FcNPtCl \cdot PPh_3$ [1]. We proved that the FcN -group, which is particularly suitable to form metal chelates, is σ -bound to the gold atom (Au-C- σ -bonding), whereas in the case of $(FcN)_2Pt$ both FcN -groups are chelate-bound to the platinum atom [1].

Transition metal compounds with metal-carbon σ -bonds are sterically sensitive and tend to decompose *via* β -hydride elimination. However, if the organic moiety also possesses donor atoms able to contribute to metal chelation, such a decomposition mechanism can be successfully blocked [3].

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FcN = 2-(Dimethylaminomethyl)ferrocenyl; FcN' = 2,2'-Bis(dimethylaminomethyl)ferrocenediyl;
 Fc' = 1,1'-Ferrocenediyl

Scheme 1

The ferrocenyl ligand (Fc), because of its electron donating ability, can form σ -ferrocenyl transition metal derivatives with metals in high oxidation states, *e.g.* $C_5H_5WO_2(Fc)$ [4] and $Cp_2V(Fc)_2$ [5]. In contrast, the 2-(dimethylaminomethyl)-ferrocenyl group (FcN) is suitable to form heterobimetallic organo metal chelates of selected main group [6] and transition metals even in low oxidation states [1, 7, 8]. The unexpected thermal stability of these heterobimetal derivatives cannot only be explained with the presence of $M \leftarrow N$ interactions, but also with the low tendency of cyclopentadienyl rings substituted in 2-position to undergo β -hydride elimination reactions.

In this connection we became interested not only in the synthesis and properties of gold(I) complexes of 2-(dimethylaminomethyl)ferrocenyl (FcN) and 2,2'-(dimethylaminomethyl)ferrocenediyl (FcN') *versus* 1,1'-ferrocenediyl (Fc') (Scheme 1), but also to test their stability towards oxidation as well as the existence of their mixed-valent congeners.

Results and Discussion

Synthesis and spectroscopic characterization

We have recently found that reaction of $FcNLi$ (**I**) with $ClAu \cdot P(C_6F_5)_3$ affords the dimeric gold(I) compound $(FcNAu)_2$ through release of the weak donor molecule $P(C_6F_5)_3$. Under similar conditions, reaction of $ClAu \cdot PR_3$ ($R = C_6H_5$, C_6H_4F [1], $C_6H_3F_2$ -3,4, $C_6H_3F_2$ -3,5 [2]) can also lead to the heterometal complexes $FcNAu \cdot PR_3$.

In contrast, the use of $ClAu \cdot P(C_6H_2F_3$ -3,4,5) $_3$ as reagent leads to slow decomplexation of the donor ligand $P(C_6H_2F_3$ -3,4,5) $_3$ accompanied by gradual dimerization of two $FcNAu$ -molecules to the dimer $(FcNAu)_2$.

If two equivalents of $P(C_6H_4Cl$ -4) $_3$ react with $(FcNAu)_2$, the gold(I) derivative $FcNAu \cdot P(C_6H_4Cl$ -4) $_3$ (**1**) is formed according to Eq. (1):

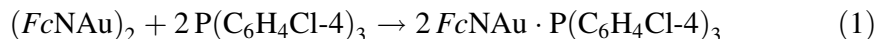


Table 1. Colours, melting points, and ^{31}P NMR chemical shifts relative to external 85% H_3PO_4 of $\text{FcNAu} \cdot \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3$ (**1**), $\text{FcN}'[\text{Au} \cdot \text{PPh}_3]_2$ (**2**), and $\text{Fc}'[\text{Au} \cdot \text{PPh}_3]_2$ (**3**)

	Colour	Fp. ($^\circ\text{C}$)	^{31}P NMR (δ (ppm), C_6D_6 , 25°C)
1	yellow-orange	203 ^a	44.36
2	orange	80–81	45.59
3	orange	121–123	45.45

^a Under decomposition and separation of gold

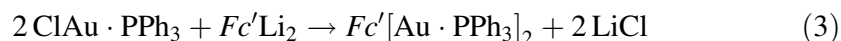
Accordingly, the α,α' -bis(dimethylaminomethyl)ferrocenediyl (FcN') ligand should also be suitable for the syntheses of heterometallic gold(I) derivatives.

