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Synthesis and NMR characterization of dinuclear Fe(II) organometallic complexes containing a non-equivalently bridging 5-aryl tetrazolate ligand

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Abstract

The synthetic routes to the formation of a wide range of dinuclear Fe(II) organometallic complexes of the general formula $[Cp(CO)(L)Fe–N_4C–C_6H_4–CN–Fe(L)(CO)Cp][SO_3CF_3]$, in which the 4-cyanophenyl-tetrazolate anion $N_4C–C_6H_4–CN$ acts as bridging ligand, are described. ^1H and ^{13}C NMR characterization of the product complexes indicate the presence of a significant interannular conjugation effect involving the aromatic rings of the organic spacer, the extent of which can be chemically modified by addition of electrophiles such as CH_3^+ and H^+. Furthermore, the reversibility of protonation reaction entails the opportunity of modulating the conjugative properties of the title compounds by a proton addition–elimination mechanism.

Keywords: Dinuclear complexes; 5-Aryl tetrazolate ligand; Interannular conjugation; Molecular switches; NMR spectroscopy

1. Introduction

Over the past two decades, the opportunity of reproducing devices (wires, switches, etc.) at the molecular level [1a–1c], as well as the chance to transfer the potentially applicable redox and optical properties of coordination compounds to a macroscopic context [2], have prompted the rapid development of di- and polynuclear arrays in which two or more metal centres are connected by organic linkers [2,3]. In all cases, the π-conjugated character of the bridging ligand plays a crucial role on determining both the presence of intramolecular electron transfer processes [4a,4b] and the enhancement of NLO response [5], as it has been shown for organometallic di- and polynuclear complexes [6a–6c]. Relative to these research areas, aromatic N-heterocyclic compounds represent one of the most important class of ligands for the design and the construction of molecular devices [7a,7b] and NLO molecules [8]. However, although a wide variety of bridging ligands have been introduced in recent years, the study of dinuclear complexes bridged by ligands comprised of two non-equivalent binding sites is less common [9]. Therefore, in this paper we report our results about the synthesis and the characterisation of dinuclear systems in which two Fe(II) organometallic fragments are connected by a non-equivalently bridging 5-aryl tetrazolate ligand. Such research can be viewed as the natural extension of our recent studies [10] in which we reported some of the first examples of mononuclear 5-aryl tetrazolate Fe(II) organometallic complexes of the type $[Cp(CO)(L)Fe(N_4C–C_6H_4–CN)]$ [L = CO; PPh_3; $P(OCH_3)_3$; $CN–2,6-Me_2C_6H_3$], the characterisation of which indicated the presence of an extended π-delocalized system involving the transition metal and the aromatic rings of the 5-substituted tetrazolate ligand. The presence of

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interannular conjugation in such class of compounds was further corroborated by the X-ray structure of complex [Cp(CO)(P(OCH$_3$)$_3$)Fe(N$_4$C–C$_6$H$_4$–CN)], which showed the tetrazole and phenyl ring to adopt a preferentially coplanar arrangement. In addition, the structural and electronic properties of aromatic 5-substituted tetrazolate ligands could be chemically modified either in permanent or in reversible way, by their reaction with electrophiles. Indeed, the addition of suitable electrophilic agents such as CH_3^+ or H^+ to complexes of the type [Cp(CO)(L)Fe(N$_4$CC$_6$H$_4$CN)] was found to regioselectively occur at the nitrogen adjacent to the tetrazole carbon, causing the out of plane rotation of the phenyl ring and the consequent strong reduction of any interannular conjugation effect. Since in mononuclear type [Cp(CO)(L)Fe(N$_4$CC$_6$H$_4$CN)] complexes the 4-cyanophenyltetrazolate moiety yet possess a free nitrile function, we have considered this ligand as an ideal candidate for the synthesis of corresponding dinuclear organometallic complexes, which could represent possible models of molecular switches. In this present work, we will report the synthetic strategies we have performed to synthesize the title compounds as well as the discussion about the changes in the properties of the bridged tetrazolate ligands as a consequence of electrophilic addition of acids and alkylating agents.

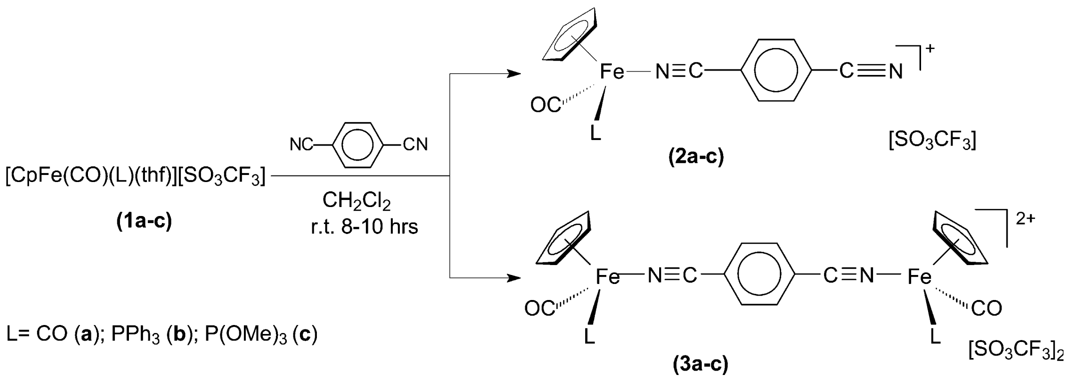
2. Discussion

2.1. Syntheses

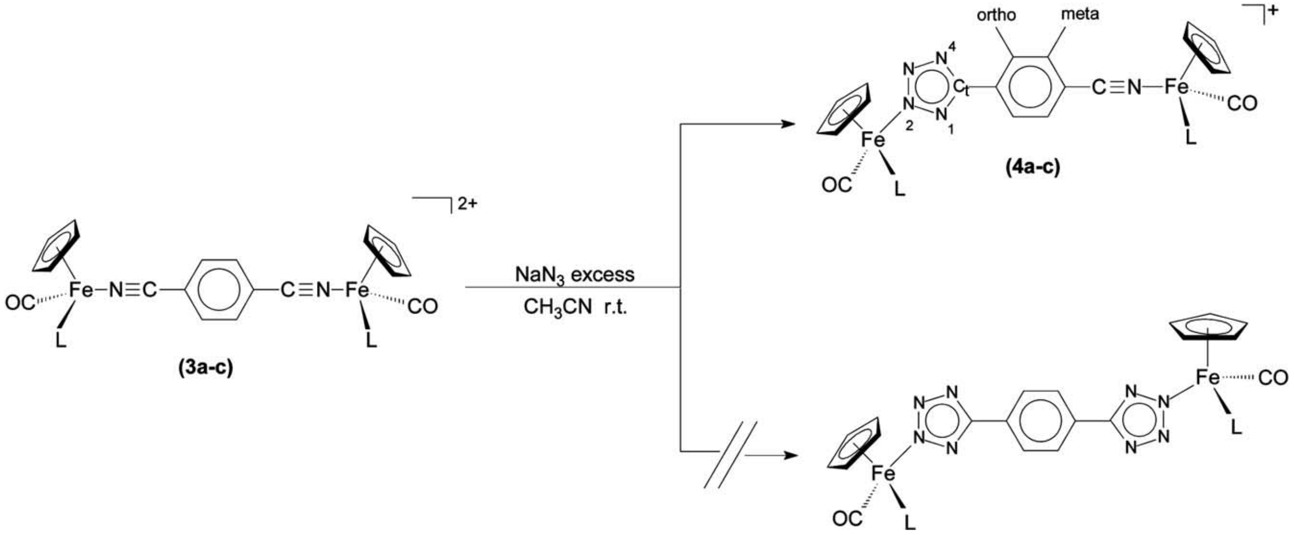
The reactions of cationic organometallic precursors such as [Cp(CO)(L)Fe(thf)][SO$_3$CF$_3$] (**1a**–**c**) (L = CO (**1a**), PPh$_3$(**1b**), P(OCH$_3$)$_3$ (**1c**)) with terephtalonitrile (Scheme 1) resulted in the formation of both of mono and dinuclear species, the relative amounts of which were not significantly influenced by the stoichiometric ratio of the starting reagents. In all cases, indeed, the purification of the reaction mixtures by alumina filled column chromatography afforded the mononuclear compounds [Cp(CO)(L)Fe(NCC$_6$H$_4$CN)][SO$_3$CF$_3$] (**2a**–**c**) as the main products, while the dinuclear complexes [Cp(CO)(L)Fe–NCC$_6$H$_4$CN–Fe(L)(CO)Cp][SO$_3$CF$_3$]$_2$(**3a**–**c**) were recovered in yield ranging from 5% (as in the case of **3a**) to 20% (Scheme 1).

