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Click Synthesis and Redox Chemistry of Mono- and Heterobimetallic Triazolyl and Triazolium-Ferrocene and Cobalticinium Complexes

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Mono- and heterobimetallic triazolylferrocene and cobalticinium complexes and triazolium derivatives were synthesized by click reactions between the ethynylmetallocenes and benzyl azide or (azidomethyl)ferrocene followed by methylation reactions, respectively. Cyclic voltammetry data shed light on the electron-withdrawing character of the 1,2,3-triazolyl and triazolium substituents of the metallocenes, and cathodic reduction of the triazolium group was found to be irreversible even at –50 °C. Chemical reduction of orange triazolylcobalticinium hexafluorophosphate using $NaBH_4$ yielded a mixture of red isomeric triazolyl η^4-cyclopentadiene–cobalt–η^5-cyclopentadienyl complexes, whereas reduction by the single-electron reductant $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ yielded the brown 19-electron triazolylcobaltocene.

Introduction

The concept of “click” reactions by Sharpless el al. proposes to easily assemble molecular fragments.[1] The Cu^I-catalyzed regioselective azide–alkyne cycloaddition (CuAAC),[2,3] which is presently the most frequent example,[4–22] was reported in 2002 by the research groups of Sharpless et al.[2] and Meldal et al.[3] This synthetic advantage is not the only one, since the resulting 1,2,3-triazolyl derivatives that are selectively produced are also good ligands in a variety of transition-metal complexes that have new luminescent,[23–26] sensor,[27–29] or catalytic properties.[30,31] In this context, one of the key functions of transition-metal complexes is their redox behavior,[32–38] and in particular late transition-metal sandwich complexes are known to withstand stability under two or three oxidation states.[36,39–41] The latter property indeed allows their use as redox reagents,[36] redox catalysts,[42] and redox sensors.[43–47] Therefore, we wish to investigate the redox behavior of simple ferrocene and cobalticinium complexes bound to 1,2,3-triazolyl using click (CuAAC) reactions of the ethynylmetallocene precursors and the related triazolium derivatives subsequently obtained by the methylation of the latter. The investigation of these syntheses and that of the redox properties of the metallocene triazolyl and triazolium derivatives are the subject of this article, and the results are a key step towards potential analytical and synthetic redox chemistry of large nanosystems involving click assemblies.[47]

The alkylation of triazole (trz) to yield the triazolium (trz*) group has been reported as well as the properties of trz and trz* derivatives as molecular sensors.[27–29] The redox chemistry of ferrocene and cobalticinium have been known since Wilkinson’s seminal reports on these metallocenes,[48,49] and these properties have been extensively studied by cyclic voltammetry and used in organometallic synthesis, sensing, and catalysis.[32–36,42,50] However, we are not aware of redox or electrochemical studies of trz and trz* derivatives.

Results and Discussion

1. CuAAC Reactions and Syntheses of the Mono- and Heterobimetallic Triazole Compounds

The CuAAC reactions were conducted between benzyl azide and the known ethynylmetallocenes[51,52] to produce the triazolyl derivatives **1** and **3** [Equation (1)], and with ethynylbenzene to produce the reference organic compound **5**.

This CuAAC click reaction is, as is well known, completely selective in the formation of 1,4-disubstituted trz, contrary to the non-catalyzed Huisgen azide–alkyne dipolar cycloaddition that produces both 1,4 and 1,5 isomers.[53] As a Cu^I catalyst, we used a mixture of $CuSO_4\cdot 5H_2O$ and the reductant sodium ascorbate that is the initial Sharpless catalyst.[2] (Azidomethyl)ferrocene[54] was also used in the CuAAC reaction with ethynylcobalticinium to produce the heterobimetallic triazolyl complex **7**; see Equation (2).

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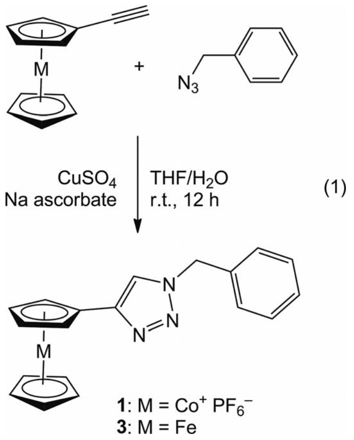