(α,α' -Bis(dimethylaminomethyl)ferrocenediyl)dilithium ($\text{FcN}'\text{Li}_2$), prepared by *ortho*-metallation of bis(dimethylaminomethyl)ferrocene ($\text{FcN}'\text{H}_2$) with *n*-BuLi, consists of three isomers: 2,2'-, 5,5'-, and 2,5'- $\text{FcN}'\text{Li}_2$; 2,5'- $\text{FcN}'\text{Li}_2$ is of the *meso* type, 2,2'- and 5,5'- $\text{FcN}'\text{Li}_2$ are chiral.

Reactions of the complex $\text{ClAu} \cdot \text{PPh}_3$ with $\text{FcN}'\text{Li}_2$ (**II**) lead to $\text{FcN}'[\text{Au} \cdot \text{PPh}_3]_2$ (**2**) according to Eq. (2):



The reaction pathway parallels that already described for the synthesis of $\text{Fc}'[\text{Au} \cdot \text{PPh}_3]_2$ (**3**) making use of $\text{Fc}'\text{Li}_2$ (**III**) [9] (Eq. (3)):



The properties of these moisture sensitive gold(I) derivatives which are relatively soluble in benzene, toluene, and dichloromethane are summarized in Table 1. The melting point of **3** is appreciably higher than the value of $104/105^\circ\text{C}$ previously reported [9].

Mass spectroscopic characterization of **1–3** is shown in Table 2. The molecular peak was observed only in the case of **1** ($m/z = 805$). The molecular peak of **3** at

Table 2. Molecular and fragment MS peaks (m/z ; in parentheses: intensity (%)) of $\text{FcNAu} \cdot \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3$ (**1**), $\text{FcN}'[\text{Au} \cdot \text{PPh}_3]_2$ (**2**), and $\text{Fc}'[\text{Au} \cdot \text{PPh}_3]_2$ (**3**)

1		2		3	
Peak	Assignment	Peak	Assignment	Peak	Assignment
805 (10)	$[\text{M}]^+$	^b		1104 (0.1)	$[\text{M}+2 \text{H}]^+$
878 (7)	$[(\text{FcNAu})_2]^+$	758 (1)	$[\text{FcN}'(\text{H})\text{Au} \cdot \text{PR}_3]^+$	922 (0.2)	$[(\text{Fc}')_5+2 \text{H}]^+$
761 (1.5)	$[\text{M-NMe}_2]^+$	713 (0.5)	$[\text{FcN}'(\text{H})\text{Au} \cdot \text{PR}_3\text{-NMe}_2]^+$	738 (0.1)	$[(\text{Fc}')_4+2 \text{H}]^+$
563 (1)	$[\text{Au} \cdot \text{PR}_3]^+$	494 (0.5)	$[\text{FcN}'\text{Au-H}]^+$	554 (0.2)	$[(\text{Fc}')_3+2 \text{H}]^+$
439 (2)	$[\text{AuFcN}]^+$	459 (0.5)	$[\text{Au} \cdot \text{PR}_3]^+$	460 (0.5)	$[\text{Au} \cdot \text{PR}_3]^+$
394 (3)	$[\text{AuFeC}_{11}\text{H}_9]^+$	451 (0.4)	$[\text{FcN}'\text{Au-NMe}_2]^+$	368 (7)	$[(\text{Fc}')_2]^+$
243 (60)	$[\text{FcNH}]^+$	300 (0.5)	$[\text{FcN}'\text{H}_2]^+$	186 (10)	$[(\text{Fc}')\text{H}_2]^+$
366 (99)	$[\text{PR}_3]^+$	262 (100)	$[\text{PR}_3]^+$	262 (100)	$[\text{PR}_3]^+$
329 (4)	$[\text{PR}_3\text{-Cl}]^+$	183 (68)	$[\text{PR}_2\text{-2H}]^+$	183 (72)	$[\text{PR}_2\text{-2H}]^+$
253 (16)	$[\text{PR}_2]^+$	108 (37)	$[\text{PR}]^+$	108 (41)	$[\text{PR}]^+$
199 (59) ^a	$[\text{C}_{11}\text{H}_{11}\text{Fe}]^+$				