However, the latter bimetallic compounds **3b-c** were treated with a slight excess of NaN$_3$ to afford the target tetrazolate bridged dinuclear complexes **4b** and **4c** (Method A, Scheme 2). As in the case of the synthesis of the parent mononuclear tetrazolate compounds [Cp(CO)(L)Fe(N$_4$CC$_6$H$_4$CN)], such reaction takes place in relatively short times at room temperature and in the presence of dichloromethane or acetonitrile as solvents, being the diffusion rate of the scarcely soluble sodium azide the main limiting factor. Relative to dinuclear complexes **4b** and **4c**, we observed in all cases the formation of only one pentatomic ring, while no evidence for the presence any bis-tetrazolate [Cp(CO)(L)Fe–N$_4$CC$_6$H$_4$CN$_4$–Fe(L)(CO)Cp] type complex was detected (Scheme 2), suggesting that, in similar conditions, the 1,3 dipolar cyclization reaction takes place only in the presence of strong electron withdrawing groups in the phenyl *para* position with respect to the coordinated nitrile. Anyway, it is worth emphasizing the determining role played by the coordination of the nitrile moiety to a transition metal atom about the activation of the –C≡N group toward nucleophilic additions. In fact, the numerous and continuously updated synthetic methods for the preparation of organic tetrazole-based compounds [11a–11c], the importance of which class has hugely increased over the past two decades [12a, 12b], require the presence of lithium [11c] or zinc [11a] salts as the activating agents and, in most cases, prolonged reaction times at the solvent reflux temperature.

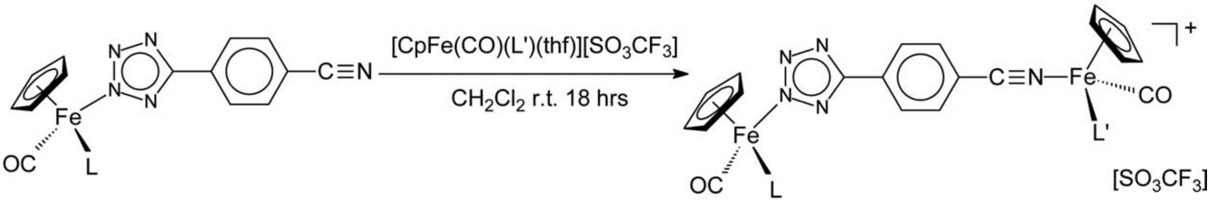
Nevertheless, the overall yields of the target dinuclear complexes **4a**–**c** were found to be seriously affected by the low quantities of the starting compounds **3a**–**c**. Therefore, it was of interest to explore some different synthetic pathways, the first of which consisted in the further complexation of mononuclear tetrazolate complexes [Cp(CO)(L)Fe(N$_4$CC$_6$H$_4$CN)] (Method B,



Scheme 1. Preparation of precursor complexes **3a**–**c**.



Scheme 2. Method A: 1,3 dipolar cyclization of NaN_3 on dinuclear precursor complexes **3a**–**c**.

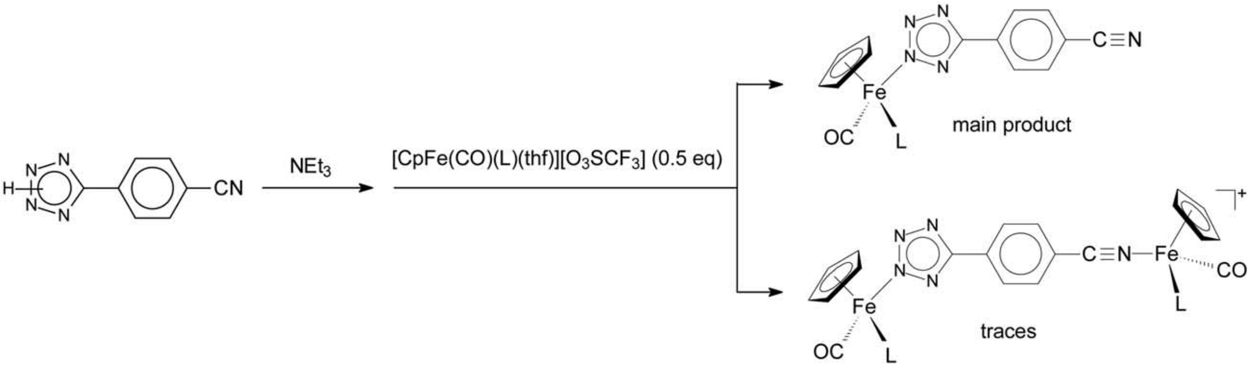


L=L'=CO (**4a**); L=CO, L'=PPh_3 (**4ab**); L=CO, L'=$P(OMe)_3$ (**4ac**); L=$P(OMe)_3$, L'=PPh_3 (**4cb**)

Scheme 3. Method B: further complexation of mononuclear tetrazolate complexes.

Scheme 3). The use of a similar two-steps protocol could also allow the introduction of different organometallic fragments, as in the case of complexes of the type $[Cp(CO)(L)Fe–N_4CC_6H_4CN–Fe(L')(CO)Cp][SO_3CF_3]$-(L = CO and L′ = PPh_3; **4ab**) (L = CO, L′ = $P(OMe)_3$; **4ac**) and **4cb** (L = $P(OMe)_3$, L′ = PPh_3). An analogous procedure was adopted for the synthesis of $[Cp(CO)_2$-$Fe–N_4CC_6H_4CN–Cr(CO)_5]$ (**4aCr**).

In a different approach, the preliminary synthesis of the nitrile complexes **3a**–**c** could be avoided by reacting the organometallic precursors with the preformed organic tetrazolate ligand (Method C, Scheme 4), which had been prepared either by the "classical" method [11c] involving the reaction of sodium azide with 1,4-dicyanobenzene in hot dimethylformamide in the presence of NH_4Cl and LiCl, or by using the more environmental friendly procedure recently reported by Demko and Sharpless [11a], in which $ZnBr_2$ acts as the promoter of the cycloaddition reaction.



Scheme 4. Method C: complexation of 4-cyanophenyl tetrazolate anion.