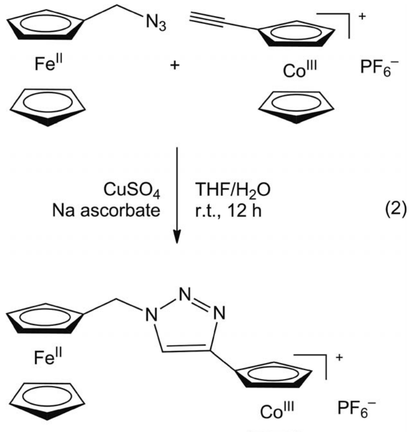

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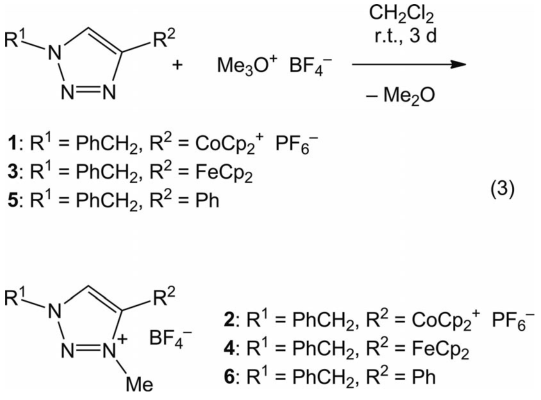
All the triazole derivatives were obtained after precipitation in an overall yield of around 80%. The infrared spectra were a very useful tool in following all these click reactions (compounds **1**, **3**, **5**, and **7**), because the characteristic peak of the azido groups at about 2094 cm^{-1} disappears at the end of each reaction confirming that these azido groups were replaced by the trz. For triazolyl cobalticinium hexafluorophosphate (**1**), which was soluble only in polar solvents such as acetone and acetonitrile, but also in THF, the characteristic band of the PF_6 anion is observed at 837 cm^{-1}. The formation of trz is clearly shown by ^{1}H NMR spectroscopy by the appearance of the trz CH peak. This is also confirmed in particular by the characteristic peaks of Cq and CH of trz in the ^{13}C NMR spectra. Finally, the structures of all of the new trz compounds were also confirmed by the observation of the molecular peak in the mass spectrum and by elemental analysis (see the Supporting Information).

2. Methylation of the Triazole Compounds to Produce Triazolium Derivatives

Further methylation of the trz rings of the compounds **1**, **3**, and **5**, using Me_3OBF_4 as the methylating agent,[29] resulted in the formation of the trz* compounds **2**, **4**, and **6**, respectively, in yields of about 90% and dimethyl ether that was removed under vacuum; see Equation (3).



The ^{1}H and ^{13}C NMR spectra of the trz* compounds **2**, **4**, and **6** show the proton and carbon signals, respectively, of the N–CH_3 methyl group. All the signals in the NMR spectra of these new trz* products were shifted downfield compared to their trz precursors, because of the cationic nature of the trz* species. However, the quaternary carbon of the cobalticinium cation linked to the trz* group was shifted upfield in the ^{13}C NMR spectrum. The infrared spectra of the trz* compounds **2**, **4**, and **6** show the appearance of the characteristic band of BF_4^- at 1070 cm^{-1}, and for trz* cobalticinium hexafluorophosphate (**2**) the characteristic band of the PF_6 anion is observed at 872 cm^{-1}. The structure of the new trz* derivatives was confirmed by the molecular peak in the mass spectra and by elemental analyses (see the Supporting Information).

3. Cyclic Voltammetry Studies

The cyclic voltammograms (CVs) of all the trz and trz* compounds have been recorded in order to investigate the redox properties of the trz and trz* groups and their influence on the redox properties of the neutral and cationic metallocenic groups to which they are directly attached. The results are reported in Table 1.

The new compound **1** shows two chemically and electrochemically reversible reduction waves in THF at the Pt electrode, assigned to the two successive single-electron reductions of cobalticinium[55] (Figure 1). The first (less cathodic) wave corresponds to the reduction of the 18-electron, d^6 Co^{III} complex to the 19-electron, d^7 Co^{II} complex. This wave at –0.85 V vs. $[FeCp_2^*]^{+/0}$ (Cp* = η^5-C_5Me_5) in THF is located at a potential that is 40 mV less negative than that of the parent cobalticinium complex, which can be attributed to the electron-withdrawing properties of the 1,2,3-triazolyl group. The second single-electron cathodic wave that is located at –1.90 V vs. $[FeCp_2^*]^{+/0}$ corresponds to the reduction of the 19-electron, d^7 Co^{II} complex to the 20-electron, d^8 Co^I species. It is remarkable that this second

Table 1. Redox potentials and chemical (i_a/i_c) and electrochemical ($E_{pa} - E_{pc} = \Delta E$) reversibility data for compounds **1**–**7**. Supporting electrolyte: [nBu$_4$N][PF$_6$] (0.1 M); working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$ (Cp* = η^5-C$_5$Me$_5$); scan rate: 0.200 V s^{-1}.

