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Article

Synthesis and Coordination Chemistry of Ferrocenyl-1,2,3-triazolyl Ligands

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"Click" reactions between ethynylferrocene and mono-, bis-, and tris-azido aromatic derivatives yielded mono-, bis-, and tris-1,2,3-ferrocenyltriazoles (**1**, **2**, and **3**, respectively) as orange crystals. The X-ray crystal structure of the monoferrocenyltriazole compound **1** was solved with two nearly identical molecules within the asymmetric unit. In both molecules, the two Cp rings make a tilt angle of 2.1(3)° [0.7(3)°], and they are roughly eclipsed with a twist angle of 2.4(3)° [1.8(3)°]. Reaction of **1** with $[PdCl_2(PhCN)_2]$ in dimethylsulfoxide (DMSO) yielded orange crystals of $[PdCl_2L_2]$ (**4**; L = **1**), for which the X-ray crystal structure shows *trans* coordination to the nitrogen atom close to the ferrocene substitution. The Pd atom is located on an inversion center and displays a nearly perfect square planar environment. In DMSO-d_6, **4** reversibly dissociates to regenerate **1**, whose ^1H NMR spectrum is then observed. The ^1H NMR study also shows that progressive addition of $PdCl_2$ or $[PdCl_2(NCR)_2]$ (R = Me or Ph) to DMSO-d_6 solutions of **1** reversibly leads to the formation of **4** and the addition of excess Pd^{II} is necessary to lead to the complete disappearance of the signals of **1**. The cyclic voltammograms of **1**, **2**, and **3** show the reversible oxidation wave of the ferrocenyl group, and that of **4** shows that this wave appears with increased intensity tentatively attributable to redox-catalyzed oxidation.

Introduction

Triazole ligands have been known for a long time, and their coordination has been investigated with a variety of transition metals.[1–3] Recently, the dipolar Huisgen-type cycloaddition[4] between alkynes and azido derivatives, made selective, catalytic, and convenient and called "click" chemistry, has been widely used in organic and bio-organic chemistry.[5] These highlighted advantages have considerably renewed the interest in 1,2,3-triazolyl derivatives. Little use has been made in inorganic chemistry, however, although the disubstituted 1,2,3-triazole ligands formed in this click reaction can also coordinate transition metals. Indeed, we recently reported the synthesis of ferrocenyl triazolyl dendrimers that can recognize and sense several transition metal ions by using the variation of the potential of the ferrocenyl wave.[6a] Titration of the ions could be carried out in order to

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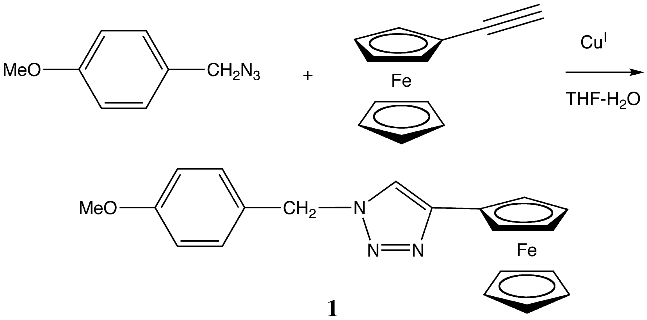
determine the number of Pd^{II} ions that bound triazole ligands inside the dendrimer.[6b] The resulting ligand−Pd^{II} interaction allowed the designing of Pd nanoparticles (NPs) of precise sizes for mechanistic investigation of their catalytic efficiency.[6b–d]

Therefore, we wished to investigate simple but precise coordination modes of nondendritic disubstituted 1,2,3-triazolylferrocene ligands resulting from click reactions between ethynylferrocene and simple terminal alkynes. Here, we report such studies involving mono-, di-, and triazides as well as ^{1}H NMR, electrochemical, and X-ray structural studies of the interaction of some mono-1,2,3-triazolylferrocene derivatives with several transition metal compounds in dimethylsulfoxide (DMSO). There are a few reports of click reactions between azido derivatives and ethynylferrocene, in polymer[7] and surface[8] chemistry.