^a $\text{C}_{11}\text{H}_{11}\text{Fe} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2$; ^b not observed

Table 3. ^1H and ^{13}C NMR chemical shifts (ppm relative to internal *TMS*) and coupling constants (Hz) of $\text{FcN}[\text{Au}(\text{PPh}_3)_2]$ (**1**), $\text{FcN}[\text{Au}(\text{PPh}_3)_2]$ (**2**), and $\text{Fc}[\text{Au}(\text{PPh}_3)_2]$ (**3**) (C_6D_6 , 25°C)

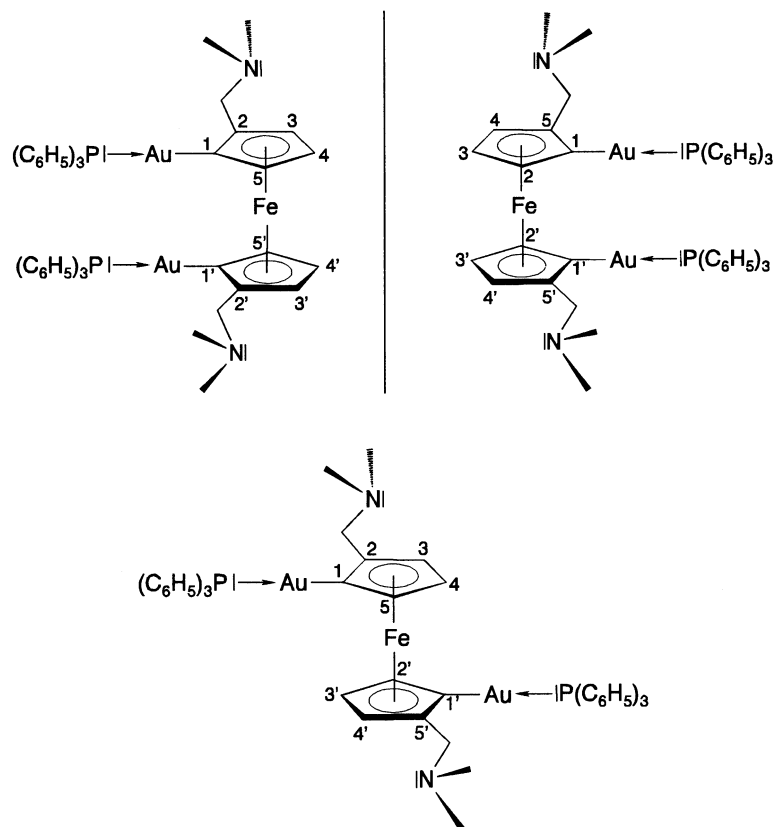
	C_5H_3	C_5H_4	C_5H_5	CH_2	CH_3	C_6H_5
^1H 1	4.39, 4.42, 4.57 (each 1H, s)		4.29 (5H, s)	3.45 (1H, d, $^2J=11.9$) 3.85 (1H, d, $^2J=11.9$) 3.98 (2H, d, $^2J=12$), 2.37 (12H, s) 4.07 (2H, d, $^2J=12$), (12H, s)	2.33 (6H, s)	6.99 (6H, d, $^3J=7.0$) 7.1 ^a
2	4.60, 4.67, 4.90 (each 2H, s)				6.98 (18H, s) 7.59 (12H, m)	
3		4.84, 4.90 (each 4H, s)				6.91 (18H, s) 7.54 (12H, m)
^{13}C 1	^b (quaternary) 70.44, 72.28, 76.98		68.34	63.80	45.59 135.56 (d, $^2J=14.8$) <i>ortho</i>	129.59 (d, $^3J=11.5$) <i>meta</i>
2	90.96 (quaternary) 70.91 (d, $J=6.4$) 72.61 (d, $J=6.3$) 76.71 (d, $J=4.6$)			64.59	45.62	129.06 (d, $^3J=10.5$) <i>meta</i> 130.79 <i>para</i> 134.77 (d, $^2J=13.9$) <i>ortho</i>
3	101.82 (d, $^1J=124.0$) (quaternary) 69.51 (d, $J=6.1$) 76.77 (d, $J=5.1$)				129.01 (d, $^3J=10.5$) <i>meta</i>	130.73 (d, $^4J=2.0$) <i>para</i> 132.13 (d, $^1J=47.9$) <i>ipso</i> 134.67 (d, $^2J=13.7$) <i>ortho</i>

