

Reactions of cyano-iron and -ruthenium compounds with *gem*-dicyano-epoxides. A new pathway to vinyl isocyanide complexes of iron and ruthenium†

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The cyano complexes $[M(CN)(cp)(dppe)]$ ($M = Fe$ or Ru , $cp = \eta-C_5H_5$, $dppe = Ph_2PCH_2CH_2PPh_2$) and the hydrogen isocyanide complex $[Fe(cp)(dppe)(CNH)]Br$ reacted with *gem*-dicyano and *gem*-cyano(ethoxycarbonyl) epoxides to give oxazol-2-yl and oxazolin-2-ylidene complexes, respectively. Treatment of the oxazol-2-yl complexes with alkyloxonium salts, $R_3O^+BF_4^-$ ($R = Me$ or Et), resulted in ring opening to give multifunctional vinyl isocyanide complexes. The complexes were characterized by mass and NMR spectral techniques; in addition, a single-crystal structure determination was carried out on a vinyl isocyanide complex.

Since our first paper in this Series² metal-stabilized hydrogen isocyanide has been successfully applied to syntheses of various functional and highly alkylated isocyanides and carbenoid heterocycles. Supplementary to the numerous additions to non-activated and activated CC double and triple bonds,^{3,4} heteroallenes,⁵ and small rings,^{2,6} surprisingly efficient three-(3CC) and four-component cycloadditions (4CC) of $[M']CNH$ ($[M'] = Cr(CO)_5$, $W(CO)_5$ or $[Fe(cp)(dppe)]$; $cp = \eta-C_5H_5$; $dppe = Ph_2PCH_2CH_2PPh_2$) with aldehydes or ketones, isocyanides, and, in case of 4CC, amines have been introduced recently.^{1,7} While the simplest reaction of the CNH species appears to be that with its conjugate base, a metal cyanide, leading to extremely strong and even symmetric H-atom bridges of the type $[(M')CN-H-NC(M')]^-$, its cluster chemistry as exemplified by $[Fe_2(CN)(cp)_2(CO)_3]^-$ gave rise to novel moieties, e.g. the doubly N-protonated cyanide in $[Fe_2(cp)_2(CO)_3(CNH_2)]^+$ or the tetraferrirozaallene ion $[{(OC)_3(cp)_2Fe_2}C=N=C\{Fe_2(cp)_2(CO)_3\}]^+$, product of a CN cleavage reaction under mild conditions.⁸⁻¹¹ The question of the existence of complexes with more than one CNH ligand was eventually answered by the X-ray structural assessment of Buff's 'ferrocyanethyl' of 1854 which revealed a homoleptic hexakis(hydrogen isocyanide)iron(2+) system containing six strong hydrogen bonds to six molecules of ethanol.¹²

We continue the early work with the reactions between the hydrogen isocyanide complexes $[M(cp)(dppe)(CNH)]Br$ and their conjugate bases $[M(CN)(cp)(dppe)]$ ($M = Fe$ or Ru) and *gem*-dicyano and -cyano(alkoxycarbonyl) epoxides described in this paper.

Results and Discussion

Oxazolin-2-ylidene (carbene) and oxazol-2-yl complexes

We had shown earlier that the hydrogen isocyanide complex $[Cr(CO)_5(CNH)]$ reacts with functionalized epoxides of the type **1a** or **1c** to give the respective oxazolin-2-ylidene complexes with a 4-aryl-5-cyano substitution pattern. In the case of **1b**,

however, the same reaction resulted in an open-chain 2-hydroxyalkyl isocyanide ligand.² While recording its ¹³C NMR spectrum, this obvious intermediate was later found to undergo a slow ring closure with elimination of HCN finally to afford the expected 4-aryl-5-ethoxycarbonyloxazolin-2-ylidene species.^{7,13}

With a view to extend this chemistry, we have now treated the epoxides **1a** and **1b** with $[Fe(cp)(dppe)(CNH)]Br$ and obtained the complex carbenoid heterocycles **1a** and **1b**. Bromide was chosen as counter anion because the more common BF_4^- salt had repeatedly caused complications. Thus, in several cases, the Lewis-acid adduct $[Fe(CNBF_3)(cp)(dppe)]$ in which cyanide is blocked has been isolated as a by-product or even as the only product.^{3,14} A more direct and convenient approach to cycloaddition products between cyanide and activated ('dielectrophilic'¹⁵) epoxides leading to carbanionic oxazol-2-yl complexes **2** and **3** starts from the cyano complexes $[M(CN)(cp)(dppe)]$ ($M = Fe$ or Ru). Both the cationic complexes **1a**, **1b** as well as the neutral compounds **2a**, **2c** and **3a**, **3c** are obtained in moderate to good yields. Note that **1a** and **2a** have been converted into each other by deprotonation and protonation, respectively, and that it is also possible to protonate **2c**, **3a** and **3c** (Scheme 1). Analytical and selected IR data for the yellow to orange products are summarized in Table 1.

