Interannular Conjugation in New Iron(II) 5-Aryl Tetrazolate Complexes

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The synthesis of new Fe(II) 5-aryl tetrazolate complexes [CpFe(CO)(L)($N_4C-C_6H_4-CN$)] (**4**) [L = CO (**4a**); PPh_3 (**4b**); $P(OCH_3)_3$ (**4c**); CN-2,6-$Me_2C_6H_3$ (**4d**)] is described. The target compounds were obtained by addition of sodium azide to the parent 1,4-dicyanobenzene complexes [CpFe(CO)(L)($NC-C_6H_4-CN$)][O_3SCF_3] (**2a**−**d**). X-ray molecular structure of **4c** confirms the predictions based on NMR (^1H, ^{13}C) studies concerning the coplanarity between the tetrazole and phenyl rings, with consequent interannular conjugation effect. The multidentate nature of the tetrazole ring involves the presence of different sites that can undergo electrophilic attack; reaction of complexes **4a**−**c** with methyl triflate afforded the methylated cationic complexes [CpFe(CO)(L)($CH_3-N_4C-C_6H_4-CN$)][O_3SCF_3], **5a**−**c**, whose ^1H and ^{13}C NMR spectroscopy data suggested out-of-plane rotation of the phenyl ring and subsequent large reduction of interannular conjugation. Noteworthy, the same effect was obtained in a reversible way by addition of triflic acid to **4a**, affording the protonated cationic complex [CpFe(CO)$_2$($H-N_4C-C_6H_4-CN$)][O_3SCF_3], **6a**, which was easily converted into its neutral precursor by treatment with a base.

Introduction

Dinuclear and polynuclear metal complexes bridged by polydentate ligands have received great attention in recent years in connection with the design of molecular electronic devices. In particular, dinuclear complexes bridged by conjugated ligands have been extensively studied because they can have interesting NLO applications[1] or behave as molecular wires[2] or molecular switches.[3] Dinuclear complexes of the type [(η^5-C_5H_5)-Ru(PPh_3)$_2$(μ-CN)Ru(NH_3)$_5$]$^{3+}$, in which the cyanide ion exhibits its "end-on" coordination ability, have been reported to exhibit a large second-order response.[1c] Since the asymmetry of the bridging cyanide ligand seems to play a key role in these processes,[4] we have recently synthesized[5] numerous pairs of isomeric complexes such as CpL(CO)Fe−CN−M(CO)$_5$ and CpL(CO)Fe−NC−M(CO)$_5$ (M = Cr, Mo, W) (L = CO; PPh_3) with the aim to study the different spectroscopic properties of the two metal fragments, C- or N-coordinated to the cyanide. As an extension of these studies, we considered 1,4-dicyanobenzene as a suitable bridging ligand and obtained mononuclear LnM(NCC_6H_4CN) and, in lower yields, dinuclear complexes LnM($NC-C_6H_4-CN$)MLn. Focusing our attention on the study of the behavior of the coordinated nitrile, we have observed its transformation into a tetrazole ring by reaction with NaN_3. In this paper we report the synthesis of mononuclear iron(II) complexes bearing 1,4-dicyanobenzene and their transformation into the corresponding 5-aryl tetrazolate complexes LnM($N_4CC_6H_4CN$). Furthermore we discuss the conjugative properties of the obtained 5-aryl tetrazolate ligand, the modifications of its geometry, and electronic properties upon addition of electrophilic species. The obtained results indicate this ambidentate anionic species [$N_4C-C_6H_4-CN$]$^-$ as a suitable ligand for the synthesis of dinuclear bridged complexes, which will be the topic of the next paper.

Discussion

Cationic complexes such as [CpFe(CO)(L)(THF)][O_3SCF_3] (**1**) [L = CO (**a**), PPh_3 (**b**), $P(OCH_3)_3$ (**c**), CN-2,6-$Me_2C_6H_3$ (**d**)] react slowly, at room temperature, with a slight excess of 1,4-dicyanobenzene to afford the relative nitrile compounds (Scheme 1). In these preparative conditions prevalent formation of mononuclear complexes [CpFe(CO)(L)(NCC_6H_4CN)]$^+$ (**2**) [L = CO (**a**), PPh_3 (**b**), $P(OCH_3)_3$ (**c**), CN-2,6-$Me_2C_6H_3$ (**d**)] is observed, even with different stoichiometric ratios of the starting reagents. Small amounts of dinuclear complexes [Cp(CO)(L)Fe(NCC_6H_4CN)Fe(L)(CO)Cp]$^{2+}$ (**3**) [L = CO (**a**), PPh_3 (**b**), $P(OCH_3)_3$ (**c**)] are also recovered by chromatography on an alumina column. Compounds **2**

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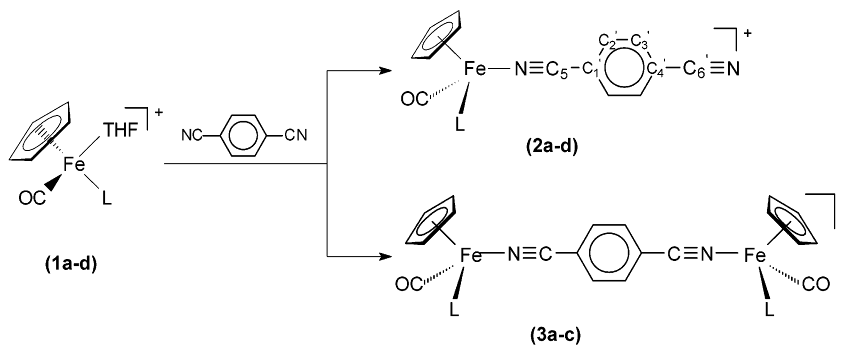
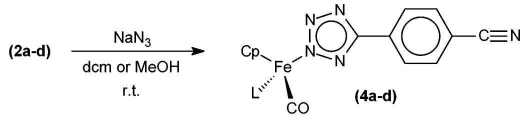
Scheme 1



L= CO (**a**); PPh_3 (**b**); $P(OMe)_3$ (**c**); CN-2,6-$Me_2C_6H_3$ (**d**)

can be distinguished from **3** because they exhibit two well-separated infrared weak absorption of the CN stretching at ca. 2255 cm^{-1} for the coordinated cyanide group and ca. 2235 cm^{-1} for the end one in CH_2Cl_2.

Compounds **2a**−**d** react in methanol with a slight excess of NaN_3 at room temperature in a few hours, to give the corresponding neutral tetrazolate derivatives $[CpFe(CO)(L)(N_4C-C_6H_4-CN)]$ [L = CO (**4a**), $P(C_6H_5)_3$ (**4b**), $P(OCH_3)_3$ (**4c**), CN-2,6-$Me_2C_6H_3$ (**4d**)]. These complexes can be easily purified by chromatography and have been well characterized by IR and ^1H and ^{13}C NMR spectroscopy.