Results and Discussion

Synthesis of Mono-, Bis-, and Tris(1,2,3-ferrocenyltriazole) Derivatives. We started from 4-methoxybenzylbromide, which was easily converted to 4-methoxybenzylazide[9] upon reaction with sodium azide in DMSO. Then, reaction of the latter with ethynylferrocene in THF/water in the presence of catalytic amounts of copper sulfate and sodium ascorbate under ambient conditions led to the formation of the 1,2,3-ferrocenyltriazole (**1**) in a 67.7% yield of orange microcrystals (eq 1). Similarly, *p*-dibromomethylbenzene was converted to *p*-diazidomethylbenzene,[9a,b] and the click reaction under the same conditions yielded bis(ferrocenyl-1,2,3-triazolylmethyl)benzene (**2**) in a 45% yield of yellow-orange microcrystals (eq 2). Finally, tris(1,3,5-bromomethyl)benzene was similarly converted to tris-1,3,5-tris(azidomethyl)benzene,[9c] and the reaction of the latter with ethynylferrocene yielded tris-1,3,5-tri(ferrocenyl-1,2,3-triazolymethyl)benzene (**3**) in a 27% yield of orange-brown microcrystals (eq 3). These 1,2,3-ferrocenyltriazole derivatives were characterized by the lack of an azide band (2095 cm^{-1}) in the IR spectrum, by the characteristic position of the triazolyl proton signal at 8.1 ppm versus TMS in DMSO-d_6 in ^{1}H NMR, and by elemental analysis. In addition, the ferrocene signals in ^{1}H NMR are characteristic, with the free Cp being found at 4.0 ppm, whereas the protons of the substituted cyclopentadienyl are located downfield at 4.70 ppm for the α protons and 4.28 ppm for the *β* proton. Finally, the X-ray crystal structure of **1** could be solved (Figure 1).



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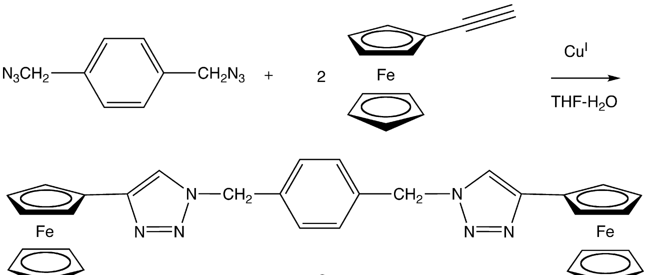

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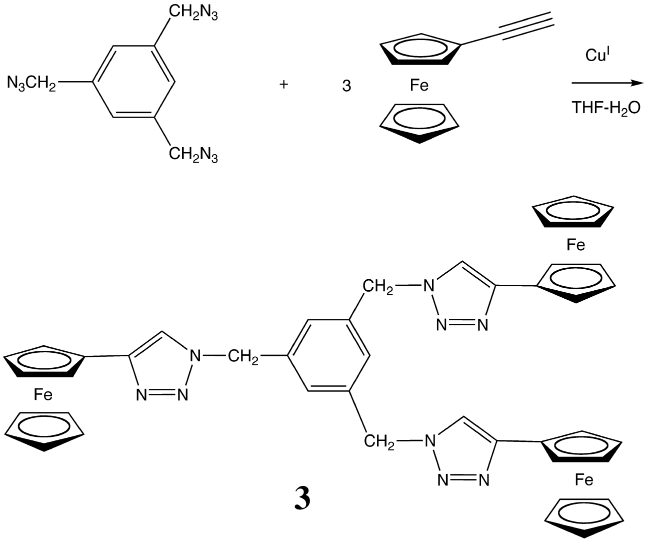

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Reaction of *p*-Methoxybenzyl-1,2,3-triazolylferrocene (1) with $PdCl_2(C_6H_5CN)_2$ and Compared X-ray Crystal Structures of 1 and Its $Pd^{II}Cl_2$ Complex 4. The reaction of $[PdCl_2(C_6H_5CN)_2]$ with **1** (eq 1) was carried out under ambient conditions in toluene. The ^{1}H NMR spectrum of the crude reaction product in DMSO-d_6 showed both series of signals of the Pd-coordinated and the noncoordinated triazole compounds. Crystallization of the crude reaction product in DMSO-d_6 yielded light brown crystals of the Pd complex **4** that were subjected to X-ray crystal structure analysis. The X-ray crystal structures of **1** and **4** are compared (Table 1).

The structure of compound **1** obtained by X-ray diffraction is presented in Figure 1 and shows the occurrence of two nearly identical molecules (**A** and **B**) within the asymmetric unit. In both molecules, the two Cp rings make a tilt angle of 2.1(3)° [0.7(3)°], and they are roughly eclipsed with a twist angle of 2.4(3)° [1.8(3)°]. The other geometrical parameters within the ferrocene framework are as usually observed. As expected, the triazole ring is planar, and it is slightly twisted with respect to the Cp ring to which it is