^a Signal partly hidden under the solvents resonance; ^b not unambiguously assigned

$m/z = 1102$ was not detected; nevertheless, a peak at $m/z = 1104$ was recorded which does not correspond to the $[M+2H]^+$ peak but to the fragmentation peak $[Fc'_6]^+$ usually associated to Fc' units. In confirmation, the fragment ion at $m/z = 643$ which should arise by removal of the $[Au \cdot PPh_3]$ appendix ($m/z = 459$) from the molecular ion ($m/z = 1102$) could not be detected.

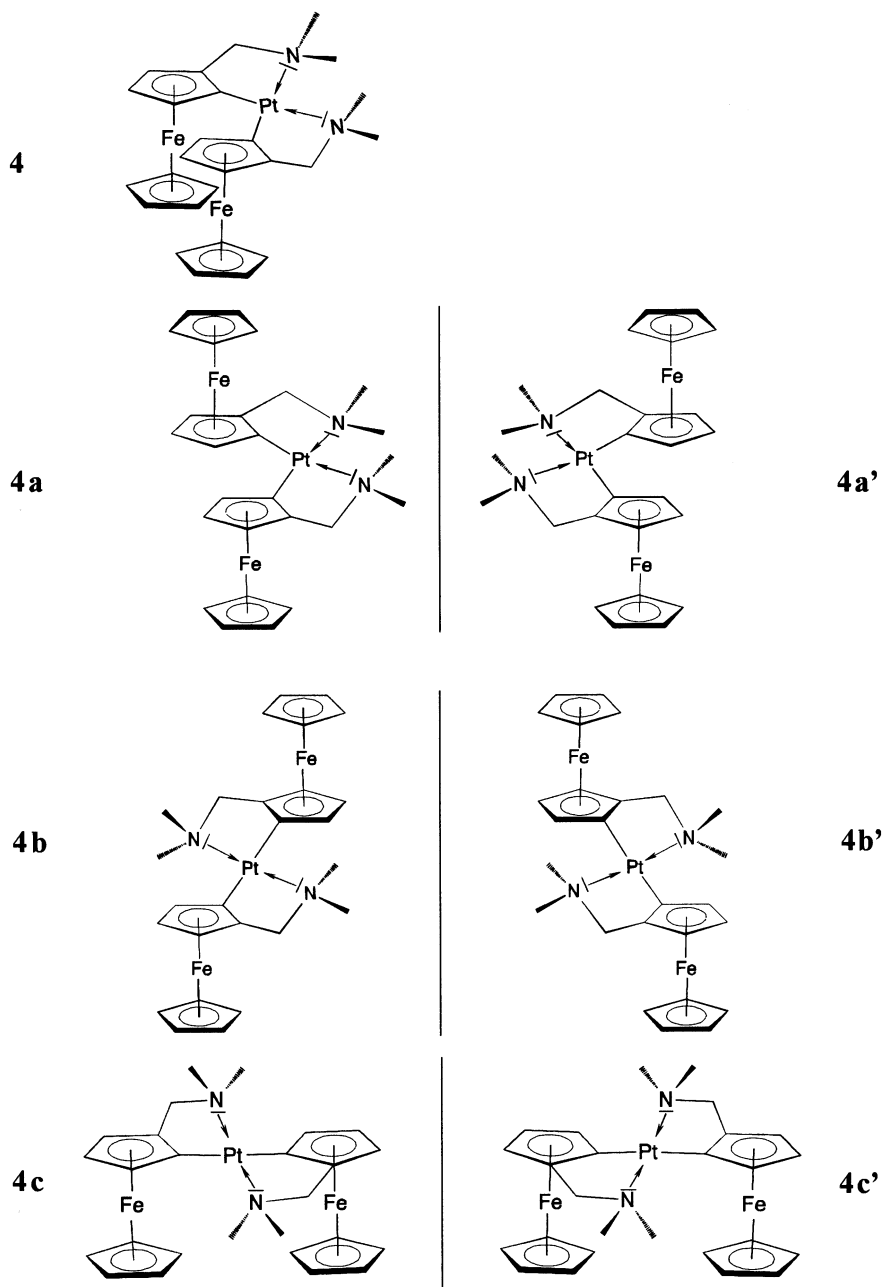
In agreement with our findings concerning the NMR spectra of $FcNAu \cdot PR_3$ ($R = C_6H_5, C_6H_4F-3, C_6H_4F-4$ [1]; C_6H_4Cl-3 [2]), the two expected singlets of the $(CH_3)_2N$ group of the chelate-bound FcN ligand [1, 6, 10] were not observed for $FcNAu \cdot P(C_6H_4Cl-4)_3$ (**1**), neither in the 1H nor in the ^{13}C NMR spectra (^{31}P : Table 1; $^1H, ^{13}C$: Table 3). This is a first proof that the FcN group in **1** could be bound at the gold(I) atom *via* Au-C- σ -bonding.