(1)

L = CO (**a**); PPh_3 (**b**); $P(OMe)_3$ (**c**); CN-2,6-Me_2-C_6H_3 (**d**)

Recently, synthetic methodologies for the preparation of 5-substituted tetrazoles have received great attention, since it has been demonstrated that the tetrazole functionality, which is metabolically stable and with a pK_a similar to that of carboxylic acids, can replace the −COOH group in drug preparations, causing better oral bioavailability and cell penetration.[6a−c] Typically, tetrazoles are prepared from the corresponding nitriles by reaction with a hydrazoic source (e.g., sodium azide and ammonium chloride) in high-boiling solvents such as DMF,[7a] toluene,[7b] or water[7c] at high temperature (90−120 °C) and, generally, in the presence of Lewis acids as activating agents. These synthetic routes could involve evolution of hydrazoic acid, which is known to be highly toxic, extremely explosive, and volatile. Alternative strategies, involving different azide anion sources such as trimethylsilyl azide in the presence of dialkyltin oxide,[8] have been developed and promising results obtained for the conversion of amides into 1,5-disubstituted tetrazoles.[9,10] Many of these methods generally require high-boiling solvents (toluene or acetonitrile) and prolonged reaction times (even 72 h). Our reaction proceeds quickly at room temperature without the presence of any other activating agent and occurs under approximately heterogeneous conditions, the solubility of NaN_3 in methanol being very low. In a different approach, nitrile complexes **2a**−**c** are dissolved in CH_2Cl_2 and solid NaN_3 is successively added at room temperature. In both cases (using methanol or dichloromethane) complexes **4a**−**d** are obtained in good yields. The cyclization mechanism probably involves nucleophilic attack of the azide anion to the carbon of the coordinated nitrile, affording tetrazole derivatives even in the presence of coordinated isocyanides and carbonyl groups, as observed in the reaction (performed in the same conditions as complexes **2a**−**c**) of $[CpFe(CO)(CN\text{-}2,6\text{-}Me_2C_6H_3)(NCC_6H_4CN)]^+$ (**2d**) with sodium azide, in which the N-coordinated tetrazole derivative $[CpFe(CO)(CN\text{-}2,6\text{-}Me_2C_6H_3)(N_4CC_6H_4CN)]$ (**4d**) was obtained. In these conditions high chemoselectivity is observed and no traces of isocyanato complexes such as $[CpFe(CO)_2(NCO)]$, whose preparation under similar conditions was reported,[11a,b] have been detected. It is also worthy of note, relative to complexes **2a**−**e**, the high activation to nucleophilic attack exhibited by the carbon atom of the coordinated nitrile. The reaction however proceeds only in the presence of electron-withdrawing groups in the *para* phenyl position of the nitrile ligand; no reaction was observed between the benzonitrile derivative $[CpFe(CO)_2(NCC_6H_5)]^+$ and NaN_3, whereas the 4-nitrobenzonitrile complex $[CpFe(CO)(P(OCH_3)_3)(NCC_6H_4NO_2)]^+$ (**2e**) easily afforded the corresponding tetrazole derivative $[CpFe(CO)(P(OCH_3)_3)(N_4CC_6H_4NO_2)]$ (**4e**). It is well known[12a−c,13] that tetrazolate complexes are prepared by reaction of azido d^8 complexes with nitriles or isonitriles in which the intramolecular cycloaddition reaction involves the formation of an intermediate species possessing azide and nitrile

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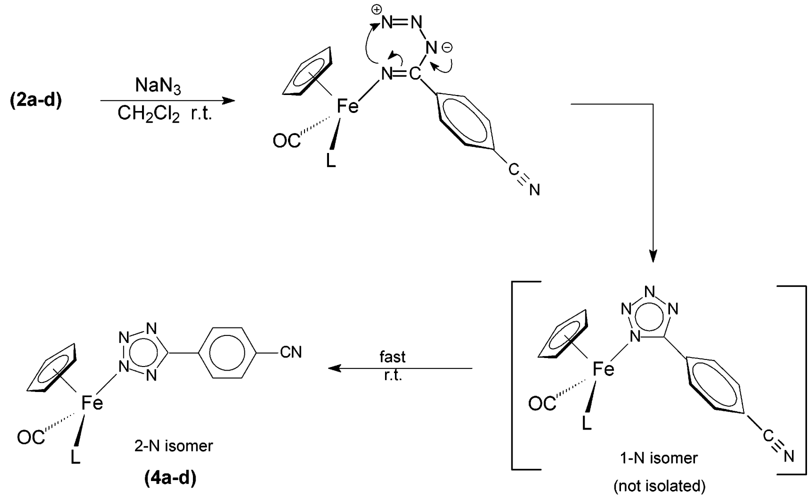
Scheme 2

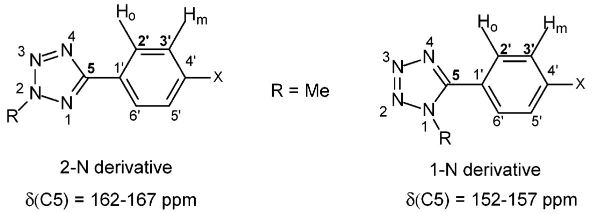


L= CO (**a**); PPh_3 (**b**); $P(OMe)_3$ (**c**); CN-2,6-$Me_2C_6H_3$ (**d**)

groups simultaneously coordinated. The iron atom of complexes **2a**−**e** is coordinatively saturated; consequently an intermolecular mechanism, with direct nucleophilic attack of the azide anion on the carbon at the carbon of the coordinated nitrile, is preferred. An analogous behavior was reported by Purcell[14] and Jackson,[15] but in those cases the cyclization reaction of nitrile complexes with sodium azide occurred in aqueous media, affording N-1 or N-2 tetrazole-coordinated Co(III) complexes. Tetrazolate complexes have also been prepared by anionic metatheses of organometallic moieties with tetrazolate salts in relative high yields.[16] Some recent examples of supramolecular structures having tetrazole rings, in which each of the four ring nitrogens can act as a coordination site, were reported.[17a−c] In our case nucleophilic attack of azide anion at the carbon of the coordinated nitrile and successive cycloaddition reaction should afford 1-N tetrazolate complexes. ^1H and ^{13}C NMR spectroscopic data however show formation of the less hindered 2-N derivatives (Scheme 2).