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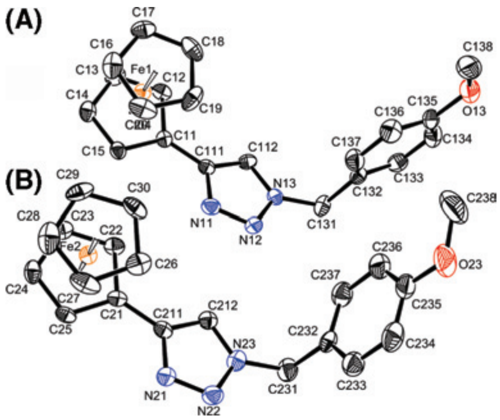

Figure 1. Molecular view of compound **1** with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Table 1. Crystal Data and Structure Refinement

	1	**4**
empirical formula	$C_{40}H_{38}Fe_2N_6O_2$	$C_{20}H_{19}ClFeN_3OPd_{0.50}\cdot 0.33(H_2O)$
fw	746.46	467.89
T, K	180(2)	180(2)
cryst syst	monoclinic	trigonal
space group	$P2_1/n$	$R\bar{3}$
a, Å	9.6335(7)	27.4194(7)
b, Å	33.4307(18)	27.4194(7)
c, Å	11.3666(8)	13.5881(4)
α, deg	90.0	90.0
β, deg	114.273(9)	90.0
γ, deg	90.0	120.0
V, Å^3	3337.1(4)	8847.2(4)
Z	4	18
D_{calcd}, Mg/m^3	1.486	1.581
μ, mm^{-1}	0.917	1.362
F(000)	1552	4272
cryst size, mm^3	0.383 × 0.115 × 0.077	0.281 × 0.222 × 0.162
θ range, deg	2.64−26.37	2.97−26.37
reflns collected	25 882	23 181
unique reflns [R_{int}]	6810 [0.0687]	4029 [0.0282]
obsd reflns [$I > 2\sigma(I)$]	2865	3133
completeness	99.9	99.8
abs correction	multiscan	multiscan
T_{min}/T_{max}	1.0/0.85835	1.0/0.69297
params	453	251
GOF on F^2	0.876	1.043
R1, wR2 [$I > 2\sigma(I)$]	0.0356, 0.0644	0.0373, 0.0936
R1, wR2 (all data)	0.1116, 0.0845	0.0542, 0.1080
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	−0.440, 0.351	−0.868, 1.206

attached, making a dihedral angle of 17.3(2)° [16.9(2)°]. The largest difference between the two molecules building the asymmetric unit is reflected in the dihedral angle between the methoxy substituted phenyl ring and the triazole, which is 87.0(1)° for molecule **A**, as compared to 69.3(1)° for molecule **B**.

The structure of the Pd complex **4** is presented in Figure 2. The Pd atom is located on an inversion center and displays a nearly perfect square planar environment with two N atoms from a symmetry-related ligand and two Cl atoms *trans* to each other. The triazolyl ring is nearly perpendicular to the Pd square plane with a dihedral angle of 84.1(1)°. The two *p*-methoxybenzyltriazolylferrocene ligands are coordinated to $PdCl_2$ in the *trans* position via a Pd−N bond in the β position with respect to the ferrocenyl ring.

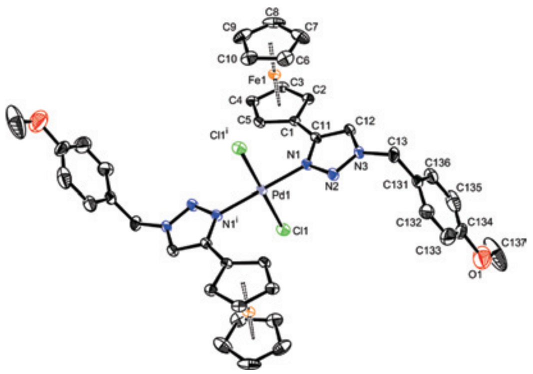

Figure 2. Molecular view of compound **4** with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Table 2. Comparison of Selected Parameters within the Free Ligand **1** and the Complex **4** (Å, deg)

	1A	**1B**	**4**
Fe(1)−Cg(1)	1.6438(16)	1.6444(16)	1.642(2)
Fe(1)−Cg(2)	1.6453(18)	1.6452(17)	1.649(3)
C(1)−N(1)			
N(1)−N(2)	1.322(3)	1.323(4)	1.328(4)
N(2)−N(3)	1.345(4)	1.333(4)	1.333(4)
N(1)−C(11)	1.362(4)	1.360(4)	1.344(4)
N(3)−C(12)	1.348(4)	1.343(4)	1.328(5)
N(3)−C(13)	1.453(4)	1.468(4)	1.475(5)
Pd(1)−N(1)			1.993(3)
Pd(1)−Cl(1)			2.2866(10)
Cg(1)−Fe(1)−Cg(2)	178.62(10)	179.47(9)	177.46(4)
N(2)−N(1)−C(11)			111.5(3)
C(12)−N(3)−N(2)			112.0(3)
N(1)−N(2)−N(3)			104.9(3)
N(2)−N(3)−C(13)			120.3(3)
C(12)−N(3)−C(13)			127.7(3)
N(3)−C(12)−C(11)			106.0(3)
N(1)−C(11)−C(12)			105.7(3)
N(1)−C(11)−C(1)			127.0(3)
C(12)−C(11)−C(1)			127.4(3)
N(1)^a−Pd(1)−Cl(1)			89.88(9)
N(1)−Pd(1)−Cl(1)			90.12(9)