The reported chemical shifts are in accordance with the formulas $FcN[Au \cdot PPh_3]_2$ (**2**) and $Fc'[Au \cdot PPh_3]_2$ (**3**), respectively. The singlets of the five protons of the unsubstituted C_5H_5 ring of the FcN group of **1** are missing in the 1H and ^{13}C NMR spectra of **2** and **3**. As far as the protons of the substituted cyclopentadienyl ring are concerned, unexpectedly only three and two singlets were observed for **2** and **3**, respectively in the 1H and ^{13}C NMR spectra. X-ray analysis essentially proved the composition of **3**, although the crystal structure of **3** cannot yet be published because of its bad R -value ($>11\%$).



Scheme 2

Given that only three CH signals of the two disubstituted cyclopentadienyl rings of the FcN' group are observed in **2**, it can be expected that the $CH_2N(CH_3)_2$ appendices occupy the same positions in the upper as well as in the lower C_5H_3 rings. Accordingly, as Scheme 2 shows, the gold(I) derivative $FcN'[Au \cdot PPh_3]_2$ (**2**) may exist as a pure racemate (2,2'- and 5,5'-isomer) or as a pure *meso* form (2,5'-isomer). This is reminiscent of the isomeric mixtures (2,2'-, 2,5'-, 5,5'-isomers) found in the platinum(II) complex $FcN'[PtCl]_2$ [11].



Scheme 3

Table 4. ^1H , ^{13}C , and ^{195}Pt NMR chemical shifts (ppm relative to internal *TMS* or Na_2PtCl_6 , respectively) and coupling constants (Hz) of $(\text{FcN})_2\text{Pt}$ (**4**) (**4**: *meso* form; **4'**: one of the possible racemates **a/a'**, **b/b'**, or **c/c'**) at 25°C

	C_5H_3	C_5H_5	CH_2	CH_3
^1H 4 ^a	3.85, 4.11, 4.16 (each 1H, s)	4.00 (5H, s)	3.27 (1H, d, $^2J=13.6$) 3.73 (1H, d, $^2J=13.6$)	3.12 (3H, s, $^3J=44.0$) 3.38 (3H, s, $^3J=46.9$)
4' ^b	4.08, 4.10, 4.28 (each 1H, s)	5.17 (5H, s)	3.61 (1H, d, $^2J=13.2$) 3.1 (under CH_3)	2.65 (3H, s, $^3J=ca. 15$) 3.15 (4H, s, $^3J=ca. 15$)
^{13}C 4 ^a	103.76, 98.25, (quat.) 67.59, 68.95, 70.68	68.25	62.47	55.95 56.58
4' ^b	^c (quaternary) 66.43, 67.71, 71.02	68.88	61.02	50.95 51.19
^{195}Pt 4 ^b	−4521			
4' ^b	−4521			

^a CD_2Cl_2 , ^b CDCl_3 , ^c not unambiguously assigned

On the other hand, in the case of complex $(\text{FcN})_2\text{Pt}$ (**4**), the *meso* form was determined by X-ray analysis after its separation from an isomeric mixture [1]. Further crystallization of a concentrated solution of $(\text{FcN})_2\text{Pt}$ by addition of *n*-hexane afforded within eight weeks also diastereomer pairs **4'** (**4a/a'**, **4b/b'**, or **4c/c'**; Scheme 3).