Unfortunately, the use of the alternative method C reported so far did not result in significant improvement of the overall yields of the target dinuclear complexes **4a**–**c**, which were always obtained as minor side products in the formation of the corresponding mononuclear derivatives.

2.2. Characterization

Some selected NMR and IR data of all compounds are summarized in Table 1. Some of the complexes (**4a**, **4ac**, **5ac**) we prepared were not recovered in sufficient amounts to allow a clear ^{13}C NMR spectroscopic characterization.

In general, the IR spectra of the title dinuclear complexes show carbonyls band wavenumbers in agreement with the formation of cationic species (Table 1). In addition, the presence of the different coordination sites in the non-equivalently bridging ligand $^{-}N_4C–C_6H_4–CN$ allowed to observe distinct carbonyl absorptions even in the case of the homodinuclear [Cp(CO)(L)Fe–$N_4CC_6H_4CN$–Fe(L)(CO)Cp][SO_3CF_3] type complexes **4b** (L = PPh_3) and **4c** (L = $P(OMe)_3$). As for example, the IR spectrum of the bimetallic compound [Cp(CO)(PPh_3)Fe–$N_4CC_6H_4CN$–Fe(PPh_3)(CO)Cp][SO_3-CF_3] (**4b**) (Fig. 1, left), shows different CO absorptions attributable to differently coordinated Cp(CO)(L)Fe–

Table 1
Selected NMR[a] and IR[b] data of the title dinuclear complexes

Entry	$\delta(C_t)$ (ppm)	$\Delta(\delta C_{meta} - \delta C_{ortho})$ (ppm)	$\Delta(\delta H_{ortho} - \delta H_{meta})$ (ppm)	CO absorption (cm^{-1})
4a	–	–	0.45	2070; 2022
4b	163.6	5.9	0.64	1990; 1973
4c	163.9	6.5	0.46	2003; 1989
4ab	165.8	5.5	0.84	2064; 2019; 1991
4ac	–	–	0.47	2066; 2019; 2000
4cb	164.2	5.6	0.50	1990
5ab	157.0	3.3	–[c]	2074; 2030; 1994
5ac	–	–	0.07	2074; 2029; 2009
6ab	158.2	4.7	0.57	2078; 2036; 1995
4aCr	166.0	5.6	0.48	2066; 2021 (FeCO); 2072; 1994; 1909 (CrCO)

See Scheme 2 for numbering.

[a] ^{1}H and ^{13}C NMR experiments were performed using $CDCl_3$ as solvent.

[b] CH_2Cl_2 as solvent.

[c] Overlapping of PPh_3 signals.

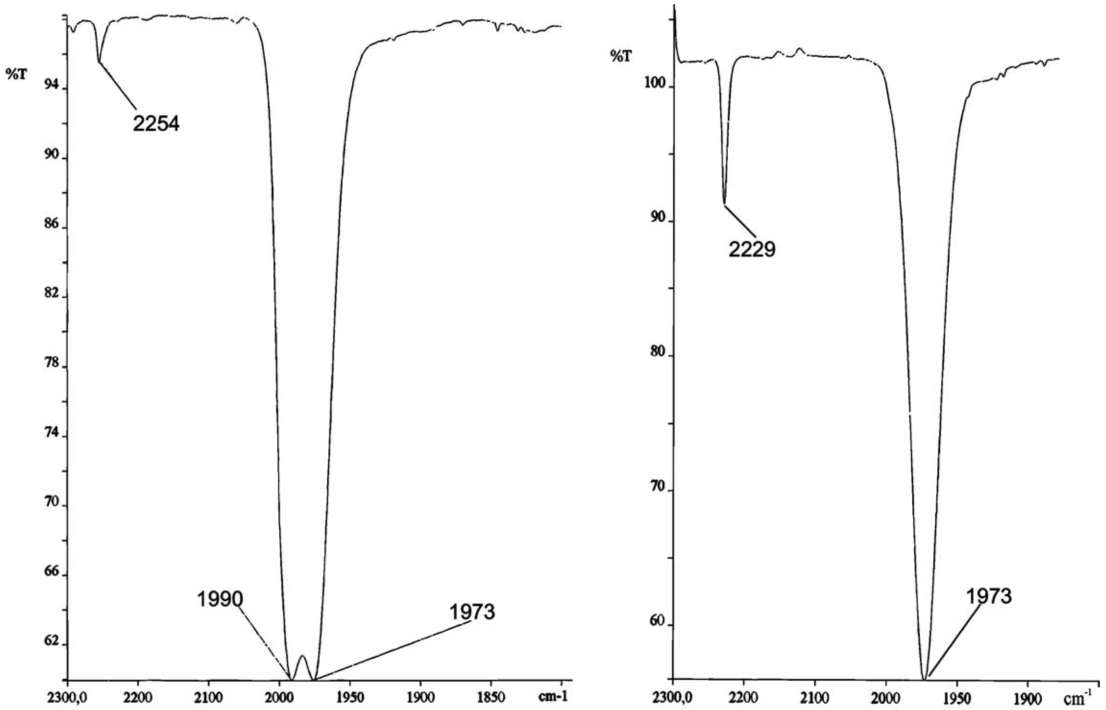


Fig. 1. IR spectra of [Cp(CO)(PPh_3)Fe–$N_4CC_6H_4CN$–Fe(PPh_3)(CO)Cp][SO_3CF_3] (**4b**) (left) and [Cp(CO)(PPh_3)Fe–$N_4CC_6H_4CN$] (right).

units. Such data, if compared with those relative to the parent mononuclear compound [Cp(CO)(PPh_3)Fe–$N_4CC_6H_4CN$] (Fig. 1, right), suggest the attribution of the more energetic CO stretching band at 1990 cm^{-1} in the spectrum of **4b** to the nitrile-coordinated metal fragment.

The NMR (^1H and, particularly, ^{13}C) spectroscopy represents a powerful tool to gain information about the main electronic and structural properties of 5-aryl substituted tetrazolate complexes [12b,13]. As for example, we report the ^1H and ^{13}C NMR spectra (Figs. 2 and 3) of the dinuclear complex [Cp(CO)($P(OMe)_3$)Fe–