	Solvent	Fe$^{II/III}$ [V]			Co$^{III/II}$ [V]			Co$^{II/I}$ [V]			trz*$^{(0/+1)}$	
	–	$E_{1/2}$	ΔE	i_a/i_c	$E_{1/2}$	ΔE	i_a/i_c	E	ΔE	i_a/i_c	E_p	ΔE
1	MeCN	–	–	–	–0.75	0.60	1	E_p = –1.76	0	0	–	–
1	THF	–	–	–	–0.85	0.65	1	$E_{1/2}$ = –1.90	0.90	0.9	–	–
2	MeCN	–	–	–	–0.46	0.50	1	E_p = –1.32	0	0	–2.20	0
3	MeCN	0.55	0.50	1	–	–	–	–	–	–	–	–
3	THF	0.43	0.60	1	–	–	–	–	–	–	–	–
4	MeCN	0.84	0.50	1	–	–	–	–	–	–	–1.64	0
6	MeCN	–	–	–	–	–	–	–	–	–	–1.60	0
6	THF	–	–	–	–	–	–	–	–	–	–1.72	0
7	MeCN	0.62	0.50	1	–0.76	0.50	0.5	E_p = –1.81	0	0	–	–
7	THF	0.48	0.65	1	–0.88	0.65	1	$E_{1/2}$ = –1.92	0.80	0.3	–	–

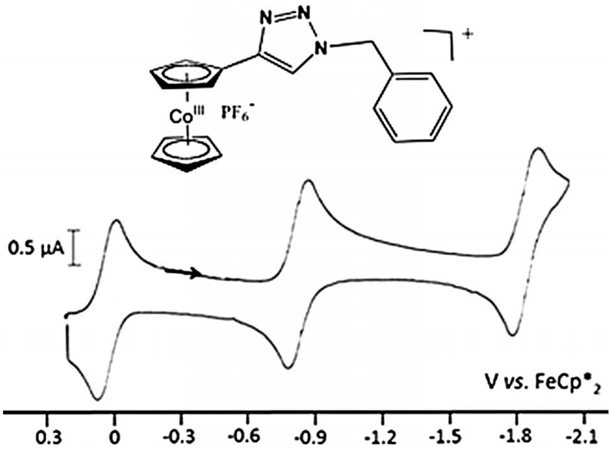


Figure 1. CV of **1** in THF. The wave at 0.0 V corresponds to the internal reference FeCp*$_2$. Solvent: THF; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V s^{-1}; supporting electrolyte: [nBu$_4$N][PF$_6$].

cathodic wave is also chemically and electrochemically reversible, which means that both the 19-electron and 20-electron species are stable on the electrochemical time scale, and the trz substituent does not destabilize these oxidation states that are already rendered fragile by the presence of electrons in the antibonding e$_1$* orbitals. The influence of the electron-withdrawing properties of the trz substituent on the redox potentials appears to be the same for both the first and second reduction wave. In MeCN, the reduction waves are chemically irreversible, which can be attributed to fast ligand substitution by the MeCN ligand in high concentration. Indeed, MeCN is a much stronger ligand than THF, and we know that ligand substitution of π-hydrocarbon ligands in 19-electron late transition-metal complexes by good ligands such as MeCN is of the order of 10^9 faster than the analogous exchange in the 18-electron complexes.[56,57] Thus the 19-electron Co^{II} complexes are kinetically very unstable in MeCN even on the electrochemical time scale, and the 20-electron Co^{I} species even more so. This irreversibility in MeCN (partial for the first wave, total for the second one) is observed for all the compounds containing the cobalticinium group (**1**, **2**, and **7**). For the triazolylferrocene complex **3**, oxidation of the ferrocenyl group is found at a more positive potential than ferrocene itself in MeCN (Table 1), whereas for **7** (Figure 2) the additional influence of the cobalticinium group shifts the oxidation of the ferrocenyl group anodically (Table 1).

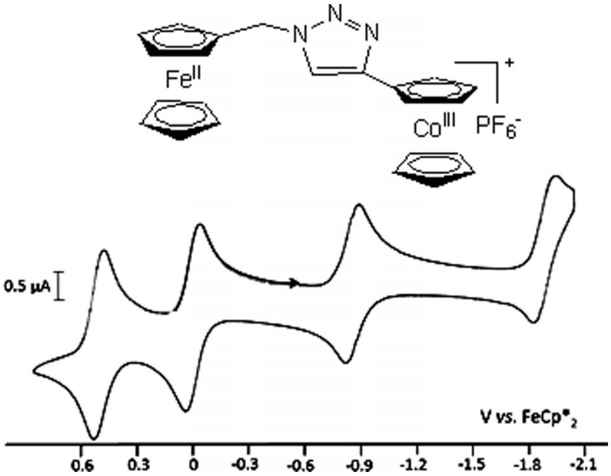


Figure 2. CV of **7** in THF. The wave at 0.0 V corresponds to the internal reference of FeCp*$_2$. Solvent: THF; reference electrode, Ag; working and counter electrodes: Pt; scan rate: 0.2 V s^{-1}; supporting electrolyte: [nBu$_4$N][PF$_6$].

Cathodic reduction of the trz ring in the triazolyl derivatives **1**, **3**, **5**, and **7** was not observed until –2.5 V vs. [FeCp$_2$*]$^{+/0}$. On the other hand, cathodic reduction of the

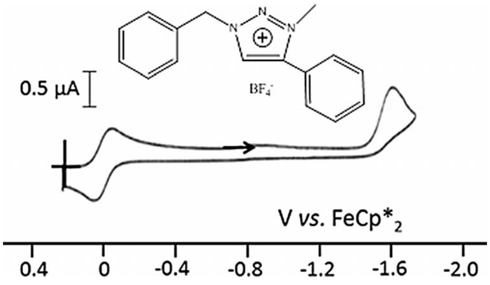


Figure 3. CV of **6** in CH$_3$CN. The wave at 0.0 V corresponds to the internal reference of FeCp*$_2$. Solvent: CH$_3$CN; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V s^{-1}; supporting electrolyte: [nBu$_4$N][PF$_6$].