The ^1H and ^{13}C NMR chemical shifts of the *meso* form of $(\text{FcN})_2\text{Pt}$ (**4**) as well as of the racemate pairs **4'** are compiled in Table 4.

Their interpretation is not straightforward in that each of the enantiomeric pairs of **4'** (**4a/a'**, **4b/b'**, **4c/c'**) gives rise to the same spectra in optically inactive solvents. Two ^1H as at ^{13}C NMR signals for the $(\text{CH}_3)_2\text{N}$ group of the *FcN* system in **4** and **4'** support chelation of the *FcN* ligands to the platinum atom. These Pt←N interactions result in a decrease of the electron density either at H or at C atoms of the methyl groups of the $(\text{CH}_3)_2\text{NCH}_2$ fragments in the *FcN* ligands. In comparison with $\text{FcNAu} \cdot \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3$ (**1**) (Table 3) this leads to a lowfield shift of the $(\text{CH}_3)_2\text{N}$ signals of **4** and **4'**.

Electrochemistry

Paralleling the electrochemical behaviour of the previously reported series of the gold(I) derivatives $\text{FcNAu} \cdot \text{P}(\text{C}_6\text{H}_5\text{-}n\text{X}_n)_3$ [2], complex **1** exhibits a ferrocene-centred one-electron oxidation, followed by slow decomposition of the corresponding monocation [**1**]⁺. As deducible from the cyclic voltammetric profile shown in Fig. 1, in acetonitrile solution the ferrocenediyl complex **3** exhibits an oxidation process in which the electrogenerated monocation [**3**]⁺ undergoes decomposition reactions even faster than those of [**1**]⁺. So controlled potential coulometry ($E_w = +0.05$ V) consumes one electron *per* molecule, the original yellow-orange solution turns pale pinky, and cyclic voltammetry after exhaustive oxidation displays no more traces of the original system.

Analyses of the cyclic voltammograms with scan rates ν varying from $0.02 \text{ V} \cdot \text{s}^{-1}$ to $2 \text{ V} \cdot \text{s}^{-1}$ are consistent with an $E\tau C_{\text{irr}}$ mechanism [12]: (i) the current function $i_{\text{pa}}/\nu^{1/2}$ is constant, (ii) the peak-to-peak separation does not depart appreciably

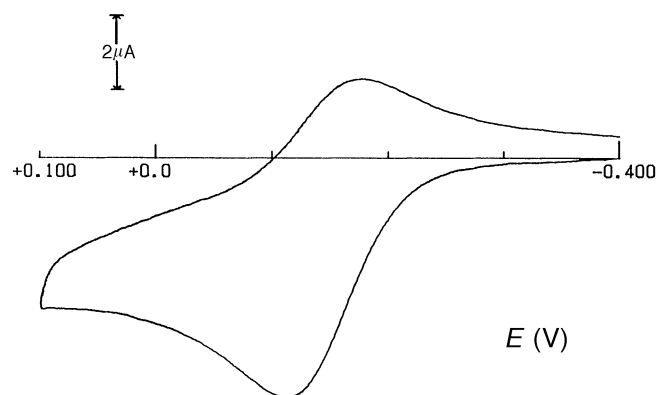


Fig. 1. Cyclic voltammetric response recorded at a platinum electrode of a MeCN solution containing $Fc'[Au \cdot P(C_6H_5)_3]_2$ (**3**) ($5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) and $[NEt_4][ClO_4]$ ($0.1 \text{ mol} \cdot \text{dm}^{-3}$); scan rate: $0.2 \text{ V} \cdot \text{s}^{-1}$