The isomerization reaction of 1-N tetrazolate complexes in 2-N derivatives has been studied in the case of tetrazolate complexes of cobalt(III),[14,15,18] whose rate of transformation was slow enough to be monitored by spectrophotometric techniques. In our case we had no evidence of the presence of the kinetic intermediate, probably very labile because of the relevant bulkiness of the metallic fragment. Indeed, ^{13}C chemical shift values ($\delta C_5 \approx 165$ ppm) of the tetrazole carbon clearly indicate that in the synthesized compounds the metal atom is bound to the 2-N tetrazole. As reported by Butler,[19a] the chemical shift of C_5 tetrazole has been assumed as a probe to distinguish 1-N ($\delta C_5 = 152-157$ ppm) from 2-N ($\delta C_5 = 162-167$ ppm) derivatives in an isomeric series of organic 5-aryltetrazoles (Scheme 3).

Scheme 3



The hindrance of the substituents in 1-N isomers causes out-of-plane rotation of the tetrazole ring with respect to the phenyl ring resulting in reduced interannular conjugation, which is, on the contrary, present in the 2-N isomers and is increased by the presence of electron-withdrawing groups on the phenyl ring. Interannular conjugation makes *ortho* (relative to tetrazole group, see Scheme 4) phenyl protons deshielded and *meta* and *para* protons shielded in the 2-N isomer relative to the 1-N isomer, resulting in a larger separation between the chemical shifts of *ortho* and *meta* protons. The same indications are given by ^{13}C NMR data; it has been assumed that large differences between $\delta C_3'$ and $\delta C_2'$, in the range 2.9−3.7 ppm, involve interannular conjugation.[19a−c] All these features were observed in the complexes prepared by us, confirming the formation of a conjugated 5-aryltetrazolate moiety (see Table 1).

All spectra present a large difference between the phenyl proton chemical shifts, for example, relative to complex **4a**, $\Delta\delta_H(H_0-H_m) = 0.49$ ppm and $\Delta\delta_C(C_3'-C_2') = 5.7$ ppm. Such a large separation of δ_C values, not observed in organic tetrazole derivatives, could indicate a strong interannular conjugation with the participation in the delocalized system of the d-electrons of the metal atom. The presence of a non-negligible back-bonding interaction to the tetrazolate ligand is also inferred by the analysis of the IR data (see Table 1), which show carbonyl bands at high wavenumbers, 2065 and 2020 cm^{-1} in CH_2Cl_2, in **4a**, with respect to parent compounds such as $[CpFe(CO)_2X]$. These values can be compared,

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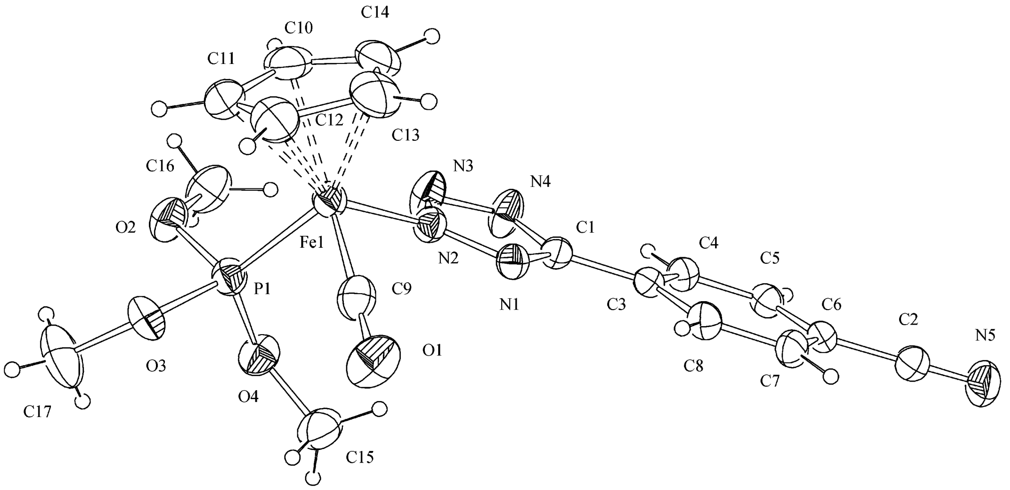
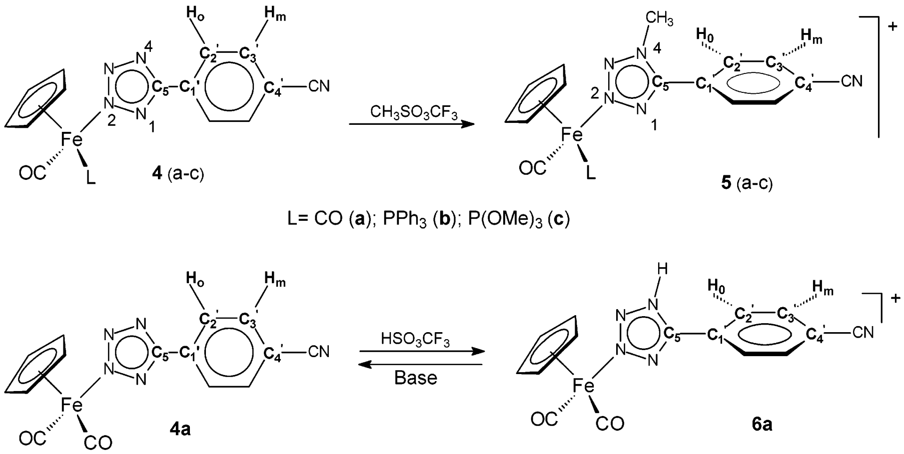


Figure 1. ORTEP plot of the molecular structure of **4c**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 4



L= CO (**a**); PPh3 (**b**); P(OMe)3 (**c**)

Table 1. Selected NMR[a] and IR[b] Data of Complexes 4a−d and 5a−c (for numbering scheme see Scheme 3)

entry	$\delta(C_5)$ (ppm)	$\Delta(\delta H_o - \delta H_m)$ (ppm)	$\Delta(\delta C_3' - \delta C_2')$ (ppm)	CO absorption (cm^{-1})
4a	165.1	0.48	5.67	2065; 2020
5a	157.2	0.07	2.69	2074; 2029
4b	164.4	0.30	5.71	1973
5b	156.1	0.16	3.09	1987
4c	164.2	0.49	5.79	1985
5c	156.4	0.13	2.68	1999
4d	164.4	0.49		2004

[a] ^1H and ^{13}C NMR experiments were performed using $CDCl_3$ as solvent. [b] CH_2Cl_2 as solvent.