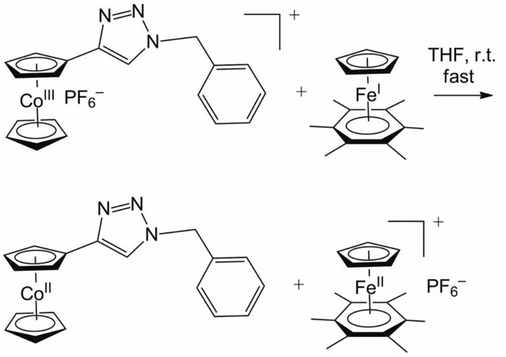
trz* derivatives **2**, **4**, and **6** was observed, but it was totally chemically irreversible even at –50 °C. The trz* group in the organic compound **6** (Figure 3) was reduced at a slightly less negative potential (E_p) than the trz* group in the ferrocene derivative **4** because of the electron-releasing property of the ferrocenyl group (compared to the phenyl group), although the comparison between the E_p values does not reflect the exact difference of the E^0 values that are not easily accessible. The trz* group in the cobaltocenyltriazole complex **2** was reduced at a much more negative potential because the 20-electron cobaltocene anionic species that is generated at a less negative potential is strongly electron-releasing. Finally, the trz* group behaves as an even more electron-withdrawing substituent than trz because of the cationic charge of the former. For instance, reversible single-electron anodic oxidation of the ferrocenyl group in MeCN occurs at a potential 220 mV more positive for **4** than for the ferrocenyl group in **7**.

4. Reduction of Triazolylcobalticinium 2 with NaBH$_4$ and Single-Electron Reductants

Reduction of the orange cationic triazolylcobalticinium complex **1** by NaBH$_4$ at 0 °C in THF, in which it was soluble, produced the red, air-sensitive compound **8** that was soluble in diethyl ether enabling its extraction under N$_2$ [Equation (4)]. Its thermal stability under N$_2$ is modest under ambient conditions, allowing standard spectroscopic analysis.

The disappearance of the PF$_6^-$ band in the infrared spectrum of **8** is consistent with the formation of a neutral compound in 95% yield, the structure being confirmed by observation of the molecular peak in the mass spectrum. Compound **8** has a rather complex ^{1}H NMR spectrum showing the formation of a mixture of isomeric triazolyl η^4-cyclopentadiene–cobalt–η^5-cyclopentadienyl complexes.[58] Indeed the hydride reduction of the cationic cobalt sandwich can occur either on the *ipso* 1,2 or 1,3 position of the cyclopentadienyl ligand to which the trz group is attached or to the free cyclopentadienyl ligand. No attempt was made to separate the isomers. The cyclic voltammogram in CH$_2$Cl$_2$ shows two totally irreversible oxidation waves at 0.3 V and 0.65 V vs. [FeCp$_2$*]$^{+/0}$. It is suggested that these two waves correspond to the oxidation of the triazolylcyclopentadiene–cobalt–Cp and triazolylcyclopentadienyl–cobalt–cyclopentadiene, respectively. The first wave at 0.3 V is more intense than the other, which would be in agreement with the preferential hydride reduction of the substituted ring that is more electron poor than the free ring.

Reduction of **1** by Na/Hg in THF led to decomposition, probably because of the thermal instability of the 20-electron triazolylcobaltocene anion, which is easily formed with reduction by Na/Hg. Therefore we synthesized the known crystalline forest-green 19-electron complex [Fe^{I}Cp(η^5-C$_6$Me$_6$)].[59] This complex has a potential E^0 of –1.53 V in THF vs. [FeCp$_2$*]$^{+/0}$[60–61] that is much more cathodic than the first potential of the reduction of **1** but less negative than its second reduction potential. Reduction of **1** by a stoichiometric amount of [Fe^{I}Cp(η^5-C$_6$Me$_6$)] in THF instantaneously provoked a color change from orange to brown and formation of a yellow precipitate of [Fe^{II}Cp(η^5-C$_6$Me$_6$)][PF$_6$]; see Equation (5).[58] The reduced brown, air-sensitive compound **9** (the color of cobaltocene) was soluble in diethyl ether and was characterized by UV/Vis and EPR (Figure 4) spectroscopy as well as mass spectrometry. It was also characterized by its re-oxidation in air to the 18-electron complex as shown by ^{1}H NMR spectroscopy (the shape of the signal of the trz proton therein is broad and different from that of the peak observed in **1**, which may tentatively be assigned to a change of anion for OH$^-$ that forms a hydrogen bond with the trz proton).