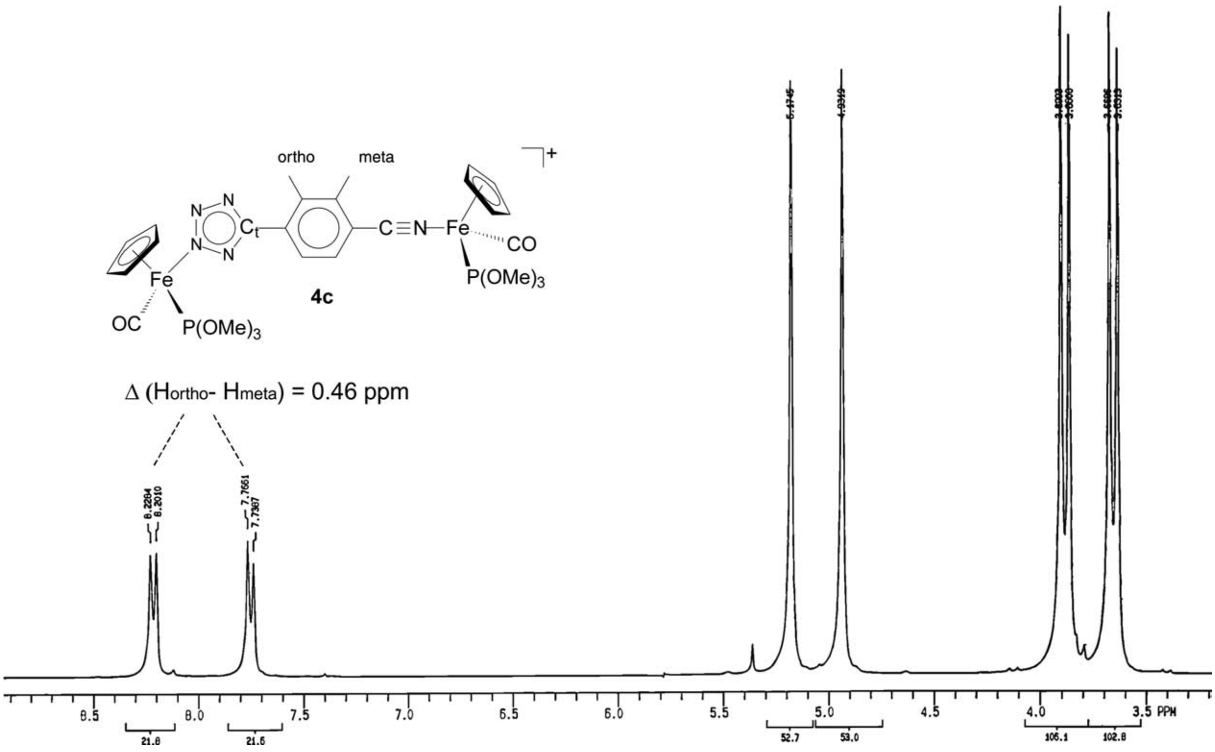


Fig. 2. ^1H NMR spectrum ($CDCl_3$) of [Cp(CO)($P(OMe)_3$)Fe–$N_4CC_6H_4CN$–Fe($P(OMe)_3$)(CO)Cp][SO_3CF_3] (**4c**).

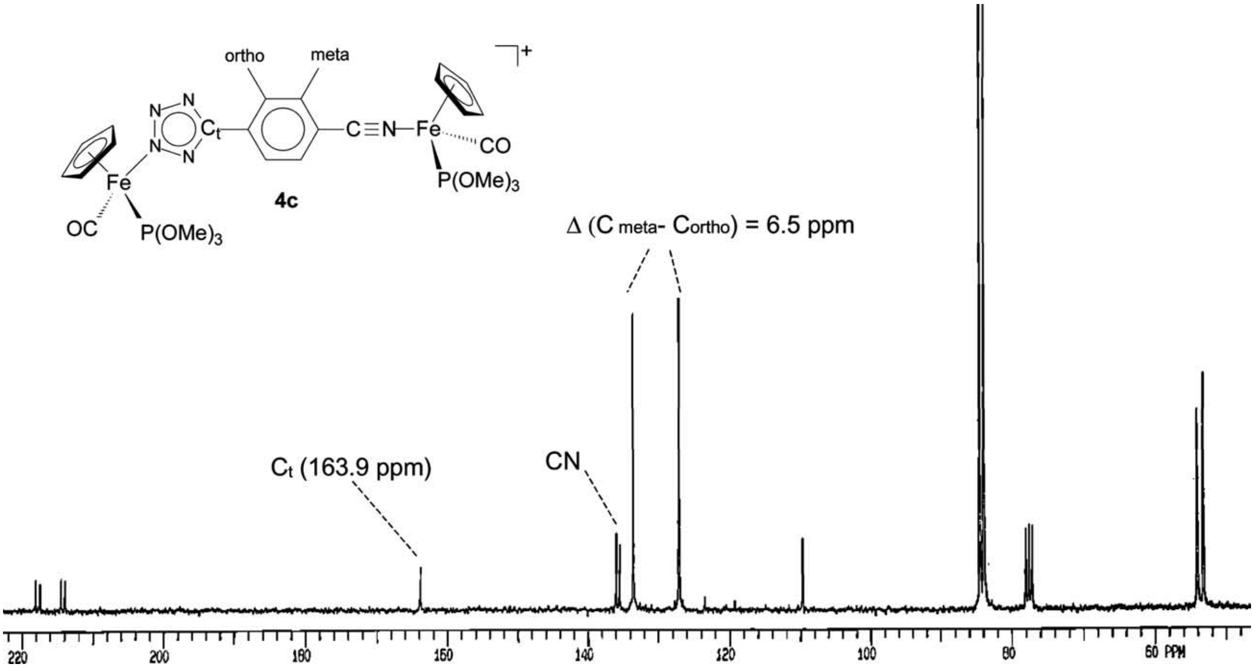


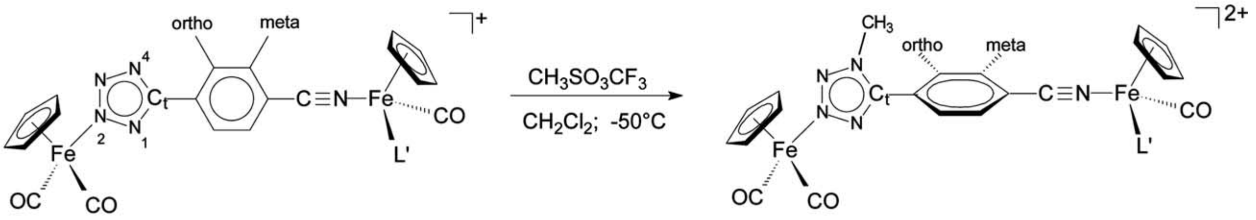
Fig. 3. ^{13}C NMR spectrum ($CDCl_3$) of [Cp(CO)($P(OMe)_3$)Fe–$N_4CC_6H_4CN$–Fe($P(OMe)_3$)(CO)Cp][SO_3CF_3] (**4c**).