in the same solvent, with the ones relative to cationic species such as $[CpFe(CO)_2(THF)]^+$ (2067 and 2024 cm^{-1}) or neutral $[CpFe(CO)_2(CN)]$ (2054 and 2014 cm^{-1}) and $[CpFe(CO)_2(CNW(CO)_5)]$ (2064 and 2024 cm^{-1}).[5] π-electron delocalization between the tetrazole and phenyl rings, as evidenced by NMR data, requires coplanarity, and evidence for this has been looked for in an X-ray diffraction study on the complex $[CpFe(CO)(P(OCH_3)_3(N_4CC_6H_4CN)]$ (**4c**). The molecular stereogeometry, Figure 1, shows the expected structure, with the iron atom exhibiting a pseudotetrahedral asymmetric coordination. The crystal is centric and therefore contains the racemic mixture. The *p*-cyanophenyltetrazolate ligand is coordinated through N(2) and the Fe−N bond, 1.950(2) Å long, and is indicative of a substantially σ character, especially if compared to the Fe−C (carbonyl) interaction, 1.758(3) Å.The presence of a π-bond

Table 2. Crystal Data and Experimental Details for $[CpFe(CO)(P(OCH_3)_3(N_4CC_6H_4CN)]$ (4c)

formula	$C_{17}H_{18}Fe_1N_5O_4P_1$
M	443.18
temperature, K	293(2)
wavelength, Å	0.71073
cryst symmetry	monoclinic
space group	$P2_1/c$
a, Å	7.6329(4)
b, Å	18.0130(8)
c, Å	14.7402(7)
α, deg	90
β, deg	98.927(2)
γ, deg	90
cell volume, Å^3	2002.1(2)
Z	4
D_c, Mg m^{-3}	1.470
μ(Mo Kα), mm^{-1}	0.866
F(000)	912
cryst size, mm	0.45 × 0.40 × 0.30
θ limits, deg	2.66−29.99
no. of reflns collected	24 324 ($\pm h, \pm k, \pm l$)
no. of unique obsd reflns $[F_o > 4\sigma(F_o)]$	5846
goodness of fit on F^2	0.795
$R_1(F)$,[a] $wR_2(F^2)$[b]	0.0369, 0.0811
weighting scheme	$a = 0.0457$, $b = 0.0000$[b]
largest diff peak and hole, e Å^{-3}	0.347 and −0.226

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4c

Fe(1)−P(1)	2.1499(7)	N(5)−C(2)	1.131(3)
Fe(1)−N(2)	1.950(2)	P(1)−O(2)	1.627(2)
Fe(1)−C(9)	1.758(3)	P(1)−O(3)	1.588(2)
C(1)−C(3)	1.466(3)	P(1)−O(4)	1.573(2)
C(2)−C(6)	1.446(3)		
C(9)−Fe(1)−N(2)	94.75(9)	N(2)−Fe(1)−P(1)	93.63(5)
C(9)−Fe(1)−P(1)	93.19(8)		

Table 4. Some C(tetrazole)−C(phenyl) Distances and Corresponding Interplanar Angles

	C−C (Å)	dihedral angle (deg)	ref
[CpFe(CO)(P(OMe)$_3$)(N$_4$C−4-CN−C$_6$H$_4$)]	1.467(2)	3.3(2)	this work
[Pd(N−N−S)(N$_4$C−4-OMeC$_6$H$_4$]	1.467(6)	10.4(8)	24
[Sn(n-Bu)$_3$(N$_4$C−4-py)(H$_2$O)]	1.468(9)	4.4(8)	17b
[Sn(Et)$_3$(N$_4$C−3-py)(H$_2$O)]	1.463(8)	9.4(7)	17b
[Sn(Et)$_3$(N$_4$C−4-py)]	1.465(7)	19.8(7)	17b

component in the Fe−N interaction can be postulated by comparison with other experimental values of Fe(II)−N(sp^2) distances, for example, a series of octahedral complexes containing borylated dioximate ligands in the equatorial plane and pyridines in the axial positions.[20] The Fe−N(dioxime) and Fe−N(pyridine) distances are found in the ranges 1.88−1.90 and 2.00−2.06(1) Å, respectively. The tetrazole ring is flat, with deviations from the average plane in the range +0.004, −0.003, and regular. In fact N−N and N−C distances are not distinguishable [range 1.319−1.338(2), average 1.329(3) Å]. The C(tetrazole)−C(phenyl) inter-ring distance is 1.467(2) Å, and the dihedral angle between the rings is 3.3(2)°. Also the phenyl ring does not exhibit measurable deviations from a regular geometry, despite being *para*-disubstituted [C−C distances in the range 1.373−1.388(3), average 1.380(3) Å]. The flat conformation of the ligand is indicative of inter-ring conjugation, but the C(tetrazole)−C(phenyl) distance does not seem to be significantly dependent on the inter-ring angle, as illustrated by the examples in Table 4.

The delocalization showed by 5-aryl tetrazole moiety in these mononuclear complexes led us to consider this ligand an ideal system to allow electronic communication between two metal atoms in dinuclear complexes having this ligand in a bridging bonding mode. Launay et al. reported an example[21] of a dinuclear complex having 4-cyanophenylimidazole as bridging ligand, in which the end-to-end $Ru^{2+} \rightarrow Ru^{3+}$ electron transfer across this bridge can be transiently switched off by a very short flash of light that makes the coplanar phenyl and imidazolyl rings twisted. In our case the 4-cyanophenyltetrazolate anion, NC−C$_6$H$_4$−CN$_4^-$, being capable of pluricentric interactions with all the ring nitrogen atoms, could represent a more versatile ligand with respect to 4-cyanophenylimidazole; thus we considered very interesting to investigate the possibility of removing interannular conjugation by addition of electrophilic species to the nitrogen atoms of the tetrazole ring. We supposed the ring nitrogen in position 4 of the ring, which suffers less from the steric encumbrance of the metal fragment, as the most accessible to electrophilic addition. In this case a significant rotation of the tetrazole ring out of the plane of the phenyl ring should be observed. Reaction of complexes [CpFe(CO)(L)(N$_4$CC$_6$H$_4$CN)] (**4a**, **4b**, **4c**) with CH$_3$O$_3$SCF$_3$ afforded the methylated cationic complexes [CpFe(CO)(L)(CH$_3$N$_4$CC$_6$H$_4$CN)][O$_3$SCF$_3$] (**5a**, **5b**, **5c**), in which the addition of the methyl group occurred at 4-N (see Scheme 4).[22] This feature was evidenced by the upfield shift of δC_5, which falls at about 157−159 ppm, as expected in tetrazoles having a substituent on the nitrogen adjacent to the tetrazole carbon.[23a]