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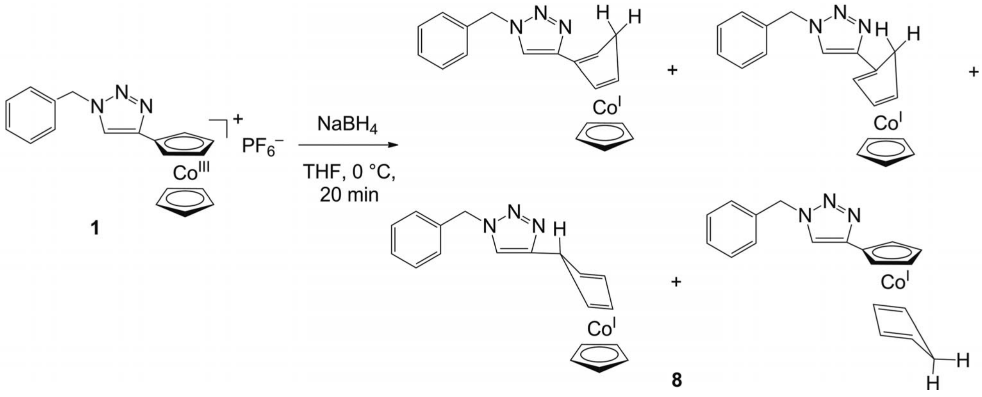

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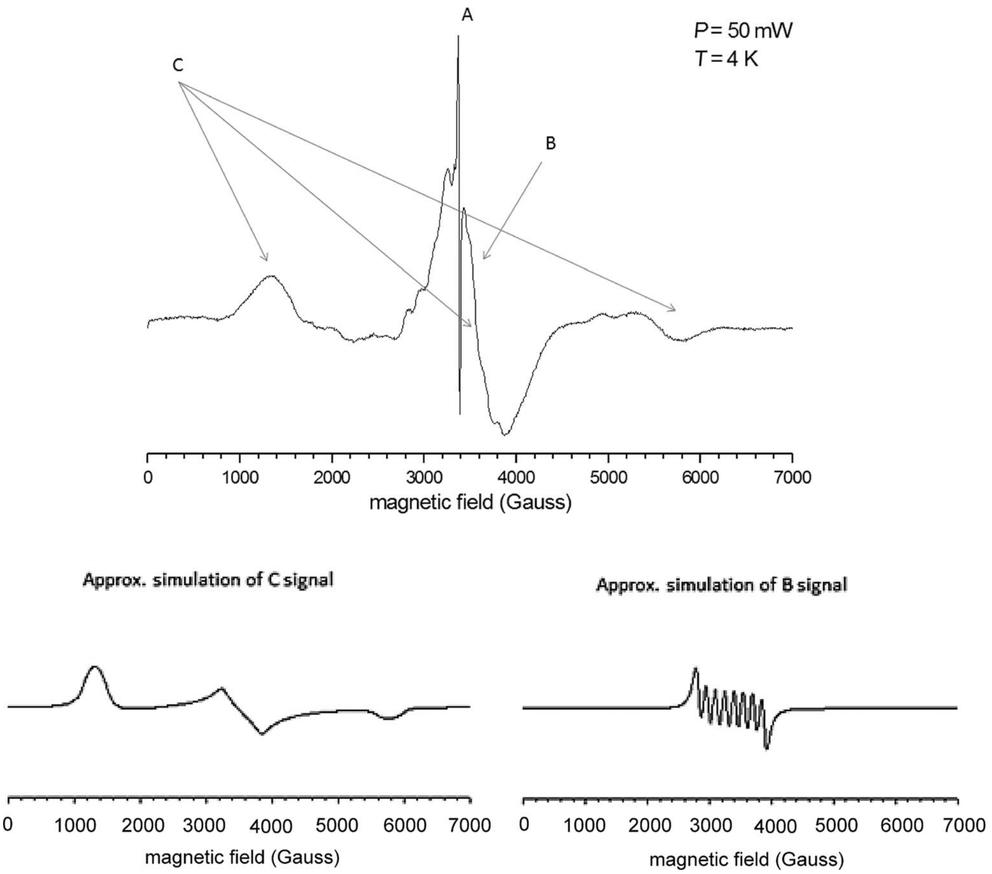

Figure 4. EPR analysis of **9** and approximate simulations of signals B and C[62]. Signal A gives $g_{\parallel} = 2.037$ and $g_{\perp} = 2.003$. Signal B gives $g = 2.015$ and the hyperfine coupling constant A (Co – I = 7/2) = 150 G. The g values of signal C are $g_1 = 1.17$, $g_2 = 1.9$, and $g_3 = 5.09$.

Conclusions

Three triazolylmetallocenes, including a heterobimetallic complex, have been synthesized by CuAAC click reactions, and their redox chemistry has been investigated including the determination of the oxidation/reduction potentials of the redox-active groups and the nature of the products of reduction by $NaBH_4$ and the electron-reservoir complex $[Fe^{I}Cp(\eta^5\text{-}C_6Me_6)]$. The relatively strong electron-withdrawing nature of trz shifts the redox potentials of the metallocenes anodically. The reduction potential of the trz group itself in the trz-containing compounds was not localized until –2.5 V in THF.