$N_4CC_6H_4CN–Fe(P(OMe)_3)(CO)Cp][SO_3CF_3]$ (**4c**). The interpretation of such NMR data gives rise to a number of features, the general validity of which can be extended to all dinuclear complexes: (i) the ^1H NMR spectra clearly indicate the presence of the expected bimetallic compounds (see Fig. 2) and, relative to all complexes, the chemical shifts separation between the phenyl protons $\Delta(\delta H_{ortho} - \delta H_{meta})$ (relative to the tetrazole group, see Scheme 2) is very similar to those of the parent mononuclear derivatives [10]; (ii) in all cases, the $C{\equiv}N$ carbon resonance experiences an evident downfield shift on going from the mononuclear complex, i.e. $[Cp(CO)(P(OMe)_3)Fe(N_4C–C_6H_4–CN)]$ ($\delta CN = 119$ ppm) [10], to the corresponding dinuclear species, i.e. $[Cp(CO)(P(OMe)_3)Fe–N_4CC_6H_4CN–Fe(P(OMe)_3)(CO)$-$Cp][SO_3CF_3]$ (**4c**) ($\delta CN = 135.5$ ppm) (see Fig. 3); (iii) the regioselective coordination of a metal fragment to the N-2 nitrogen atom of the tetrazolate ring (see Scheme 2 for numbering) is unambiguously indicated by the presence of a unique resonance of the tetrazole carbon (δC_t) in the chemical shifts range (162–167 ppm) typical of both N-2 coordinated tetrazolate complexes [10,14,15] and of 2-N methyl derivatives of organic 5-aryl-tetrazoles [12b,13]; (iv) the large chemical shifts separation $\Delta(\delta C_{meta} - \delta C_{ortho})$ (see Table 1) between the carbons *meta* and *ortho* (relative to the tetrazole group, see Scheme 2) in the target dinuclear complexes can suggest the presence of a significant interannular conjugation effect involving both the tetrazolate and the benzonitrile ring. In facts, the magnitude of such parameter has been introduced by Butler [13] for determining the extent of interannular conjugation in a series of organic 5-aryl tetrazoles. In the case of $[Cp(CO)(P(OMe)_3)Fe–N_4CC_6H_4CN–Fe(P(OMe)_3)(CO)Cp][SO_3CF_3]$ (**4c**) the value of $\Delta(\delta C_{meta} - \delta C_{ortho})$ is of 6.5 ppm (Fig. 3) and it is even greater than that we recently observed ($\Delta(\delta C_{meta} - \delta C_{ortho}) = 5.7$ ppm) for the mononuclear analogue $[Cp(CO)(P(OCH_3)_3)Fe–N_4CC_6H_4CN]$, the structural determination of which showed the aromatic rings of the 5-substituted tetrazolate ligand to adopt a totally coplanar arrangement [10]. In light of these results, the NMR data of dinuclear complexes may suggest the participation of metal orbitals to the π-delocalized system of the conjugated linker and, consequently, the 5-aryltetrazolate bridging ligand may act as a mediator of electron transfer processes between the peripheral metal centres. Thus, in order to determine the presence of any metal-to-metal electronic interaction, the dinuclear complexes **4b** and **4c** were preliminary studied by cyclic voltammetry. Unfortunately, we only had evidence of the formation of decomposition products arising from chemically irreversible redox processes, which did not provide any information about the presence and/or the eventual stability of mixed valence species.

2.3. Addition of electrophiles

Relative to mono and dinuclear 5-aryl tetrazolate complexes, the presence of three pyridine-type nitrogen atoms in the 2-N coordinated five-membered ring offers different sites which could undergo alkylation and/or protonation reactions. Therefore, it was of interest to perform electrophilic additions on our dinuclear complexes in order to establish if they exerted the same chemical reactivity we previously observed in the case of the analogous mononuclear derivatives [10].

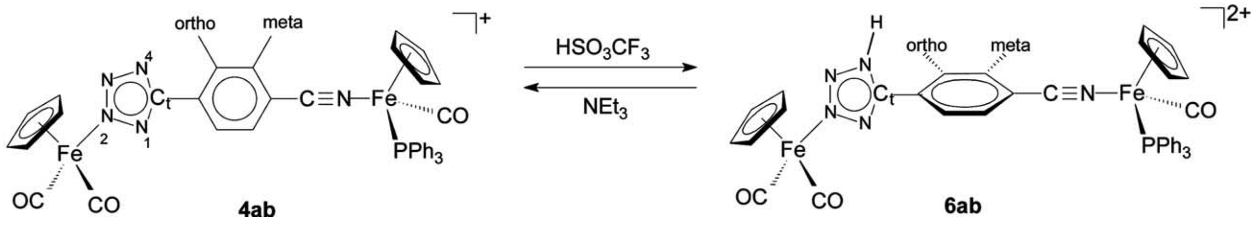
The addition of methyl triflate to dinuclear complexes $[Cp(CO)_2Fe–N_4CC_6H_4CN–Fe(PPh_3)(CO)Cp][SO_3CF_3]$ (**4ab**) and $[Cp(CO)_2Fe–N_4CC_6H_4CN–Fe(P(OMe)_3)(CO)$-$Cp][SO_3CF_3]$ (**4ac**) resulted in the formation of dicationic species **5ab** and **5ac** (Scheme 5) in which the increase of ionic charge was found to be distributed on the entire molecule, as evidenced in the IR spectra by the carbonyl absorptions which are found at higher wavenumbers, in particular the ones of the carbonyls coordinated to the iron directly bonded to the tetrazole moiety of the bridging ligand. The addition of a methyl group also determines the disappearance of the weak $\nu(C{=}N)$ absorption of the tetrazole ring, which is observed in the starting derivatives at about 1620 cm^{-1}. The NMR characterization of the addition products reveal some interesting features, the more relevant of which is given by the upfield shift of the tetrazole carbon resonance on



4ab L'=PPh$_3$ **5ab**

4ac L'=P(OMe)$_3$ **5ac**

Scheme 5. Methylation reactions.



Scheme 6. Protonation of complex **4ab**.

going from the starting compound **4ab** ($\delta C_t = 165.8$ ppm) to the methylated product **5ab** ($\delta C_t = 157.0$ ppm). A similar behaviour indicates the regioselective addition of the methyl group to the N-4 tetrazole nitrogen [10,13,15] (see Scheme 5), the one which less suffers of the encumbrance of the metal fragment. Moreover, as it has been reported both for 5-aryltetrazolate complexes [10,14,15] and 1-N methyl derivatives of organic 5-aryltetrazoles [12b,13], the presence of a substituent in such position causes the out-of-plane rotation of the aromatic 5-substituent ring and, consequently, the removal or the strong diminution of any interannular conjugation effect. This latter feature is further evidenced in complex **5ab** by the chemical shifts of the phenyl carbons *meta* and *ortho* ($\Delta(\delta C_{meta} - \delta C_{ortho})$), the separation of which, if compared to that of the cationic precursor **4ab**, have decreased to 3.3 ppm. Relative to methylated compound **5ac** some further evidences about the decreasing of the conjugative properties of the 5-aryl tetrazolate ligand might be deduced by the analysis of the phenyl ^{1}H NMR signals [12b]. Indeed, in perfect agreement with the case of the analogues mononuclear derivatives [10], the ^{1}H NMR spectra of the methylated complex **5ac** showed protons *ortho* and *meta* to resonate in a much narrower chemical shift range ($\Delta(\delta H_{ortho} - \delta H_{meta}) = 0.07$ ppm) than what observed for the cationic precursor **4ac** ($\Delta(\delta H_{ortho} - \delta H_{meta}) = 0.47$ ppm). This latter feature is not clearly observable in complex **5ab**, in which the phenyl protons resonances are overlapped by the signals pattern of the coordinated triphenylphosphine (see Table 1).

Analogous considerations can be extended to the characterization of protonated complex **6ab** (Scheme 6).

In fact, the NMR evidences indicate the selective N-4 tetrazole quaternization ($\delta Ct = 158.2$ ppm), while the low steric hindrance of the proton substituent probably accounts for the minor changes observed about the chemical shifts separation between the phenyl protons *ortho* and *meta* ($\Delta(\delta H_{ortho} - \delta H_{meta})$) on going from the starting compound **4ab** ($\Delta(\delta H_{ortho} - \delta H_{meta}) = 0.84$), to the dication product complex **6ab** ($\Delta(\delta H_{ortho} - \delta H_{meta}) = 0.57$). However, the addition of a proton should result in changes of both structural and electronic properties of the tetrazolate ligand, as we previously evidenced in the case of the protonated complex $[Cp(CO)_2Fe–(H)N_4C–C_5H_4N–H]^{2+}$, the X ray diffraction study of which allowed to establish the partial twisting (dihedral angle = 21°) of the pyridyl ring with respect to the tetrazole plane [15]. It is important to notice that the protonated dinuclear complex **6ab** can be re-converted into its cationic precursor by treatment with a stoichiometric amount of a base such as triethylamine. Interestingly, the reversibility of the protonation reaction (Scheme 6) offers the opportunity to modulate both the structural and the electronic properties of the aromatic 5-substituted tetrazolate ligands by a simple acid-base mechanism.