Appreciable chemical shift variations are also observed in ^{1}H NMR spectra, in which the separation of the phenyl proton signals becomes significantly smaller. For example, the difference of 0.48 ppm between the two phenyl signals in [CpFe(CO)$_2$(N$_4$CC$_6$H$_4$CN)] (**4a**) becomes 0.07 ppm in the methylated compound [CpFe(CO)$_2$(CH$_3$N$_4$CC$_6$H$_4$CN)][O$_3$SCF$_3$] (**5a**); analogous behavior is observed in the phosphine derivatives (**5b**, **5c**). Furthermore, the difference between the chemical shift of the phenyl C_2' and C_3' is reduced in the cationic methylated complex ($\Delta = 2.69$ ppm in **5a**) with respect to the starting neutral derivative ($\Delta = 5.67$ ppm in **4a**). All these data strongly support removal of interannular conjugation due to out-of-plane rotation of the tetrazole ring in the methylated compounds **5a**−**c** (see Table 1). We have considered stimulating studying the effect of proton addition to this kind of complexes. Addition to tetrazolate complex **4a** of stoichiometric quantities of HO$_3$SCF$_3$ at low temperature has not resulted in decomplexation and formation of free organic tetrazole HN$_4$CC$_6$H$_4$CN. On the contrary, we have observed proton addition with formation of the cationic complex [CpFe(CO)$_2$(HN$_4$CC$_6$H$_4$CN)][O$_3$SCF$_3$] (**6a**, see Scheme 4), as shown by the shift of carbonyl absorptions to higher wavenumbers, 2078 and 2036 cm^{-1} versus 2065 and 2020 cm^{-1}, of the correspondent carbonyl bands of the starting neutral derivative (**4a**). Organic 5-aryl tetrazoles show a fast proton annular tautomerism; comparison of tetrazole carbon chemical shifts between 1-N methyl and 2-N methyl isomers has been used to monitor the relative percentage of the two isomers at equilibrium.[23b] In the protonated complex (**6a**) we have observed general and significant changes of the ^{13}C chemical shifts, in particular, an upfield shift of the tetrazole C$_5$ chemical shift, 159.5 ppm versus 165.1 ppm, of the neutral precursor (**4a**), indicating a preferential protonation of 4-N. We also note an upfield shift of C_1', the *ipso* phenyl carbon bonded to the tetrazole ring, $\Delta\delta = 6.7$ ppm, whereas the nitrile carbon is deshielded by 3.7 ppm. Moreover, we observe a significant decrease of the value of $\Delta(\delta C_3' - \delta C_2')$, even if smaller than that observed in the analogous methylated complex (**5a**). A smaller separation between the phenyl proton chemical shifts is also observed in the ^{1}H NMR spectra, $\Delta\delta = 0.152$ ppm in **6a** versus 0.478 ppm of the precursor **4a**. As evidenced before, these data indicate a preferential protonation of 4-N, suggesting partial out-of-plane rotation of the tetrazole ring with loss, or massive reduction,

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[20] Vernik, I.; Stynes, D. V. *Inorg. Chem.* **1996**, *35*, 6210.

[21] Hatzidimitriou, A.; Gourdon, A.; Devillers, J.; Launay, J. P.; Mena, E.; Amouyal, E. *Inorg. Chem.* **1996**, *35*, 2212.

[22] In some cases, addition of methyl iodide to Ru(II) tetrazolate complexes was reported to cause cleavage of an organometallic fragment. See: Chang, K. H.; Lin, Y. C.; Liu, Y. H.; Wang Y. *J. Chem. Soc., Dalton Trans.* **2001**, 3154.

[23] (a) Butler, R. N.; Garvin, V. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 390. (b) Butler, R. N.; Garvin, V. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 721.

of interannular conjugation. Noteworthy, this feature occurs by addition of electrophiles smaller than the methyl group and in a perfectly reversible way; indeed, addition of a base quantitatively re-forms the starting complex $[CpFe(CO)_2(N_4C-C_6H_4-CN)]$ (**4a**), in which tetrazole and phenyl rings are coplanar.

Conclusions

The synthesis of organometallic complexes having a 5-(4-cyanophenyl)tetrazolate ligand, by a simple and selective addition of the azide anion to the relative nitrile cationic complexes, represents an interesting route to the formation of a tetrazolate ring in which the transformation of the activated nitrile is carried out in very mild conditions. The NMR data and X-ray diffraction studies have established that in these complexes the metal is bonded to the 2-N atom of the tetrazole ring, for steric reasons. This feature involves coplanarity between the tetrazole and the phenyl ring and, consequently, a strong interannular conjugation, which can be removed by addition of electrophilic agents (CH_3^+ or H^+) to the nitrogen adjacent to the tetrazole carbon; moreover, the proton addition is reversible by addition of a base. The just described properties of this ligand could permit an efficient electronic communication between metal centers in dinuclear complexes. The reversible removal of this communication, by proton addition−elimination, should make these complexes good models of pH-dependent molecular switches. The synthesis of cyanophenyl tetrazole bridged dinuclear complexes and the description of their spectroscopic and electronic features will be reported in a successive paper.

Experimental Section

Materials and Procedures. All reactions with organometallic reagents or substrates were carried out under 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 (^1H, ^{13}C) were always recorded using a Varian Gemini 300 instrument (^1H, 300.1; ^{13}C, 75.5 MHz). The spectra were referenced internally to residual solvent resonance and were recorded at 298 K for characterization purposes. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. 1,4-Dicyanobenzene and 4-nitrobenzonitrile were purchased from Aldrich and used as received. Cationic precursors such as $[CpFe(CO)(L)(THF)]^+$ [L = CO (**1a**), PPh_3 (**1b**), $P(OMe)_3$ (**1c**), CN-2,6-$Me_2C_6H_3$ (**1d**)] were prepared from the corresponding iodides[25] by reaction with a stoichiometric amount of $Ag(CF_3SO_3)$ in a THF solution (15 mL) at room temperature. Filtration over Celite and subsequent evaporation to dryness afforded a mixture, which was used without any further purification. All reactions were monitored by IR spectroscopy. Petroleum ether (Etp) refers to a fraction of bp 60−80 °C. Typically, all chromatographies were performed on an alumina column (diameter 1.5 cm; height 15 cm) under argon atmosphere and using dichloromethane−acetonitrile mixtures as eluent.