The reaction pathway postulated in our earlier work, *i.e.* attack of the nucleophilic cyano nitrogen at the aryl-substituted carbon of the oxirane, ring opening and cyclization by intramolecular O(H) addition across the isocyano group with concomitant elimination of HCN, appears to be valid also in the present case.^{2,7} That the (hydrogen isocyanide)iron complex could be replaced by the corresponding cyano species without changing the basic reaction course shows that in contrast to mono- and di-alkylated oxiranes, O-protonation is not an indispensable prerequisite for nucleophilic attack with ring opening in the case of oxiranes with geminal electron-withdrawing substituents.

As already pointed out, there is a remarkable difference between the IR patterns of protonated (carbenoid) and deprotonated (carbanionic) N,O- or N,N-heterocycles in organometallic complexes. While for the former, the $\nu_{asym}(N\equiv C\equiv O)$ vibration mode gives rise to a strong and broad

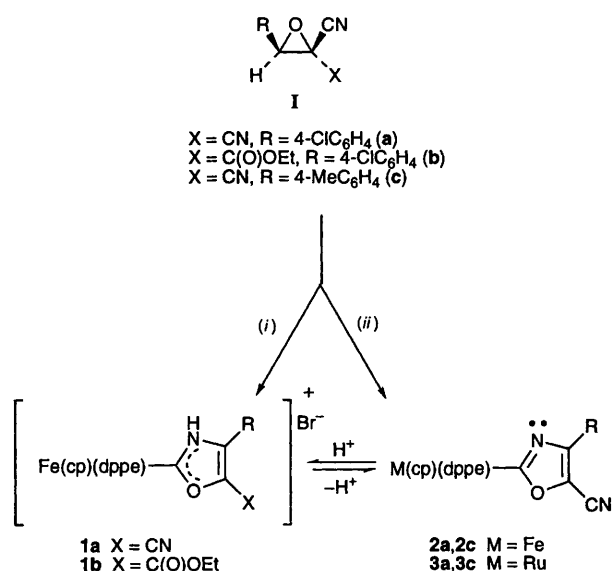
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‡ Chemistry of hydrogen isocyanide. Part 12.¹

Table 1 Analytical and IR data

Compound	Analysis (%) ^a			<i>M</i> ^{a,b}	M.p./°C	IR data (cm ⁻¹) ^c			
	C	H	N			<i>v</i> (CN)	<i>v</i> (MCNR)	<i>v</i> (C=C, N=C)	Other
1a	61.0 (61.25)	4.35 (4.25)	3.60 (3.50)		214	2190s		1579m	1480s [<i>v</i> (NCO)] 3400 (br) [<i>v</i> (NH)]
1b	60.4 (60.7)	4.70 (4.60)	2.00 (1.65)		202			1650m	1490s [<i>v</i> (NCO)], 3400 (br) [<i>v</i> (NH)], 1700s [<i>v</i> (CO ₂ Et)]
2a^d	67.0 (68.1)	4.95 (4.60)	3.65 (3.85)	722 (723)	178	2192s		1600w, 1580m, 1560w, 1540w, 1482s	
2c^e	71.45 (71.4)	5.30 (5.35)	4.30 (3.85)	702 (703)	183	2195s		1600w, 1578m, 1558w, 1482m	
3a^f	60.5 (59.15)	4.45 (4.15)	3.40 (3.30)	768 (768)	192	2192s		1603m, 1589m, 1503m, 1482m	
3c	66.7 (67.45)	5.20 (4.85)	3.45 (3.75)	748 (748)	205	2190s		1610w, 1590w, 1510m, 1480m	
4a	60.95 (61.15)	4.90 (4.40)	3.70 (3.40)	737 (738)	162	2208w	2045vs	1588m	
4a'^g	64.5 (64.5)	5.95 (5.00)	3.15 (3.00)	751 (751)	159	2206w	2050vs	1587m	
5a	55.95 (58.0)	4.80 (4.15)	3.15 (3.20)	783 (783)	184	2223w	2059vs	1586m	
5a'	58.0 (58.4)	6.55 (4.35)	3.40 (3.15)	797 (797)	187	2207w	2061vs	1589m	
5c	60.4 (60.8)	5.10 (4.65)	3.40 (3.30)	763 (763)	179	2220w	2062vs	1636m	