3. Conclusions

Even though the formation of the relative dinuclear organometallic complexes is rather difficult, the 4-cyanophenyl tetrazolate bridging ligand shows some main features – i.e the presence of a reversibly switchable interannular conjugation effect – which could favour the use of this compound in the construction and in the design of bimetallic arrays. Thus, in order to explore the potential of 5-aryl tetrazolates as mediators of electron transfer processes between the end-on coordinated metal fragments, we are currently engaged in the synthesis and in the spectro-electrochemical characterization of dinuclear species in which the 4-cyanophenyl tetrazolate anion act as conjugated linker between efficient redox centres such as Ruthenium polypyridyl units.

4. Experimental

4.1. Materials and procedures

All reactions with organometallic reagents were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. The prepared derivatives were characterized by elemental analysis and spectroscopic methods. IR spectra were recorded with a Perkin Elmer Spectrum 2000 FT-IR spectrometer. The routine NMR spectra (^{1}H, ^{13}C) were always recorded using a Varian Gemini 300 instrument (^{1}H, 300.1; ^{13}C, 75.5 MHz). The spectra were referenced internally to residual solvent resonance and were recorded at 298 K for characterisation purposes. Elemental analyses were performed on a Thermoquest Flash 1112 Series EA instrument. Unless otherwise stated, chemicals were obtained commercially (e.g. Aldrich) and used without any further purification. Cationic precursors like [CpFe(CO)(L)(thf)][SO_3CF_3] [L = CO (**1a**), PPh_3 (**1b**), $P(OMe)_3$ (**1c**)] were prepared from the corresponding iodides [16] by reaction with a stoichiometric amount of Ag(SO_3CF_3) in a thf solution (15 mL) at room temperature. Filtration through Celite and subsequent evaporation to dryness afforded a mixture that was used without any further purification. The ligand 4-(*1-H*-tetrazol-5-yl)-benzonitrile was prepared (yield ranged from 80% to 90% with respect to starting terephtalonitrile) by following the literature procedures [11a,11c]. The preparation of mononuclear derivatives [Cp(CO)(L)-Fe($N_4CC_6H_4CN$)] (L = CO; PPh_3; $P(OMe)_3$) has been reported elsewhere [10]. All reactions were monitored by IR spectroscopy. Petroleum ether (Etp) refers to a fraction of b.p. 60–80 °C. Typically, all chromatographies were performed on alumina filled columns (diameter 1.5 cm; height 15 cm) under argon atmosphere and using dichloromethane–acetonitrile mixtures as eluent.

*4.1.1. Preparation of [Cp(CO)(L)Fe–NCC_6H_4CN–Fe(L)(CO)Cp][SO_3CF_3]$_2$ complexes (L = CO (**3a**), PPh_3(**3b**), $P(OMe)_3$ (**3c**))*

The title compounds were always obtained as byproducts in the preparation of the relative mononuclear [Cp(CO)(L)Fe(NCC_6H_4CN)][O_3SCF_3] (**2a**–**c**) derivatives by reacting the cationic [CpFe(CO)(L)(thf)]$^+$ (**1a**–**c**) complexes with terephtalonitrile in 15 mL of dichloromethane. Although the formation of the desired dinuclear compounds **3a**–**c** should be prevalent toward that of the mononuclear derivatives by mixing the starting reagents in 2/1 (complex/ligand) ratio, appreciable amounts of complexes **3a**–**c** were obtained only when the reactions were performed in the presence of a slight excess (1.1 equiv.) of terephtalonitrile with respect of precursors **1a**–**c**. The reaction mixtures were stirred overnight at r.t. Then, filtration through a Celite pad and evaporation of the filtrate to dryness afforded a residue which was purified by chromatography on alumina filled column using dichloromethane–acetonitrile mixtures as eluent. The target dinuclear complexes were recovered as the last fraction by eluting with pure acetonitrile.

*4.1.2. [Cp(CO)$_2$Fe–NCC_6H_4CN–Fe(CO)$_2$Cp]-[SO_3CF_3]$_2$ (**3a**)*

Yellow oil. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2082s, 2040s (CO); NMR: δ_H (CD_3CN) 7.92 (4H, s, C_6H_4), 5.45 (10H, s, Cp) ppm. Anal. Calc. for $C_{24}H_{14}N_2O_{10}Fe_2F_6S_2$: C, 36.95; H, 1.81; N, 3.59. Found: C, 36.8; H, 1.83; N, 3.6%.

*4.1.3. [Cp(CO)(PPh_3)Fe–NCC_6H_4CN–Fe(PPh_3)-(CO)Cp][SO_3CF_3]$_2$ (**3b**)*

Orange powder. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2254w (CN), 1993s (CO); NMR: δ_H ($CDCl_3$) 7.40–7.20 (34H, m, PPh_3, C_6H_4), 4.99 (10H, s, Cp) ppm; δ_C ($CDCl_3$) 216.3 (CO, d, $J_{CP} = 29$ Hz), 134.5–129.5 (PPh_3, C_6H_4), 127.3 (CN), 115.5 (C*ipso*-CN), 86.0 (Cp). Anal. Calc. for $C_{58}H_{44}N_2O_8Fe_2F_6P_2S_2$: C, 55.78; H, 3.55, N, 2.24. Found: C, 55.9; H, 3.51, N, 2.3%.

*4.1.4. [Cp(CO)($P(OMe)_3$)Fe–NCC_6H_4CN–Fe-($P(OMe)_3$)(CO)Cp][SO_3CF_3]$_2$ (**3c**)*

Orange-green powder. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2256w (CN), 2008s (CO); NMR: δ_H ($CDCl_3$) 8.08 (4H, s, C_6H_4), 5.18 (10H, s, Cp), 3.89 (18H, d, OMe, $J_{HP} = 9$ Hz) ppm. Anal. Calc. for $C_{28}H_{32}N_2O_{14}Fe_2F_6P_2S_2$: C, 34.58; H, 3.32; N, 2.88. Found: C, 34.6; H, 3.32; N, 2.8%.

*4.1.5. Preparation of [Cp(CO)(L)Fe–$N_4CC_6H_4CN$–Fe(L)(CO)Cp][SO_3CF_3] complexes (L = PPh_3 (**4b**), $P(OMe)_3$ (**4c**)) [Cp(CO)(PPh_3)Fe–$N_4CC_6H_4CN$–Fe(PPh_3)(CO)Cp][SO_3CF_3] (**4b**)*

A stirred solution of **3b** (0.210 g, 0.168 mmol) in acetonitrile (20 mL) at room temperature was added of a little excess of NaN_3 (0.033 g, 0.508 mmol). The resulting suspension was stirred at r.t. for 12 h. The mixture was filtered through Celite and evaporated to dryness. Subsequent chromatography of the residue on alumina with CH_2Cl_2 as eluent gave a first fraction containing traces of the mononuclear derivative [Cp(CO)(PPh_3)Fe($N_4CC_6H_4CN$)]. Further elution with a mixture CH_2Cl_2–CH_3CN (1:1, v/v) afforded the complex **4b** (0.120 g, 62.5%), obtained as a red oily solid. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2254w (CN), 1990s, 1973s (CO), 1609w (C=N); NMR: δ_H ($CDCl_3$) 7.77 (2H, H$_{ortho}$, d, $J_{HH} = 12$ Hz), 7.13 (2H, H$_{meta}$, d, $J_{HH} = 12$ Hz), 7.60–7.20 (30H, PPh_3), 4.98 (5H, s, Cp), 4.68 (5H, s, Cp) ppm; δ_C ($CDCl_3$) 219.6 (CO, d, $J_{CP} = 29$ Hz), 216.0 (CO, d, $J_{CP} = 21$ Hz), 163.6 (C$_t$), 136.0 (C*ipso*–C$_t$), 135.2 (CN), 134.2–126.0 (PPh_3), 132.1 (C$_{meta}$), 126.2 (C$_{ortho}$), 109.0 (C*ipso*-CN), 85.2 (Cp), 84.1 (Cp). Anal. Calc. for $C_{57}H_{44}N_5O_5Fe_2F_3P_2S$: C, 59.96; H, 3.88; N, 6.13. Found: 60.1; H, 3.95; N, 6.2%.