[a] The symmetry code used to generate equivalent atoms: $-x + 1, -y, -z + 2$.

The asymmetric unit is built up from half of the complex and contains 0.33 solvate water molecules. As observed in Table 2, the coordination to the Pd atom through the N1 atom does not affect significantly the geometry of the ligand. The largest differences appear in the dihedral angle between the triazolyl ring and the Cp ring to which it is attached, 14.2(3)° compared to 17° (mean value), and the tilt angle between the two Cp rings, 3.7(4)° in place of 1.5° (mean value). A ConQuest search of the Cambridge Structural

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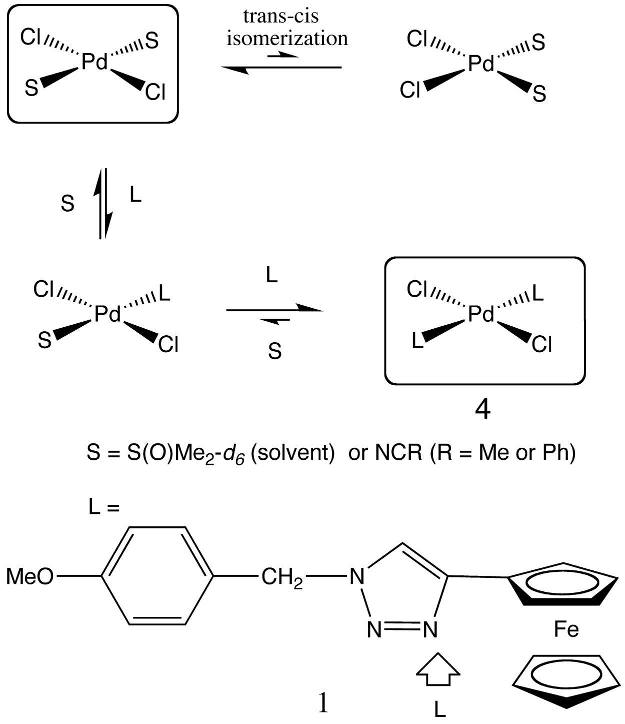
Scheme 1



Database (CSD) reveals that such an eclipsed conformation for a substituted ferrocene is quite common.

^{1}H NMR Study of the Interaction of Transition Metal Complexes with 1 in DMSO. The complexes $[MCl_2(DMSO)_2]$ (M = Pd or Pt) are well-known[11–16] and have been largely studied. DMSO is a solvent that solubilizes both **1** and transition metal mono- or dichlorides or acetates. $PdCl_2$ is a chloro-bridged polymer that depolymerizes in DMSO solution. It forms the square-planar 16-electron d^8 complex $[PdCl_2(DMSO)_2]$ in which *cis/trans* isomerization rapidly proceeds by pseudorotation of five-coordinate intermediates in the presence of excess DMSO.[15] The complex $[PdCl_2(DMSO)_2]$ is preferably *trans* with S coordination, whereas the complex $[PtCl_2(DMSO)_2]$ is preferably *cis* with S coordination.[15] Although dinuclear chloro-bridged Pd complexes are known to form in solution, they lead to the mononuclear complexes in the presence of a neutral donor.[15,16] Thus, in the present situation, where DMSO is in large excess, essentially the mononuclear *trans* Pd^{II} (and *cis* Pt^{II}) complexes are present. The situation is summarized in Scheme 1 for Pd^{II}, with only the framed Pd^{II} complexes being observed.