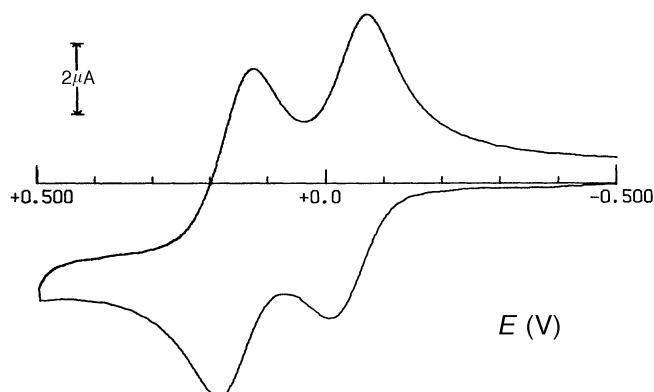


Fig. 2. Cyclic voltammetric response recorded at a platinum electrode of a CH_2Cl_2 solution containing $(FcN)_2Pt$ (**4**) ($5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) and $[NEt_4][PF_6]$ ($0.2 \text{ mol} \cdot \text{dm}^{-3}$); scan rate: $0.2 \text{ V} \cdot \text{s}^{-1}$

from the theoretical value of 59 mV, and (iii) the peak current ratio i_{pc}/i_{pa} , which is 0.1 at $0.1 \text{ V} \cdot \text{s}^{-1}$, progressively increases to 0.9 at the highest scan rate.

In contrast to the behaviour of the above mentioned ferrocene-gold derivatives, the platinum compounds **4** and **5** exhibit higher redox stability. Compound **5** undergoes a reversible one-electron oxidation either at the cyclic voltammetric or at the controlled potential coulometric timescale. As Fig. 2 illustrates, complex **4** displays two consecutive oxidations, each of them displaying features of chemical reversibility.

Step-by-step controlled potential coulometry shows that each process involves a one-electron removal. Cyclic voltammetry of progressively oxidized solutions proved that the monocation $[4]^+$ is quite stable, whereas the dication $[4]^{2+}$ undergoes slow decomposition reactions. The appearance of two separated oxidations suggests that the central platinum atom allows electronic communication between the two ferrocene units. In this connection, a K_{com} value of about $2 \cdot 10^3$, which has been calculated from the difference in the redox potentials of the two sequential one-electron transfer, allows the monocation $[4]^+$ to be classified as

Table 5. Electrochemical parameters for the oxidation process of $FcNAu \cdot P(C_6H_4Cl-4)_3$ (**1**), $Fc'[Au \cdot PPh_3]_2$ (**3**), $(FcN)_2Pt$ (**4**), and $FcNPtCl \cdot PPh_3$ (**5**)

	$E_{0/+}^{o'}$ (V)	i_{pc}/i_{pa}^a	ΔE_p^a (mV)	$E_{+/2+}^{o'}$ (V)	i_{pc}/i_{pa}^a	ΔE_p^a (mV)	solvents
1	+0.09	0.75	78				CH ₂ Cl ₂ ^b
3	-0.15	0.3	70				MeCN ^c
	-0.20	0.4	82				CH ₂ Cl ₂ ^b
4 ^d	-0.04	1.0	66	+0.15	1.0	66	CH ₂ Cl ₂ ^b
5	+0.17	1.0	92				CH ₂ Cl ₂ ^b
Fe(C ₅ H ₅) ₂	+0.39	1.0	94				CH ₂ Cl ₂ ^b
	+0.38	1.0	75				MeCN ^c

^a Measured at 0.2 V · s⁻¹; ^b [NBu₄][PF₆], 0.2 mol · dm⁻³; ^c [NEt₄][ClO₄], 0.1 mol · dm⁻³; ^d mixture of **4** (*meso* form) and **4'** (see Scheme 3)

a slightly delocalized *Robin-Day* Class II mixed-valent species [13]. By way of speculation, biferrocene displays higher communication (K_{com} value of about $5 \cdot 10^5$ [14]), whereas diferrocenylmethane exhibits lower electronic interaction (K_{com} value of about 10^2 [15]).