^a Calculated values are given in parentheses. ^b Mass spectrometrically determined; *M* denotes the molecular mass of the complex or of the complex cation, respectively. ^c In KBr. ^d + 1 CH₂Cl₂ (from ¹H NMR spectrum). ^e + ½ Me₂CO (¹H NMR spectrum). ^f + 1 Et₂O (¹H NMR spectrum). ^g + 1 C₆H₅Me (¹H NMR spectrum).



Scheme 1 (i) [Fe(cp)(dppe)(CNH)]⁺ Br⁻; (ii) [M(CN)(cp)(dppe)] (M = Fe or Ru)

band below 1500 cm⁻¹ which dominates the spectrum and is well separated from the feature assigned to the C=C stretching vibration, the deprotonated analogues only exhibit a set of equally weak to medium intensity bands in the aromatic (heteroaromatic) region thereby precluding any further assignment (Table 1). It is interesting that these observations correspond to the stereochemical findings from crystal structure analyses of a number of *carbenoid* imidazole and triazole complexes.¹⁶⁻¹⁸ Though formally 6π aromates, these C-co-ordinated heterocycles unanimously feature markedly different bond lengths reflecting the existence of two more or less localized π systems, the bis(heteroatom)-stabilized metal-carbene moiety and the transannular C-C double bond, tied together by relatively long (C-N) bonds. We have repeatedly drawn attention to this kind of 'metal activation of heterocycles' and were actually able to demonstrate its chemical consequence

recently.¹ On the other hand, no such deviation from the expected uniformity of bond distances has been reported for C-metallated *carbanionic* heterocycles which obviously retain their aromaticity. The positive-ion FAB mass spectra show the required parent peaks and, in most cases, one line corresponding to loss of the heterocyclic ligand.

The ¹H and ¹³C NMR data for the new compounds (Table 2) are in accord with the assumed structures. Thus, for the iron N,O-carbene complexes **1a** and **1b** the signals of the carbene carbon atoms (C²) appear at the expected low-field positions, *i.e.* much lower than those of the related imidazolin-2-ylidene (N,N'-carbene) species (δ ≈ 150), though not quite as low as C² in 4-amino-Δ³-oxazolin-2-ylidene complexes with their unprecedented π-electron delocalization along the O=C²-N²-C²-N^{exo} atomic sequence (δ > 250),^{1,19} while the signals of the C² atoms of the carbanionic heterocycles in **2a**, **2c** and **3a**, **3c** are shifted by some 15 (Fe) to 25 ppm (Ru) to higher fields. The triplet nature of these signals is a clear consequence of the presence of the two equivalent phosphorus atoms in the dppe ligand as is the virtual triplet of its ethylene bridge. The small range of δ 112-118 is characteristic for cyano-carbon resonances; the assignment of signals to the ring carbon atoms C⁴ (δ ≈ 140) and C⁵ (δ ≈ 120) was made by comparison with those of other oxazolin- and oxazolidin-2-ylidene complexes.²

Vinyl isocyanide complexes

Having learned that deprotonation and reprotonation of the carbenoid and carbanionic ligands in complexes **1** and **2**, **3** were clean, straightforward processes, we turned to N-alkylations of **2** and **3**. The intention was to generate potential sources of free carbenes, an objective which we had only recently achieved with an N-alkylated N,N' analogue from the 4-aminoimidazolin-2-ylidene pentacarbonylchromium family.²⁰ Very surprisingly, however, the yellow to orange powdery products which were recovered from dichloromethane solution after treatment of the oxazole complexes **2**, **3** with R'₃O⁺BF₄⁻ (R' = Me or Et) showed strong IR bands above 2000 cm⁻¹ instead of the characteristic carbene feature [*v*_{asym}(N²=C²=O)] around 1500 cm⁻¹. Obviously, ring opening to give the cationic vinyl