Upon addition of $PdCl_2$ to **1** in DMSO-d_6, a major set of new signals (deshielded when compared to the signals of **1**) is observed in addition to the signals of **1**. The triazole proton at 8.6 ppm (deshielded by 0.35 ppm relative to **1**) and the two protons of the cyclopentadienyl in the α position at 5.6 ppm (deshielded by 0.9 ppm) are especially characteristic. The signals of **1** progressively decrease as more $PdCl_2$ is added, and it is necessary to add up to 4 equiv of $PdCl_2$ to see the signals of **1** disappearing. This is the sign of an equilibrium, as indicated in Scheme 1. Consistently, the spectrum of **4** in DMSO-d_6 shows a high proportion of dissociated **1** in addition to the same new spectrum. If $[PdCl_2(MeCN)_2]$ or $[PdCl_2(PhCN)_2]$ is added to **1** in DMSO-d_6, this same new set of signals is observed, and their intensity increases as more Pd−nitrile complex is added until complete disappearance with 2 equiv of Pd−nitrile complex (Figure 3). The fact that the same new spectrum appears in these different conditions is consistent with the formula of **4** that does not contain solvent ligand but only the two triazoles in the *trans* positions shown in the X-ray crystal structure of **4**. In DMSO- d_6 only, minor signals are also observed. The relative intensity of these minor signals remains constant compared to those of the major signals as more $PdCl_2$ is added, which discards the presence of a monotriazole complex. Their attribution is uncertain, but they might be due to a chloro-bridged dinuclear Pd complex formed in small amounts.

The fact that a monosubstituted complex $[PdCl_2(S)L]$ (S = DMSO-d_6 or PhCN; L = **1**) is not observed by ^{1}H NMR, indicating that its formation may only occur in a small amount, is presumably due to the *trans* effect of the triazole ligand that favors substitution of the ligand in the *trans* position.[17,18]

With $[Pd(OAc)_2]$, a similar behavior is observed. A yellow-orange color appears as well as a single set of new ^{1}H NMR signals shifted downfield, and full coordination of **1** is observed after adding 4 equiv of $[Pd(OAc)_2]$ to **1**. For instance, the triazole proton is shifted downfield by 0.45 ppm. With $[Pd(OAc)_2]$, this downfield shift is 0.4 ppm. This downfield shift is only 0.23 ppm with $[PdCl_2(MeCN)_2]$ in CD_3CN.

With $[Cu(MeCN)_4][BF_4]$, a yellow color develops, and the addition of 1 equiv to **1** in DMSO-d_6 provokes a downfield shift of all the signals of **1**; the triazole proton is shifted by 0.2 ppm.

With $[PtCl_2(DMSO)_2]$, a yellow solution forms, but full complexation of **1** is never completely reached even after addition of 8 equiv of metal complex to **1** in DMSO-d_6 (only 84% complexation), although all the ^{1}H NMR signals are shifted downfield as well upon complexation of **1** with Pt^{II}.

With $Cu(BF_4)_2$, $Cu(NO_3)_2$, $CuSO_4 \cdot 5H_2O$, $NiCl_2$, $HgCl_2$, $FeCl_2$, $AgNO_3$, $CdCl_2$, and $SnCl_2$, which are soluble in DMSO, the interaction of these salts with **1** or **2** in homogeneous DMSO-d_6 solutions does not result in any ^{1}H NMR signal shift when up to a 4-fold excess of **1** is added. Thus, it appears that the DMSO-d_6 ligands are not substituted by **1** in the presence of excess DMSO-d_6 with these metal salts.

Electrochemical Study of Complexes 1−4 in DMSO. Complexes **1**−**4** were studied by cyclic voltammetry in DMSO solution on a Pt anode with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, and the classic reversible ferrocenyl wave[19a,b,20] of the Fe^{III}/Fe^{II}