Table 5 summarizes the electrochemical parameters of the oxidation processes exhibited by the investigated derivatives **1** and **3–5**.

In all cases, incorporation of the present gold or platinum fragments in the ferrocene backbone makes the oxidation much easier than that of unsubstituted ferrocene, thus testifying the strong electron-donating ability of such fragments.

Experimental

Since the investigated compounds are moderately sensitive to air and moisture, all operations were carried out under argon as an inert gas. The synthesis of (2-(dimethylaminomethyl)-ferrocenyl)-lithium (FcN)Li was carried out by lithiation of dimethylaminomethylferrocene (Fluka Chemie GmbH) with *n*-BuLi [16]; the tetramethylenediamino complex of 1,1'-(ferrocenediyl)-dilithium ($Fc'Li_2$) was prepared by reaction of ferrocene (Fluka Chemie GmbH) with *n*-BuLi in the presence of tetramethylethylenediamine [17]. The synthesis of (α,α' -bis(dimethylaminomethyl)ferrocenediyl)-dilithium ($FcN'Li_2$) was carried out by dilithiation of 1,1'-bis(dimethylaminomethyl)ferrocene $FcNH_2$ [17] with *n*-BuLi according to Ref. [16].

The syntheses of ClAu · PPh₃ [18], $(FcN)_2Pt$, and $(FcNAu)_2$ [1] were performed according to literature procedures. $P(C_6H_4Cl-4)_3$ was a commercial product (Lancaster Synthesis GmbH).

Mass spectra were recorded on an AMD 402 (Sector Field, EI, 70 eV) Intectra GmbH spectrometer. NMR spectra were measured with a Gemini XL-300 Varian spectrometer. Apparatus and materials for electrochemistry have been described elsewhere [19]; all potential values are referred to a saturated calomel electrode (SCE).

$FcNAu \cdot P(C_6H_4Cl-4)_3$ (**1**)

70 mg (0.08 mmol) of $(FcNAu)_2$ were dissolved in 10 ml diethyl ether. 57 mg (0.16 mmol) of $P(C_6H_4Cl-4)_3$ were added at room temperature under stirring. After stirring for 30 minutes, the solvent was removed by oil pump vacuum. *n*-Pentane was added, and the resulting solution was stored in refrigerator for two days at 0°C. The separated brown precipitate was filtered and the

solvent reduced to a volume of 30 ml. Storage at 0°C for approximately 10 days afforded yellow-orange crystals which were filtered and dried by oil pump vacuum. Yield: 110 mg (85%); Fp.: 203°C (decomposition).

$FcN[Au \cdot P(C_6H_5)_3]_2$ (**2**)

A suspension of 0.67 g (1.35 mmol) of $ClAu \cdot P(C_6H_5)_3$ in 30 ml diethyl ether was added to 0.22 g (0.70 mmol) of solid $FcN'Li_2$ at $-20^\circ C$ under stirring. Stirring was continued for 3 h at this temperature; then the solution was warmed to room temperature. After 18 h the solution was filtered. Solvent evaporation by application of vacuum afforded 0.83 g of an orange, viscous product. This mixture of isomers possesses only low tendency towards crystallization. Addition of *n*-heptane gave 10 mg of pure diastereomers of **2** which were crystallized for approximately 8 weeks at room temperature. Yield: 0.82 g (99%, raw material), 10 mg (1% pure racemate); Fp: 80–85°C.

$Fc^l[Au \cdot P(C_6H_5)_3]_2$ (**3**)

0.41 g (1.02 mmol) of solid $Fc^lLi_2(tmeda)_2$ were added to a suspension of 1 g (2.02 mmol) of $ClAu \cdot P(C_6H_5)_3$ in 100 ml diethyl ether at $-20^\circ C$ under stirring. Stirring was continued for 3 h at this temperature; then the solution was warmed to room temperature and filtered. After solvent evaporation, the resulting solid residue was extracted with *n*-pentane. Crystallites of **3** separated from the pentane extract. Yield: 0.82 g (74%); Fp: 121–123°C.

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