*4.1.6. [Cp(CO)($P(OMe)_3$)Fe–$N_4CC_6H_4CN$–Fe-($P(OMe)_3$)(CO)Cp][SO_3CF_3] (**4c**)*

This complex was prepared using the above procedure and starting from 0.105 g (0.107 mmol) of **3c**. It was finally obtained as an orange oily solid (0.048 g, 52%), m.p. 142–146 °C (dec.). IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2003, 1989 (CO), 1610w (C=N). NMR: δ_H ($CDCl_3$): 8.21 (2H, d, H$_{ortho}$, $J_{HH} = 9$ Hz), 7.75 (2H, d, H$_{meta}$, $J_{HH} = 9$ Hz), 5.17 (5H, s, Cp), 4.93 (5H, s, Cp), 3.88 (9H, d, OMe, $J_{HP} = 12$ Hz), 3.65 (9H, d,

$OC\mathit{H}_3$, $J_{HP} = 12$ Hz) ppm. δ_C ($CDCl_3$) 217.8 (CO, d, $J_{CP} = 45$ Hz), 214.2 (CO, d, $J_{CP} = 45$ 0Hz), 163.9 (C_t), 136.0 (C*ipso*–C_t), 135.5 (CN), 133.6 (C_{meta}), 127.1 (C_{ortho}), 109.7 (C*ipso*-CN), 84.5 (Cp), 83.9 (Cp), 54.1 (OMe, d, $J_{CP} = 6$ Hz), 53.2 ($OC\mathit{H}_3$, d, $J_{CP} = 5$ Hz). Anal. Calc. for $C_{27}H_{32}N_5O_{11}Fe_2F_3P_2S$: C, 37.48; H, 3.73; N, 8.09. Found: C, 37.4; H, 3.70; N, 8.2%.

4.1.7. Preparation of $[Cp(CO)(L)Fe–N_4CC_6H_4CN–Fe(L')(CO)Cp][SO_3CF_3]$complexes (L = L′ = CO (**4a**); L = CO, L′ = PPh_3 (**4ab**); L = CO, L′ = $P(OMe)_3$ (**4ac**); L = $P(OMe)_3$, L′ = PPh_3 (**4cb**))

These complexes were synthesized by reacting the mononuclear derivatives $[Cp(CO)(L)Fe(N_4CC_6H_4CN)]$ (L = CO, $P(OMe)_3$) with a slight excess of the appropriate cationic fragment $[CpFe(CO)(L')(thf)][SO_3CF_3]$ [L′ = CO (**1a**), PPh_3 (**1b**), $P(OMe)_3$ (**1c**)] in 15 mL of dichloromethane. The reaction mixture was stirred for 18 h, filtered on Celite and the products were separated by chromatography with the procedure above described. This is also the best procedure for the synthesis of (**4a**). Yields : 10% (**4a**), 15% (**4ac**), 40% (**4ab** and **4cb**).

4.1.8. $[Cp(CO)_2Fe–N_4CC_6H_4CN–Fe(CO)_2Cp]$-$[SO_3CF_3]$ (4a)

Light yellow powder. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2233vw (CN), 2070, 2022 (CO). NMR: δ_H ($CDCl_3$): 7.87 (2H, H_{ortho}, d, $J_{HH} = 6$ Hz), 7.72 (2H, H_{meta}, d, $J_{HH} = 6$ Hz), 5.39 (Cp), 5.17 (Cp) ppm. Anal. Calc. for $C_{23}H_{14}N_5O_7Fe_2F_3S$: C, 41.04; H, 2.10; N, 10.40. Found: C, 41.2; H, 2.14; N, 10.5%.

4.1.9. $[Cp(CO)_2Fe–N_4CC_6H_4CN–Fe(PPh_3)(CO)Cp]$-$[SO_3CF_3]$ (4ab)

Orange powder. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2064s, 2019s, 1991s (CO), 1610w (C═N). NMR: δ_H ($CDCl_3$): 8.10 (2H, H_{ortho}, d, $J_{HH} = 5$ Hz), 7.63–7.44 (15H, m, PPh_3), 7.26 (2H, H_{meta}, d, $J_{HH} = 5$ Hz), 5.33 (5H, s, Cp), 5.04 (5H, s, Cp) ppm. δ_C ($CDCl_3$): 216.6 (CO, d, $J_{CP} = 28$ Hz), 211.3 (CO), 165.8 (C_t), 136.6 (C*ipso*–C_t), 135.5 (*C*N), 133.8–129.5 (PPh_3), 132.8 (C_{meta}), 127.3 (C_{ortho}), 110.3 (C*ipso*-CN), 86.7 (Cp), 85.7 (Cp). Anal. Calc. for $C_{40}H_{29}N_5O_6Fe_2F_3PS$: C, 52.94; H, 3.22; N, 7.71. Found: C, 53.0; H, 3.18; N, 7.6%.

4.1.10. $[Cp(CO)_2Fe–N_4CC_6H_4CN–Fe(P(OMe)_3)$-$(CO)Cp][SO_3CF_3]$ (4ac)

Orange oil. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2066s, 2019s, 2000sh (CO), 1610w (C═N). NMR: δ_H ($CDCl_3$): 8.12 (2H, H_{ortho}, d, $J_{HH} = 6$ Hz), 7.65 (2H, H_{meta}, d, $J_{HH} = 6$ Hz), 5.23 (5H, s, Cp), 5.07 (5H, s, Cp), 3.79 (9H, d, OMe, $J_{HP} = 15$ Hz). Anal. Calc. for $C_{25}H_{23}N_5O_9Fe_2F_3PS$: C, 39.03; H, 3.01; N, 9.1. Found: C, 39.2; H, 2.98; N, 9.0%.

4.1.11. $[Cp(CO)(P(OMe)_3)Fe–N_4CC_6H_4CN–Fe(PPh_3)(CO)Cp][SO_3CF_3]$ (4cb)

Red oily powder. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 1990vs (CO), 1609w (C═N), NMR: δ_H ($CDCl_3$): 8.02 (2H, H_{ortho}, d, $J_{HH} = 6$ Hz), 7.52–7.18 (17 H, m, PPh_3, H_{meta}), 4.98 (Cp), 4.88 (Cp), 3.61 (9H, d, $OC\mathit{H}_3$, $J_{HP} = 12$ Hz). δ_C ($CDCl_3$): 217.9 (CO, d, $J_{CP} = 45$ Hz), 216.9 (CO, d, $J_{CP} = 28$ Hz), 164.2 (C_t), 136.8 (C*ipso*–C_t), 135.7 (CN), 133.8–129.9 (PPh_3), 132.7 (C_{meta}), 127.1 (C_{ortho}), 110.14 (C*ipso*-CN), 84.8 (Cp), 84.2 (Cp), 53.62, 53.56 (OCH_3, d, $J_{CP} = 5$ Hz). Anal. Calc. for $0C_{42}H_{38}N_5O_8Fe_2F_3P_2S$: C, 50.27; H, 3.82; N, 6.98. Found: C, 50.4; H, 3.80; N, 7.1%.