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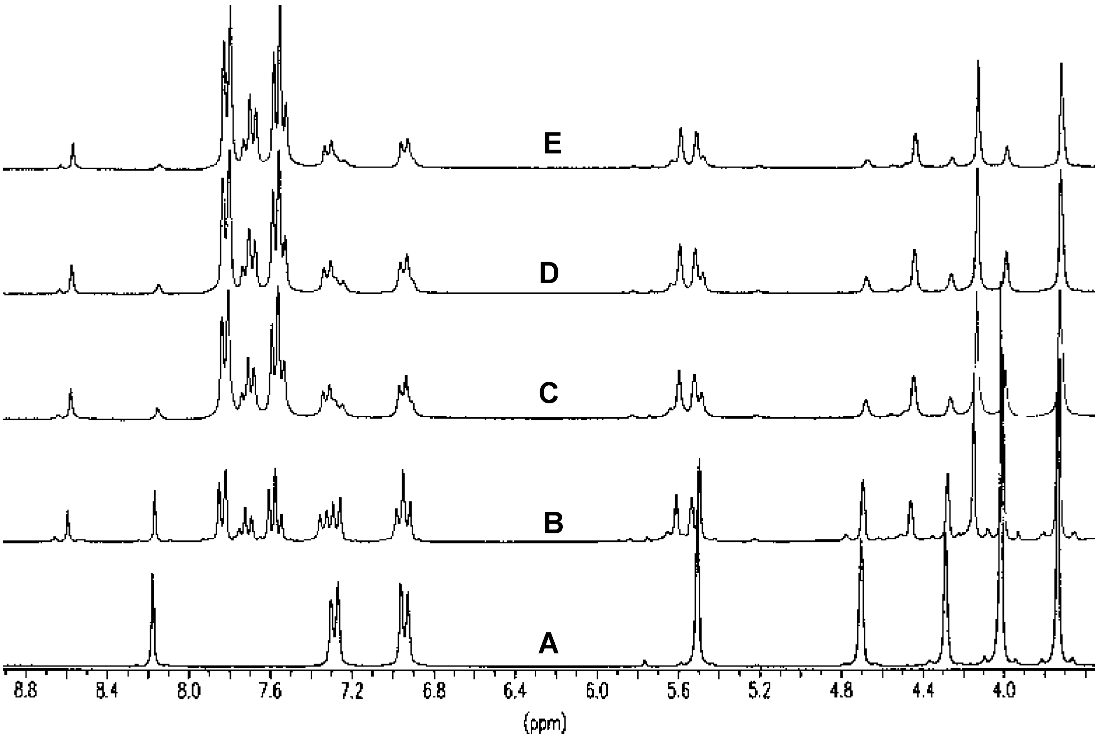

Figure 3. ^{1}H NMR spectrum of **1** in DMSO-d_6 upon addition of [$PdCl_2(C_6H_5CN)_2$]: (A) **1** alone; (B) 1 equiv of **1** and 0.5 equiv of [$PdCl_2(C_6H_5CN)_2$]; (C) 1 equiv of **1** and 1 equiv of [$PdCl_2(C_6H_5CN)_2$]; (D) 1 equiv of **1** and 1.5 equiv of [$PdCl_2(C_6H_5CN)_2$]; (E) 1 equiv of **1** and 2 equiv of [$PdCl_2(C_6H_5CN)_2$].

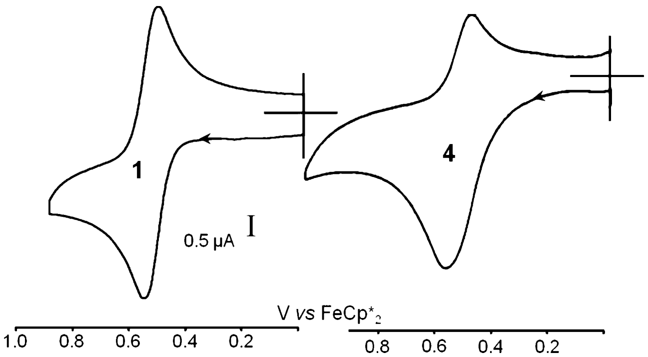

Figure 4. Cyclic voltammetry of **1** and **4** (that partly dissociates in DMSO solution to **1** and [$PdCl_2(DMSO)_2$], as shown by ^{1}H NMR (see text and Scheme 1). Solvent, DMSO; temperature, 20 °C; supporting electrolyte, 0.1 M [n-Bu_4N][PF_6]; working and counter electrodes, Pt; reference electrode, Ag; scan rate, 0.200 V·s^{-1}; internal reference, decamethylferrocene.

redox system was recorded at 0.5 V versus decamethylferrocene used as an internal reference.[21] Only one reversible ferrocenyl wave is observed for each of the four compounds, indicating that the ferrocenyl redox systems are independent in **2** and **3** (the electrostatic factor is extremely small). In the case of **4**, the anodic part of the ferrocenyl wave is broader, which may be attributed to an electrocatalytic process corresponding to the oxidation of chloride to chlorine.[19a,c] This process should be facilitated by the fact that the ferrocenyl and the chloride are connected (inner-sphere process) via the Pd^{II}. This same electrocatalytic wave also appears when $PdCl_2$ is added to the electrochemical cell containing the DMSO solution of **1** (Figure 4).

Concluding Remarks. Click chemistry now very easily provides access to disubstituted 1,2,3-triazoles that serve as linkers in bio-organic chemistry. Given the potential of these ligands to bind, recognize, and sense transition metals, it was informative to investigate the synthetic and structural aspects of Pd^{II} complexes, probably the most studied metal with this series of ligands. The compared crystal structures of **1** and **4** show the weak structural changes within the triazole ring occurring upon coordination, the coordination site of the triazole nitrogen atom in the α position, and finally the remarkable shielding of the imidazole and the ferrocenyl protons in ^{1}H NMR. From the ^{1}H NMR study, we also learn the fragility of the ligand binding probably related to the steric effect of the disubstituted Pd^{II} complex, for which equilibriums are observed between the DMSO, nitriles, and triazole ligands. In electrochemistry, the behavior in DMSO is strongly induced by this special solvent and is very different from the trends observed in methylene chloride, which allowed sensing the oxo-anions and metal cations.