Additionally, trz* tetrafluoroborate derivatives, including those attached to the metallocenes, have been synthesized. The cationic charge of the trz* renders it even more electron-withdrawing than the trz group, which is reflected in the cyclic voltammetry data. The reduction potential of the trz* group is reported here, but the trz* cathodic reduction is totally chemically irreversible, even at –50 °C. In 1-benzyl-3-methyl-4-cobalticinium hexafluorophosphate-1*H*-triazolium (**2**) the addition of the third electron (reduction of trz* group) is hifted cathodically, i.e. reduction is rendered much more difficult (E_p = –2.20 V), because of the negative charge of cobaltocene than in compounds **4** and **6** for which the reduction of the trz* group attached to a neutral ferrocenyl or phenyl takes place around E_p = –1.60 V.

In conclusion, this study has afforded useful information concerning the electronic properties of trz and trz* groups and their effect on the redox potentials of late transition-metal metallocenes. The stability of reduction products synthesized using specific reductants is of the utmost importance if similar procedures are envisaged for large nanosystems such as metallodendrimers and nanoparticles.[47] The satisfying results show that such further steps can be undertaken in the future.

Experimental Section

General: Reagent-grade diethyl ether and tetrahydrofuran (THF) were predried with Na foil and distilled from sodium/benzophenone under argon immediately prior to use. Dichloromethane was distilled from calcium hydride just before use. All other solvents and chemicals were used as received. Ethynylferrocene, styrene, benzyl azide, and Me_3OBF_4 were purchased from Aldrich. ^1H NMR spectra were recorded at 25 °C with a Bruker AC 300 MHz spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a Bruker AC 300 spectrometer. The NMR spectra were recorded in d^6 acetone unless noted otherwise. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). The mass spectra were recorded at the CESAMO (Univ. Bordeaux) with a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temp. Samples were introduced by injection through a 20 µL sample loop into a 4500 µL min^{-1} flow of methanol from the LC pump. Mass spectra of **8** were performed by the CESAMO with an AccuTOF-GcV (JEOL), which is a GC-TOF. The instrument is equipped with a sample introduction system named FD (Field Desorption). The EPR spectrum was recorded with a Bruker EMX X-band spectrometer (microwave frequency 9.46 GHz). Parameters: microwave power: 50 mW; modulation frequency (magnetic field): 100 kHz; modulation amplitude: 8 Gauss; magnetic field sweep width (Gauss): [0; 7000]; $T = 4$ K. All electrochemical measurements were recorded under nitrogen in dry CH_3CN, THF, or CH_2CH_2 at 20 °C. Supporting electrolyte: $[n\text{Bu}_4\text{N}][\text{PF}_6]$ (0.1 м); working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$; scan rate: 0.200 V s^{-1}.

Click Synthesis of 1: A mixture of 1 equiv. of benzyl azide (70 mg, 0.53 mmol) and 1 equiv. of ethynyl cobalticinium hexafluorophosphate[52] (189.79 mg, 0.53 mmol) were dissolved in 3:2 distilled THF/H_2O. At 0 °C, $CuSO_4$ was added (1 equiv.; 1 м aqueous solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv.; 1 м aqueous solution). The solution was allowed to stir for 12 h at room temp. under N_2. An aqueous solution of ammonia was added, and the mixture was allowed to stir for 10 min. The organic phase was washed twice with water, dried with sodium sulfate, filtered through paper, and the solvent was removed under vacuum. Complex **1** was purified by precipitation with diethyl ether, and obtained as an orange-red powder; yield 80%. ^{1}H NMR (1D, 1 H): δ = 8.55 (1 H, C*H* of trz), 7.39 (5 H, C*H* of Ar), 6.38 (2 H, C*H* of Cp sub.), 5.97 (2 H, C*H* of Cp sub.), 5.70 (7 H, C*H* of Cp and Ar-CH_2) ppm. ^{13}C NMR (1D 1 H): δ = 138.28 (*Cq* of trz), 135.5 (*Cq* of Ar), 128.98, 128.52, 128.21 (*C*H of Ar), 124.52 (*C*H of trz), 96.04 (*Cq* of Cp sub.), 85.96 (*C*H of Cp), 84.53, 80.92 (*C*H of Cp sub.), 53.82 (Ar-*C*H_2) ppm. MS (*m*/*z*): calcd. for $C_{19}H_{17}N_3Co$ 346.0748; found 346.0746.