4.1.12. Reaction between $[CpFe(CO)(L)(thf)]^+$ complexes and 4-(1-H-tetrazol-5-yl)cyanobenzene

As a general method 2 mmol of the tetrazole were suspended in 10 mL of dimethylformamide and treated with 2 mmol of triethylamine. The solution becomes immediately clear because of the formation of the corresponding tetrazolate. This solution is added dropwise to 4 mmol of the cationic $[CpFe(CO)(L)(thf)]^+$ [L = CO (**1a**), PPh_3 (**1b**), $P(OMe)_3$ (**1c**)] complexes, dissolved in 10 mL of DMF. After 4 h, the solvent is evaporated to dryness. The resulting mixture was dissolved in 10 mL of CH_2Cl_2, filtered, and purified by alumina filled column. With this method, very low yields of homodinuclear **4a**, **4b** and **4c** complexes were obtained, the mixture containing predominantly the corresponding mononuclear derivatives.

4.1.13. Synthesis of $[Cp(CO)_2Fe–N_4CC_6H_4CN–Cr$-$(CO)_5]$ (4aCr)

0.100 g (0.29 mmol) of $[Cp(CO)_2Fe(N_4CC_6H_4CN)]$, dissolved in 20 mL of thf, were treated under stirring with a solution of $Cr(CO)_5(thf)$, obtained by irradiation of $Cr(CO)_6$ in tetrahydrofurane (0.188 g, 0.85 mmol). After 12 h the solvent was removed in vacuo and the yellow residue, dissolved in CH_2Cl_2, was chromatographed on an alumina column. After elimination of a first fraction containing $Cr(CO)_6$, eluted with a Etp/CH_2Cl_2 mixture, the desired product **4aCr**, 0.065 g (42%), was eluted with a CH_3CN/CH_2Cl_2 mixture. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2230 (CN), 2066s, 2021s (FeCO), 2072sh, 1994vs, 1909sh (CrCO); δ_H ($CDCl_3$): 8.42 (2H, br s, H_{ortho}), 7.94 (2H, br s, H_{meta}), 5.53 (5H, s, Cp); δ_C ($CDCl_3$): 220.4 ($Cr\mathit{C}O_{ax}$), 215.9 (Fe*C*O), 214.9 ($Cr\mathit{C}O_{eq}$), 166.0 (C_t), 133.5 (C_{meta}), 127.9 (C_{meta}), 120.0 (*C*N), 112.01 (C*ipso*-CN), 86.97 (Cp). Anal. Calc. for $C_{20}H_9N_5O_7FeCr$: C, 44.54; H, 1.68; N, 12.98. Found: C, 44.7; H, 1.80; N, 12.8%.

4.1.14. Methylation reactions: synthesis of $[Cp(CO)_2$-$Fe–(Me)N_4CC_6H_4CN–Fe(L)(CO)Cp][SO_3CF_3]_2$, L = PPh_3 (5ab), $P(OCH_3)_3$ (5ac)

(**5ab**) A solution of **4ab** (0.110 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was treated with $CH_3O_3SCF_3$ (0.013

mL, 0.12 mmol) with stirring at −50 °C for 30 min. The mixture was then allowed to warm at r.t. and stirred for an additional 4 h. After filtration on Celite the solvent is removed in vacuo. **5ab** (0.105 g, 87%) was recovered as an orange solid that was crystallized from CH_2Cl_2/Et_2O, m.p. 136 °C. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2074s, 2030s, 1994s (CO); δ_H ($CDCl_3$): 8.05 (2H, H_{ortho}, d, $J_{HH} = 5$ Hz), 7.90–7.20 (17 H, m, H_{meta}, PPh_3), 5.47 (5H, s, Cp) 5.00 (5H, s, Cp) 4.15 (3H, s, Me); δ_C ($CDCl_3$): 216.3 (CO, d, $J_{CP} = 28$ Hz), 209.45 (CO), 157.0 (C_t), 136.0 (C*ipso*–C_t), 135.0 (CN), 134.4–130.1 (PPh_3), 133.4 (C_{meta}), 131.1 (C_{ortho}), 114.3 (C*ipso*-CN), 87.6 (Cp), 85.9 (Cp) 38.2 (Me). Anal. Calc. for $C_{42}H_{32}N_5O_9Fe_2F_6PS_2$. C, 47.08; H, 3.01; N, 6.53. Found: C, 47.2; H, 3.04; N, 6.7%. Compound **5ac** was analogously prepared from **4ac**. IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2074s, 2029s, 2009s (CO), 1607w (C=N); δ_H ($CDCl_3$): 8.04 (2H, H_{ortho}, d, $J_{HH} = 5$ Hz), 7.97 (2H, H_{meta}, d, $J_{HH} = 6$ Hz), 5.46 (5H, s, Cp), 5.15 (5H, s, Cp), 4.20 (3H, s, Me), 3.87 (9H, d, OCH_3, $J_{HP} = 15$ Hz). Anal. Calc. for $C_{27}H_{26}N_5O_{12}Fe_2F_6PS_2$. C, 34.74; H, 2.81; N, 7.50. Found: C, 34.6; H, 2.84; N, 7.7%.

*4.1.15. Protonation reaction: synthesis of $[Cp(CO)_2Fe–(H)N_4CC_6H_4CN–Fe(PPh_3)(CO)Cp][O_3SCF_3]_2$ (**6ab**)*

While a stirred solution of **4ab** (0.100 g, 0.11 mmol) in 15 mL of CH_2Cl_2 was kept at −60 °C, two drops of triflic acid were added. After 30 min the mixture was allowed to warm at r.t. and stirred for additional 4 h, after which time the solvent was removed in vacuo. The resulting solid was re-dissolved in CH_2Cl_2 and layered with diethyl ether, causing the formation an orange microcrystalline powder, identified as the protonated complex **6ab** (0.080 g, 70%). IR(CH_2Cl_2) ν_{max} (cm^{-1}): 2078s, 2036s, 1995s (CO); δ_H (CD_2Cl_2): 7.90 (2H, H_{ortho}, d, $J_{HH} = 5$ Hz), 7.75–7.43 (15H, m, PPh_3), 7.33 (2H, H_{meta}, d, $J_{HH} = 5$ Hz), 5.47 (5H, s, Cp), 5.00 (5H, s, Cp); δ_C (CD_2Cl_2): 216.5 (CO, d, $J_{CP} = 28$ Hz), 209.6 (CO), 158.2 (C_t) 138.4 (C*ipso*-C_t) 135.1 (CN), 134.5–129.2 (PPh_3), 131.9 (C_{meta}), 127.2 (C_{ortho}), 114.6 (C*ipso*-CN), 87.5 (Cp), 85.9 (Cp). Anal. Calc. for $C_{41}H_{30}N_5O_9Fe_2F_6PS_2$. C, 46.56; H, 2.86; N, 6.62. Found: C, 46.6; H, 2.90; N, 6.8%.

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