Experimental Section

General Data. p-Methoxybenzylazide and p-diazidomethylbenzene were synthesized from p-methoxybenzylbromide and p-dibromomethylbenzene, respectively, according to Sommers and Barnes (i.e., by reaction with NaN_3 in DMF under ambient conditions).[9a,b] The same procedure was used with 1,3,5-tris(bromomethyl)benzene for the synthesis of 1,3,5-tris(azidomethyl)benzene.[9c] [$PdCl_2(CH_3CN)_2$] was synthesized according to Komiya.[22] The complex [$Cu(CH_3CN)_4BF_4$] was synthesized according to Kubas.[23] Ethynylferrocene, phenylacetylene, and [$Cu(BF_4)_2$] were purchased from Sigma-Aldrich. [$PdCl_2(C_6H_5CN)_2$],

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(23) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

$FeCl_2$, $CuSO_4 \cdot 5H_2O$, $NiCl_2$, $AgNO_3$, and $CdCl_2$ were purchased from Strem and used as received. The ^{1}H NMR spectra were recorded at 25 °C with a Brucker AC (300 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a Brucker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). All the electrochemical measurements were recorded on a PAR 273 apparatus under a nitrogen atmosphere. The conditions are as follows: solvent, DMSO; temperature, 20 °C; supporting electrolyte, 0.1 M [n-Bu_4N][PF_6]; working and counter electrodes, Pt; reference electrode, Ag; internal reference, $FeCp^*_2$ ($Cp^* = \eta^5$-C_5Me_5); scan rate, 0.200 $V \cdot s^{1-}$.

General Procedure for the Click Reactions. The benzylazido derivative (1 equiv) and ethynylferrocene (1.5 equiv *per* branch) were dissolved in THF, and water was added (THF/water = 1:1). At 208 °C, $CuSO_4$ (1 M aqueous solution, 1 equiv *per* azido group) was added, and then, a freshly prepared solution of sodium ascorbate (1 M aqueous solution, 2 equiv *per* azido group) was added dropwise. The solution was then stirred for 2 h at room temperature. After removing the THF under vacuum, dichloromethane and an aqueous solution of ammonia were added. The mixture was stirred for 10 min to remove all the Cu^I derivative trapped inside the product as $[Cu(NH_3)_6]^+$. The organic phase was washed twice with water and filtered through Celite, and the solvent was removed under vacuum. The product was washed with pentane to remove the excess of ethynylferrocene and precipitated by addition of dichloromethane/pentane. The ferrocenyl triazoles were obtained as orange-brown microcrystals. The elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France.

Synthesis of 1. The reaction between p-methoxybenzylazide (0.32 g, 1.96 mmol) and ethynylferrocene (0.62 g, 2.94 mmol) was carried out using the above general procedure for click reactions. Ferrocenyltriazole (**1**) was obtained as orange microcrystals (0.5g, 67.7% yield). ^{1}H NMR (DMSO-d_6, 300 MHz): 8.17 (s, 1H, triazole), 7.28 (d, 2H, $^3J = 9$, arom), 6.94 (d, 2H, $^3J = 9$, arom), 5.55 (s, 2H), 4.7 (s, 2H, H_α of Cp), 4.28 (s, 2H, H_β of Cp), 4.02 (s, 5H, Cp), 3.73 (s, 3H). ^{13}C NMR (DMSO-d_6, 75.5 MHz): 159.04 (Cq, arom), 145.51 (Cq, triazole), 129.27 (CH, arom), 120.39 (CH, triazole), 114.08 (CH, arom), 75.94 (Cq, Cp), 69.16 (CH, Cp), 68.17 (CH, Cp), 66.26 (CH, Cp), 55.09 (CH_3), 52.29 (CH_2). Anal. Calcd for $C_{20}H_{19}FeN_3O$: C, 64.36; H, 5.13. Found: C, 64.12; H, 5.19. $E_{1/2} = 0.53$ V versus decamethylferrocene, reversible.