Click Synthesis of 7: The compound **7** was synthesized according to the same procedure as for **1** above by the click synthesis between (azidomethyl)ferrocene[53] (80 mg, 0.33 mmol) and ethynylcobalticinium hexafluorophosphate[52] (118.84 mg, 0.33 mmol) and obtained as orange-red needles after precipitation in ether; yield 84%. ^{1}H NMR (1D 1 H): δ = 8.48 (1 H, C*H* of trz), 6.39 (2 H, C*H* of Cp sub. of $CoCp_2^+PF_6^-$), 5.98 (2 H, C*H* of Cp sub. of $CoCp_2^+PF_6^-$), 5.71 (5 H, C*H* of Cp of $CoCp_2^+PF_6^-$), 5.46 (2H of trz-CH_2), 4.42 (2 H, C*H* of Cp sub. of $FeCp_2$), 4.23 (2 H, C*H* of Cp sub. of $FeCp_2$), 4.22 (5 H, C*H* of Cp of $FeCp_2$) ppm. ^{13}C NMR (1D 1 H): δ = 138.75 (*Cq* of trz), 124.81 (*C*H of trz), 97.30 (*Cq* of Cp sub. of $CoCp_2^+PF_6^-$), 86.85 (*C*H of Cp of $CoCp_2^+PF_6^-$), 85.39, 81.85 (*C*H of Cp sub. of $CoCp_2^+PF_6^-$), 82.65 (*Cq* of Cp sub. of $FeCp_2$), 69.98 (*C*H of Cp sub. of $FeCp_2$), 69.80 (*C*H of Cp of $FeCp_2$), 50.89 (trz-*C*H_2) ppm. MS (*m*/*z*): calcd. for $C_{23}H_{21}FeCoN_3$ 454.0429; found 454.0413. $C_{23}H_{21}CoF_6FeN_3P$ (599.18): calcd. C 46.10, H 3.53; found C 45.92, H 3.46.

Synthesis of 2: A mixture of 1 equiv. of **1** (120 mg, 0.24 mmol) with 1 equiv. of Me_3OBF_4 (36.14 mg, 0.24 mmol) in distilled dichloromethane (30 mL) was stirred for 3 d at room temp. under N_2. Then, the organic phase was washed twice with water, dried with sodium sulfate, and the solvent was evaporated under vacuum. Compound **2** was purified upon washing with THF; yield 90%. ^{1}H NMR (1D, 1 H): δ = 9.47 (1 H, CH of trz*), 7.62, 7.46 (5 H, CH of Ar), 6.61 (2 H, CH of Cp sub.), 6.21 (2 H, CH of Cp sub.), 6.03 (5 H, CH of Cp), 5.96 (2 H, CH of Ar-CH_2), 4.53 (3 H, CH of N-CH_3) ppm. ^{13}C NMR (1D, 1 H): δ = 136.15 (Cq of trz*), 132.25 (Cq of Ar), 131.32 (CH of trz*), 129.58, 129.46, 129.22 (CH of Ar), 87.37 (CH of Cp), 86.51, 84.96 (CH of Cp sub.), 85.63 (Cq of Cp sub.), 57.36 (Ar-CH_2), 39.64 (N-CH_3) ppm. MS (*m*/*z*): calcd. for $C_{20}H_{19}N_3Co$ 360.0905; found 360. $C_{20}H_{19}BCoF_{10}N_3P\cdot Et_2O$ (426.01): calcd. C 43.19, H 4.71; found C 43.39, H 4.11.

Synthesis of 4: The compound **4** was synthesized from 1 equiv. of **3** (120 mg, 0.35 mmol) and 1 equiv. of Me_3OBF_4 (51.72 mg, 0.35 mmol) according to the same procedure as for **2**. It was purified by precipitation in ether; yield 93%. ^{1}H NMR (1D 1 H): δ = 8.65 (1 H, CH of trz*), 7.52, 7.40 (5 H, CH of Ar), 5.67 (2 H, CH of Ar-CH_2), 4.72 (2 H, CH of Cp sub.), 4.47 (2 H, CH of Cp sub.), 4.22 (5 H, CH of Cp), 4.20 (3 H, CH of N-CH_3) ppm. ^{13}C NMR (1D 1 H): δ = 145.04 (Cq of trz*), 133.64 (Cq of Ar), 130.29, 130.12, 130.01 (CH of Ar), 128.38 (CH of trz*), 72.08 (CH of Cp sub.), 71.16 (CH of Cp), 69.96 (CH of Cp sub.), 66.98 (Cq of Cp sub.), 57.63 (Ar-CH_2), 39.73 (N-CH_3) ppm. MS (*m*/*z*): calcd. for $C_{20}H_{20}N_3Fe$ 358.1001; found 358.1000. $C_{20}H_{20}BF_4FeN_3$ (445.05): calcd. C 53.98, H 4.53; found C 53.63, H 4.44.