Typical Procedure for the Preparation of 1,4-Dicyanobenzene Iron Complexes $[CpFe(CO)(L)(NCC_6H_4CN)][O_3SCF_3]$ [L = CO (2a), PPh_3 (2b), $P(OMe)_3$ (2c), CN-2,6-$Me_2C_6H_3$ (2d)]. A solution of the complexes **1a**−**d** (0.500 g) in CH_2Cl_2 was treated with a slight excess (1.1 equiv) of 1,4-dicyanobenzene. The mixture was stirred at rt for 12 h. Filtration over Celite and evaporation to dryness afforded a residue, which was purified by column chromatography on alumina using a dichloromethane−acetonitrile (5:1) mixture. The complexes **2a**−**d** were usually obtained as a second fraction after discharging starting reagents or the compound $[Fe_2Cp_2(CO)_4]$ in the case of **2a**. Atom labeling for complexes **2a**−**d** should be referred to Scheme 1. **2a:** Yield: 0.420 g, 72%, yellow oil. NMR: δ_H($CDCl_3$) 8.14 (2H, d, $^3J_{HH}$ = 15 Hz), 7.84 (2H, d, $^3J_{HH}$ = 15 Hz), and 5.68 (5H, s, Cp) ppm. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2235w (CN), 2079s (CO), 2038s (CO). Anal. Calcd for $C_{16}H_9N_2FeO_5SF_3$: C, 42.2; H, 1.98; N, 6.16. Found: C, 42.5; H, 2.01; N,6.2. **2b:** Yield: 0.200 g, 37%, orange oil. NMR: δ_H ($CDCl_3$) 7.6−7.2 (19H, m, PPh_3, C_6H_4), 5.05 (5H, s, Cp) ppm; δ_C ($CDCl_3$) 216.68 (CO, d, $^3J_{CP}$ = 28 Hz), 133.86 (PPh_3, d), 132.23 (PPh_3, s), 132.7 (PPh_3, s), 130.1 (PPh_3, d), 134.6 ($C_{3'}$), 133.0 ($C_{2'}$), 134.5 ($C_{1'}$), 117.8−117.7 ($C_{5'}-C_{6'}$), 115. 5 ($C_{4'}$), 86.3 (Cp). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2254w (CN coord.), 2236w (CN), 1993s (CO). Anal. Calcd for $C_{33}H_{24}N_2FeO_4PSF_3$: C, 57.5; H, 3.49; N, 4.06. Found: C, 57.3; H, 3.40; N, 3.9. **2c:** Yield: 0.190 g, 40%, orange oil. NMR: δ_H ($CDCl_3$) 7.95 (2H, d, $^3J_{HH}$ = 8 Hz), 7.78 (2H, d, $^3J_{HH}$ = 8 Hz), 5.13 (5H, s, Cp), 3.81 (9H, $(OC\mathit{H}_3)_3$, d, $^3J_{HP}$ = 11 Hz); δ_C ($CDCl_3$) 214.0 (CO, d, $^3J_{CP}$ = 45 Hz), 134.6 ($C_{3'}$), 133.5 ($C_{2'}$), 133.7 ($C_{1'}$), 118.5−118.1 ($C_{5'}-C_{6'}$), 115.3 ($C_{4'}$), 85.0 (Cp), 54.44−54.38 ($O\mathit{C}H_3$, d, $^3J_{CP}$ = 5 Hz). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2254w (CN coord.), 2235w (CN), 2006s (CO). Anal. Calcd for $C_{18}H_{18}N_2FePO_7SF_3$: C, 39.3; H, 3.27; N, 5.1. Found: C, 39.2; H, 3.30; N, 5.4. **2d:** Yield: 0.310 g, 82%, yellow oil. NMR: δ_H ($CDCl_3$) 7.92 (2H, d, $^3J_{HH}$ = 9 Hz), 7.82 (2H, d, $^3J_{HH}$ = 6 Hz), 7.35−7.19 (m, 3H, $C_6\mathit{H}_3$-2,6 $(Me)_2$), 5.30 (5H, s, Cp), 2.48 (s, 6H, C_6H_3-2,6$(C\mathit{H}_3)_2$); δ_C ($CDCl_3$) 212.9 (CO), 162.9 ($C{\equiv}N-$), 136.1−129.0 (C_6H_4: C_6H_3-2,6-Me) 118.6 ($C_{1'}$), 117.8 ($C_{6'}$), 115.3 ($C_{4'}$), 85.5 (Cp), 19.3 (Me). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2258w (CN coord.), 2234w (CN), 2159s ($C{\equiv}N-$), 2027s (CO). Anal. Calcd for $C_{24}H_{18}N_3FeO_4SF_3$: C, 51.7; H, 3.23; N, 7.5. Found: C, 51.65; H, 3.20; N, 7.3. In the case of complexes **2a**−**c**, further elution with acetonitrile as eluent afforded small amounts of dinuclear derivatives **3a**−**c**, as shown by IR spectroscopy with single CN absorptions at ca. 2255 cm^{-1} and by ^1H NMR spectra ($CDCl_3$), in which a singlet in the region 7.40−8.10 ppm was observed.

Preparation of $[CpFe(CO)(L)(NCC_6H_4NO_2)][O_3SCF_3]$ (2e) [L = $P(OMe_3)_3$]. This complex was prepared in the same way as shown for compounds **2a**−**d**, using 4-nitrobenzonitrile in place of terephthalonitrile and yielding 0.164 g, 71%, of **2e** as a yellow oil. NMR: δ_H ($CDCl_3$) 8.31 (br, 2H), 8.10 (br, 2H), 5.18 (s, 5H, Cp), 3.76 (br, 9H, Me). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2255w (CN coord.), 2003s (CO), 1521s (NO_2). Anal. Calcd for $C_{17}H_{18}N_2FePO_9SF_3$: C, 35.8; H, 3.15; N, 4.9. Found: C, 35.7; H, 3.13; N, 5.1.

Cyclization Reactions: Synthesis of $[CpFe(CO)(L)(N_4CC_6H_4CN)]$ [L = CO (4a), PPh_3 (4b), $P(OMe)_3$ (4c), CN-2,6-$Me_2C_6H_3$ (4d)]. Numbering of complexes **4a**−**d** should be referred to Scheme 3. **4a**: To a solution of **2a** (0.500 g, 1.10 mmol) in dichloromethane (20 mL) at room temperature was added an excess of NaN_3 (0.210 g, 3.20 mmol). The resulting suspension was stirred at rt for 10 h. The mixture was filtered on Celite and evaporated to dryness. Subsequent chromatography of the residue on Al_2O_3 with CH_2Cl_2 as eluent gave, only in this case, a first red fraction of $[Fe_2Cp_2(CO)_4]$, which was discharged. Further elution with a mixture $CH_2Cl_2-CH_3CN$ (2:1, v/v) afforded the complex **4a** (0.291 g, 76%), obtained as a yellow microcrystalline powder. NMR: δ_H($CDCl_3$) 8.17 ($2H_{ortho}$, d, $^3J_{HH}$ = 8 Hz), 7.70 ($2H_{meta}$, d, $^3J_{HH}$ = 8 Hz), 5.29 (5H, s, Cp), δ_C($CDCl_3$) 211.2 (CO), 165.1 (C_5), 134.4 ($C_{1'}$), 133.0 ($C_{3'}$), 127.3 ($C_{2'}$), 119.5 (CN), 112.4 ($C_{4'}$), 86.5 (Cp). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2230w (CN), 2065s (CO), 2020s (CO), 1615w ($C{=}N$). Anal. Calcd for $C_{15}H_9N_5FeO_2$: C, 51.8; H, 2.59; N, 20.1.