Synthesis of 2. The reaction between p-diazidomethylbenzene (0.2 g, 1.06 mmol) and ethynylferrocene (0.67 g, 3.18 mmol) was carried out using the general procedure for click reactions and yielded yellow-orange microcrystals of bis(ferrocenyl-1,2,3-triazolylmethyl)benzene (**2**) (0.29 g, 45% yield). ^{1}H NMR (DMSO-d_6, 300 MHz): 8.20 (s, 2H, triazole), 7.31 (s, 4H, arom), 5.59 (s, 4H), 4.69 (s, 4H, H_α of Cp), 4.28 (s, 4H, H_β of Cp), 4.00 (s, 10H, Cp). ^{13}C NMR (DMSO-d_6, 75.5 MHz): 129.27 (CH, arom), 120.39 (CH, triazole), 75.94 (Cq, Cp), 69.16 (CH, Cp), 68.17 (CH, Cp), 66.26 (CH, Cp), 52.29 (CH_2). Anal. Calcd for $C_{32}H_{28}Fe_2N_6$: C, 63.18; H, 4.64. Found: C, 63.40; H, 4.93. $E_{1/2} = 0.53$ V versus decamethylferrocene, reversible.

Synthesis of 3. The reaction between 0.135 g (0.55 mmol) of tris(azidomethyl)benzene and 0.52 g (2.48 mmol) using the general procedure for click reactions gave tri(ferrocenyl-1,2,3-triazolylmethyl)benzene (**3**) as orange-brown microcrystals. The yield was 0.13 g, 27%. ^{1}H NMR (DMSO-d_6, 300 MHz): 8.16 (s, 3H, triazole), 7.22 (s, 4H, arom), 5.95 (s, 6H), 4.68 (s, 6H, H_α of Cp), 4.28 (s, 6H, H_β of Cp), 4.02 (s, 15H, Cp). ^{13}C NMR (DMSO-d_6, 75.5 MHz): 145.51 (Cq, triazole), 129.27 (CH, arom), 120.39 (CH, triazole), (CH, arom), 75.94, (Cq, Cp), 69.16 (CH, Cp), 68.17 (CH, Cp), 66.26 (CH, Cp), 52.29 (CH_2). Anal. Calcd for $C_{45}H_{39}Fe_3N_9$: C, 61.88; H, 4.5. Found: C, 61.09; H, 4.54. $E_{1/2} = 0.53$ V versus decamethylferrocene, reversible.

Synthesis of 4. $[PdCl_2(C_6H_5CN)_2]$ (0.05 g), ferrocenyltriazole (**1**, 0.12 g), and 50 mL of toluene were introduced under an inert atmosphere into a Schlenk flask. The solution was stirred at room temperature for 2.5 h. After the solvent was removed under vacuum, the product was washed twice using diethylether. The ^{1}H NMR spectrum of the crude reaction product in DMSO-d_6 showed both series of signals of the Pd-coordinated and the noncoordinated triazole compounds. Crystallization of the crude reaction product in DMSO-d_6 yielded light brown crystals of the Pd complex **4**. ^{1}H NMR (DMSO-d_6, 300 MHz): 8.59 (s, 1H of **4**), 8.16 (s, 1H of **1**), 7.22 (d, 2H, $^3J = 9$, of **1** and **4**), 6.94 (d, 2H, $^3J = 9$, of **1** and **4**), 5.61 (s, 2H of **4**), 5.50 (s, 2H of **1** and **4**), 4.69 (s, 2H of **1**), 4.46 (s, 2H of **4**), 4.28 (s, 2H of **1**), 4.15 (s, 5H of **4**), 409 (s, 5H of **1**), 3.73 (s, 3H of **1** and **4**). Anal. Calcd for $C_{40}H_{38}Cl_2Fe_2N_6O_2Pd$: C, 52.00; H, 4.14. Found: C, 53.36; H, 4.12. $E_{1/2} = 0.53$ V versus decamethylferrocene, reversible; $ip_c/ip_a = 0.45$.

X-ray Crystallography. A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using monochromatic Mo Kα radiation ($\lambda = 0.71073$).

The structures were solved by direct methods (SIR97)[22] and refined by least-squares procedures on F^2 using SHELXL-97.[23] All H atoms attached to carbon were introduced in idealized positions and treated as riding on their parent atoms in the calculations. In molecule **4**, there is a water molecule statistically distributed over three positions occupying a void in the structure located around the threefold axis, leading to a total amount of six water molecules within the unit cell. The drawing of the molecules was realized with the help of ORTEP-3 for Windows.[24] Crystal data and refinement parameters are shown in Table 1. Bond distances and angles are given in Table 2.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 685263 and 685264. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: ^{1}H NMR spectra of **1** and **4** in DMSO-d_6 and ^{1}H NMR spectra of **1** + $[Pd(CH_3CN)_2Cl_2]$, **1** + $[Cu(CH_3CN)4Cl_2]$, and **1** + $PtCl_2$ in DMSO-d_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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