Synthesis of 6: The compound **6** was synthesized from 1 equiv. of **5** (120 mg, 0.51 mmol) and 1 equiv. of Me_3OBF_4 (75.49 mg, 0.51 mmol) according to the same procedure as for **2**. It was purified by precipitation in ether; yield 91%. ^{1}H NMR (1D, 1 H) $CDCl_3$: δ_{ppm} = 9.01 (1 H, CH of trz*), 7.79 (2 H, CH of Ph), 7.66 (5 H, 2 CH of Ar and 3 CH of Ph), 7.46 (2 H, CH of Ar), 5.98 (2 H, CH of Ar-CH_2), 4.41 (3 H, CH of N-CH_3) ppm. ^{13}C NMR (1D, 1 H): δ = 144.42 (Cq of trz*), 133.54 (Cq of Ar), 132.51, 130.10 (CH of Ph), 130.47, 130.36, 130.29 (CH of Ar), 129.59 (CH of trz*), 123.75 (Cq of Ph), 57.91 (Ar-CH_2), 39.47 (N-CH_3) ppm. MS (*m*/*z*): calcd. for $C_{16}H_{16}N_3$ 250.1338; found 250.1337. $C_{16}H_{16}BFN_3$ (280.13): calcd. C 57.00, H 4.78; found C 56.75, H 4.56.

Synthesis of 8: A mixture of 1 equiv. of **1** (150 mg, 0.31 mmol) with 1.1 equiv. of $NaBH_4$ (12.71 mg, 0.34 mmol) in distilled THF (20 mL) was stirred for 20 min at 0 °C under N_2. Then, the solvent was evaporated under vacuum, and distilled diethyl ether was added to solubilize the neutral product. After filtration under N_2 and evaporation of the solvent, the product was obtained as a deep red powder; yield 95%. The complex **8** is not air stable and stored under N_2. It is thermally stable under N_2 for a few hours, then degradation appears as indicated by the ^{1}H NMR spectrum and precipitation. ^{1}H NMR (1D, 1 H) $CDCl_3$: δ = 7.41–7.31 (5 H, CH of Ph), 7.13 and 6.66 (1H of trz), 5.51–5.34 (2H of Ph-CH_2 and 2H of diene), 4.88–4.52 (5H of free Cp and 4H of substituted Cp when H$^-$ is added to free Cp), 2.93–2.88 (2H of diene), 2.09–2.04 (2H free) ppm. ^{13}C NMR (1D, 1 H) C_6D_6: δ = 149.59 (*Cq* of triazole), 133.62 (*Cq* of Ar), 129.37, 129.19 (*C*H of Ar), 121.51 (*C*H of triazole), 80.755–80.60 (*C*H of Cp), 78.84–75.16 (*C*H of cyclopentadiene), 55.14 (Ar-*C*H_2), 43.17–39.72 (*C*H_2 of cyclopentadiene) ppm. MS (*m*/*z*): calcd. for $C_{19}H_{18}CoN_3$ 347.08327; found 347.08422.

Synthesis of 9: A solution of **1** (1 equiv., 120 mg, 0.24 mmol) in distilled THF (20 mL) was prepared in a Schlenk flask. Then addition under N_2 of a solution of a stoichiometric amount of the forest-green complex $[\text{Fe}^{\text{I}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_6)]$[59] (1 equiv., 0.24 mmol, 67.97 mg) in distilled THF was performed by canula. A color change from orange to brown and a yellow precipitate of $[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_6)][\text{PF}_6]$ appeared immediately. After evaporation of the solvent under vacuum, the neutral brown product **9** was solubilized in distilled diethyl ether and filtered to obtain **9** as a brown powder; yield 97%. The paramagnetic complex **9** is not air stable and was stored under N_2. Oxidation of the product in air yielded **1** after addition of $NaPF_6$. ^{1}H NMR (1D 1 H), ([D$_6$]acetone, 300 MHz), after oxidation of **9** in air: δ = 8.57 (1 H, C*H* of triazole), 7.41 (5 H, C*H* of Ar), 6.41 (2 H, C*H* of substituted Cp), 6.01 (2 H, C*H* of substituted Cp), 5.74 (5 H, C*H* of Cp), 5.72 (2H of Ar-CH_2) ppm. MS (*m*/*z*): calcd. for $C_{19}H_{17}CoN_3$ 346.0748; found 347.0765.

Supporting Information (see footnote on the first page of this article): General data, ^{1}H, ^{13}C NMR (including HMBC spectrum of **8**), IR, UV/Vis and mass spectra and cyclic voltammograms.

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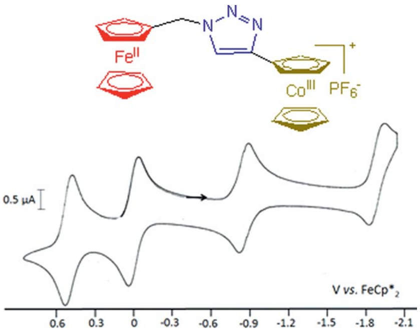
Click Reactions

The click syntheses (CuAAC) of triazole and access to triazolium derivatives containing ferrocene and/or cobalticinium allowed us to evaluate their redox chemistry by cyclic voltammetry and with the use of redox reagents.



A. Rapakousiou, C. Mouche, M. Duttine, J. Ruiz, D. Astruc* 1–8

Click Synthesis and Redox Chemistry of Mono- and Heterobimetallic Triazolyl and Triazolium-Ferrocene and Cobalticinium Complexes

Keywords: Metallocenes / Sandwich complexes / Iron / Cobalt / Redox chemistry / Click chemistry / Reduction / Nitrogen heterocycles