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(25) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38.

Found: C, 51.7; H, 2.60; N, 20.4. **4b**: This complex was prepared as **4a**, using methanol as solvent. Complex **4b** (0.223 g, 55%) was obtained as a red microcristalline powder by chromatography on alumina eluting with a $CH_2Cl_2-CH_3CN$ (5:1, v/v) mixture. NMR: δ_H ($CDCl_3$) 7.91 ($2H_{ortho}$, d, $^3J_{HH} = 7$ Hz), 7.61 ($2H_{meta}$, d, $^3J_{HH} = 7$ Hz), 7.49−7.28 (PPh_3, m), 4.71 (5H, s, Cp); δ_C ($CDCl_3$) 219.6 (CO, d, $^3J_{CP} = 28$ Hz), 164.4 (C_5), 133.7 (PPh_3, d), 133.3 (PPh_3, s), 130.9 (PPh_3, s), 128.8 (PPh_3, d), 132.6 (C_3'), 126.9 (C_2'), 134.7 (C_1'), 111.6 (C_4'), 119.5 (CN), 84.5 (Cp). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2229w (CN), 1973s (CO), 1615w (C=N). Anal. Calcd for $C_{32}H_{24}N_5FeO$: C, 69.8; H, 4.36; N, 12.7. Found: C, 69.9; H, 4.40; N, 13.0. **4c**: The same procedure as **4a** was adopted, using methanol (15 mL) as solvent. The product was obtained (0.209 g, 52%) eluting with a $CH_2Cl_2-CH_3CN$ (5:1, v/v) mixture and was successfully recrystallized from a dichloromethane solution layered with petroleum ether at rt, affording red crystals of **4c**. NMR: δ_H ($CDCl_3$) 8.18 ($2H_{ortho}$, d, $^3J_{HH} = 8$ Hz), 7.69 ($2H_{meta}$, d, $^3J_{HH} = 8$ Hz), 4.91 (5H, s, Cp), 3.63 (9H, $(OCH_3)_3$, d, $^3J_{HP} = 11$ Hz); δ_C ($CDCl_3$) 217.8 (CO, d, $^3J_{CP} = 45$ Hz), 164.2 (C_5), 132.7 (C_3'), 126.9 (C_2'), 134.6 (C_1'), 111.7 (C_4'), 119.3 (CN), 83.9 (Cp), 53.1 (OCH_3, d, $^3J_{CP} = 5$ Hz). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2229w (CN), 1985s (CO), 1616w (C=N). Anal. Calcd for $C_{17}H_{18}N_5FePO_4$: C, 46.0; H, 4.06; N, 15.8. Found: C, 46.1; H, 4.10; N, 15.5. **4d**: A workup analogous with that for complexes **4a**−**c** afforded a mixture, which was chromatographed on an alumina column. Elution with a $CH_2Cl_2-CH_3CN$ (1:1, v/v) mixture gave the product **4d** as a yellow oil (0.260 g, 64%). NMR: δ_H ($CDCl_3$) 8.16 ($2H_{ortho}$, d, $^3J_{HH} = 9$ Hz), 7.67 ($2H_{meta}$, d, $^3J_{HH} = 6$ Hz), 7.26−7.11 (m, 3H, C_6H_3-2,6$(CH_3)_2$), 5.08 (s, 5H, Cp), 2.39 (s, 6H, C_6H_3-2,6$(CH_3)_2$); δ_C ($CDCl_3$) 215.8 (CO), 170.5 ($C\equiv N-$), 164.4 (C_5), 135.2−126.9 (C_6H_4: C_6H_3-2,6-Me), 119.4 ($-C\equiv N$), 111.8 (C_4'), 84.26 (Cp), 18.9 (C_6H_3-2,6-*Me*). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2229w (CN), 2148s ($C\equiv N-$), 2004 s (CO), 1615w (C=N). Anal. Calcd for $C_{23}H_{18}N_6FeO$: C, 61.3; H, 4.0; N, 18.7. Found: C, 61.2; H, 3.95; N, 19.0.

Synthesis of [CpFe(CO)(L)($N_4CC_6H_4NO_2$)] (4e) [L = P(OMe)$_3$]. A 0.164 g (0.29 mmol) sample of **2e**, dissolved in CH_3OH (15 mL), was treated with an excess of NaN_3 (100 mg, 1.54 mmol) for 10 h at room temperature. Following the same procedure as for complexes **2a**−**d**, the product **4e** was obtained by chromatography on an alumina column eluting with a $CH_2Cl_2-CH_3CN$ (5:1, v/v) mixture and yielding 97 mg, 72%, of the complex **4e** as a dark yellow microcrystalline powder. NMR: δ_H ($CDCl_3$) 8.29 ($2H_{ortho}$, d, $^3J_{HH} = 9$ Hz), 8.27 ($2H_{meta}$, d, $^3J_{HH} = 7$ Hz), 4.94 (s, 5H, Cp) 3.67 (d, 9H, $(OCH_3)_3$, $^3J_{HP} = 11$ Hz); δ_C ($CDCl_3$) 218.0 (d, CO, $^3J_{CP} = 45$ Hz), 164.3 (C_5), 148.1 (C_4'), 136.7 (C_1'), 127.4 (C_3'), 124.6 (C_2'), 84.2 (Cp), 53.5 (d, OCH_3, $^3J_{CP} = 5$ Hz). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1985s (CO), 1606w (−C=N−), 1521s (NO_2). Anal. Calcd for $C_{16}H_{18}N_5FePO_6$: C, 41.4; H, 3.89; N, 15.1. Found: C, 41.5; H, 3.91; N, 15.3.

Methylation Reactions: Synthesis of [CpFe(CO)(L)(4-MeN$_4$C−C_6H_4−CN)][O_3SCF_3] [L = CO (5a), PPh$_3$ (5b), P(OMe)$_3$ (5c)]. Numbering for complexes **5a**−**c** is shown in Scheme 4. **5a**: A solution of **4a** (0.101 g, 0.29 mmol) in CH_2Cl_2 was treated with $CH_3O_3SCF_3$ (0.033 mL, 0.29 mmol) with stirring at −50 °C for 30 min. The mixture was then allowed to warm at rt and stirred for an additional 3 h. Evaporation of solvent and chromatography of the residue on an alumina column with CH_2Cl_2 as solvent afforded a first red fraction of [$Fe_2(Cp)_2(CO)_4$], which was discharged. Elution with a $CH_2Cl_2-CH_3CN$ (5:1, v/v) mixture gave the complex **5a** (98 mg, 67%), obtained as a pale brown oil. NMR: δ_H ($CDCl_3$) 7.94 ($2H_{ortho}$, d, $^3J_{HH} = 7$ Hz), 7.87 ($2H_{meta}$, d, $^3J_{HH} = 10$ Hz), 5.45 (5H, s, Cp), 4.20 (3H, s, CH_3); δ_C ($CDCl_3$) 209.5 (CO), 157.2 (C_5), 133.5 (C_3'), 130.8 (C_2'), 130.0 (C_1'), 126.3 (C_4'), 116.5 (CN), 87.5(Cp), 37.4 (CH_3). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2235w (CN), 2075s (CO), 2031s (CO). Anal. Calcd for $C_{17}H_{12}N_5FeO_5SF_3$: C, 39.9; H, 2.25; N, 13.7. Found: C, 40.0; H, 2.29; N, 14.0. Compounds **5b** [L = PPh_3] and **5c** [L = (P(OMe)$_3$)] were analogously prepared from **4b** and **4c**, respectively. In these cases no trace of undesired species arising from dimerization of cationic precursors was detected. **5b**: Yield: 0.131 g, 98%, dark red oil. NMR: δ_H ($CDCl_3$) 7.84 ($2H_{ortho}$, d, $^3J_{HH} = 10$ Hz), 7.67 ($2H_{meta}$, d, $^3J_{HH} = 10$ Hz), 7.49−7.28 (PPh_3, m), 4.89 (5H, s, Cp), 3.91 (3H, s, CH_3); δ_C ($CDCl_3$) 217.7 (CO, d, $^3J_{CP} = 28$ Hz), 156.1 (C_5), 133.8 (PPh_3, d), 132.4 (PPh_3, d), 131.9 (PPh_3, s), 129.5 (PPh_3, d), 133.6 (C_3'), 130.5 (C_2'), 126.3 (C_1'), 118.3 (C_4'), 116.3 (CN), 85.2 (Cp), 37.0 (N−CH_3). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2235w (CN), 1987s (CO). Anal. Calcd for $C_{34}H_{27}N_5FePO_4SF_3$: C, 54.7; H, 3.62; N, 9.4. Found: C, 54.9; H, 3.67; N, 9.6. **5c**: Yield: 0.133 g, 97%, orange oil. NMR: δ_H ($CDCl_3$) 7.95 ($2H_{ortho}$, d, $^3J_{HH} = 7$ Hz), 7.82 ($2H_{meta}$, d, $^3J_{HH} = 10$ Hz), 4.98 (5H, s, Cp), 4.19 (3H, s, CH_3), 3.70 (9H, $(OCH_3)_3$, d, $^3J_{HP} = 11$ Hz); δ_C ($CDCl_3$) 215.8 (CO, d, $^3J_{CP} = 44$ Hz), 156.4 (C_5), 133.5 (C_3'), 130.845 (C_2'), 126.4 (C_1'), 118.3 (C_4'), 116.2 (CN), 84.6 (Cp), 54.1 (OCH_3), 37.3 (N-CH_3). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2235w (CN), 1999s (CO). Anal. Calcd for $C_{19}H_{21}N_5FePO_7SF_3$: C, 37.5; H, 3.46; N, 11.5. Found: C, 37.6; H, 3.49; N, 11.8.

Preparation of Protonated Complex [CpFe(CO)(L)(4-HN$_4$C−C_6H_4−CN)] (6a) [O_3SCF_3] [L = CO]. Numbering for complex **6a** is shown in Scheme 4. To a stirred solution of **4a** (0.500 g, 1.44 mmol) in CH_2Cl_2 (20 mL) was added dropwise $HOSO_2CF_3$ (0.13 mL, 1.44 mmol, diluted in 5 mL of CH_2Cl_2) at −60 °C. After 30 min the mixture was allowed to warm at rt and the solvent removed in vacuo. The resulting mixture was redissolved in dichloromethane and layered with diethyl ether, causing the formation of yellow fine needles identified as the protonated complex **6a** (0.651 g, 91%). NMR: δ_H (CD_3CN) 8.14 ($2H_{ortho}$, d, $^3J_{HH} = 9$ Hz), 7.99 ($2H_{meta}$, d, $^3J_{HH} = 9$ Hz), 5.47 (5H, s, Cp); δ_C ($CDCl_3$) 209.5 (CO), 159.4 (C_5), 133.7 (C_3'), 128.7 (C_2'), 127.6 (C_1'), 118.5 (C_4'), 116.1 (CN), 86.9 (Cp). IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2235w (CN), 2078s (CO), 2036s (CO). Anal. Calcd for $C_{16}H_{10}N_5FeO_5SF_3$: C, 38.6; H, 2.01; N, 14.1. Found: C, 38.7; H, 1.99; N, 13.9. Addition of a stoichiometric amount of proton sponge to a solution of **6a** in acetonitrile re-forms quantitatively the neutral precursor **4a**.

X-ray Diffraction Experiments and Structure Determination of [CpFe(CO)P(OCH$_3$)$_3$)($N_4CC_6H_4CN$)] (4c). Crystal data and other experimental details for [CpFe(CO)(P(OCH$_3$)$_3$)($N_4CC_6H_4CN$)] are reported in Tables 2 and 3. The X-ray diffraction data were measured on a Bruker AXS SMART 2000 diffractometer, equipped with a CCD area detector, using Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Cell dimensions and orientation matrixes were initially determined from least-square refinements on reflections measured in three sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. Full spheres of the diffraction space were measured by 0.3° ω steps, 20 s exposures with a sample−detector distance kept at 5.0 cm. Intensity decay was monitored by re-collecting the initial 50 frames at the end of each data collection and analyzing the duplicate reflections. The collected frames were processed for integration by using the program SAINT, and an empirical absorption correction was applied using SADABS[26] on the basis of the Laue symmetry of the reciprocal space. The structure was solved by direct methods (SIR 97)[27] and subsequent Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXTL)[28] using anisotropic thermal parameters for all non hydrogen atoms. The three oxygen atoms of the phosphite ligand were found disordered over two sites, and an occupancy factor of 0.82 was refined for their main images. All hydrogen atoms except for the methyl H atoms were located experimentally, but their positions were

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idealized [C(sp^3)−H = 0.98, C(sp^2)−H = 0.93 Å] and refined riding the pertinent carbon atoms with isotropic thermal parameters, U(H) = 1.2U_{eq}(C) [U(H) = 1.5U_{eq}(C-Me)]. The final difference electron density map was featureless.

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Supporting Information Available: Further details of the structure determination of **4c**, including atomic coordinates, bond distances and angles, and thermal parameters. Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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