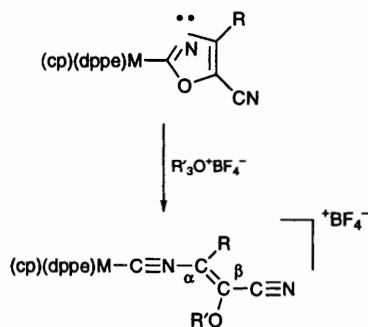
isocyanide complexes **4**, **5** had to be considered (Scheme 2) and, in fact, the purified compounds displayed the appropriate IR pattern with the four distinct stretching vibrations $\nu(\text{CN})$, $\nu(\text{MCNR}^+)$, $\nu(\text{C}=\text{C})$ and $\nu(\text{BF}_4^-)$ (Table 1). Again the mass spectra show the required parent peaks and a line corresponding to the loss of the vinyl isocyanide moiety (Table 3). In the ^{13}C NMR spectra the nitrile carbon atoms are assigned to signals between δ 112 and 118 while the isocyanide carbon appears as a triplet at about δ 190 (Fe) and 170 (Ru), respectively. Values between δ 120 and 130 for the vinylic carbon atoms compare well with the findings for other vinyl isocyanide metal complexes (Table 2).²¹

Though unexpected here and contrasting a wealth of N-deprotonation and -alkylation studies of saturated and unsaturated cyclic N,O- and N,N'-carbenes in metal complexes,^{22–24} ring-opening reactions of oxazoles have their precedents in organic and organometallic chemistry from which we can draw some (speculative) conclusions. Thus, deprotonation in the C² position of oxazoles and benzoxazoles with organolithium reagents represents an efficient route to ring-opened hydroxyisocyanides (Scheme 3).²⁵ The driving force of this reaction must certainly be attributed in parts to the high oxygenophilicity of Li^+ , but in parts also to the high electron density at the carbanionic C² removal of which is easiest by C–O cleavage. This picture also explains the observation of strong CN(isocyanide) bands in the IR spectrum after removal in a titrimetric study of 3 equivalents of acid (HCl) from the hexacarbene complex $[\text{Co}\{\text{CN}(\text{H})\text{CH}_2\text{CH}_2\text{O}\}_6]\text{Cl}_3$,²⁶ as it explains, e.g., the non-cyclization of 2-hydroxyisocyanides at electron-rich metal centres such as Cr^0 or W^0 in $[\text{M}(\text{CO})_5-$

$(\text{CNCH}_2\text{CH}_2\text{OH})]$ and Fe^{II} in $[\text{Fe}(\text{CNCH}_2\text{CH}_2\text{OH})_6]\text{[BF}_4\text{]}_2$.²⁷ A particularly illustrative example of a borderline case between cyclization and non-cyclization, i.e. sufficient and insufficient CN activation, respectively, is the recently reported cyclopentadienyliron complex which assembles all three forms of *o*-hydroxyphenyl isocyanide in its ligand sphere: the open-chain, the cyclic carbenoid and the cyclic carbanionic form.²⁸ A similarly delicate balance appears to be present in the case of **2**, **3** where the cp and dppe ligands contribute to a considerable overall electron density at the metal centre and through it at the attached C² carbon. It is conceivable that by O-alkylation we simply trap the ring-opened species which co-exists in small amounts with the respective heterocycle. Moreover, electron density on iron is more efficiently reduced by O- than by N-alkylation, for isocyanides are much better π acceptors than are N,O-carbenes. The effect of the ring substituents (aryl, CN) momentarily remains an open question; that they may have an important influence, however, is shown by the chemistry of the 5-oxooxazolin-2-yl platinum complex

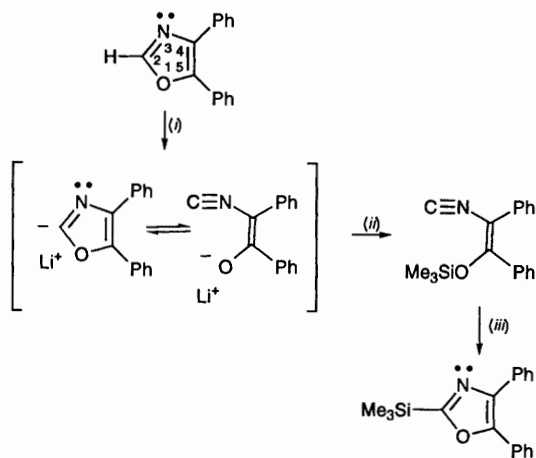
Table 2 Proton and ^{13}C NMR data

Compound	Proton and ^{13}C NMR data
1a	2.9 (m, 4 H, CH_2P), 4.8 (s, 5 H, cp), 7.2–7.8 (m, 24 H, Ph), 14.1 (s, 1 H, NH), 30.1 (t, CH_2P), 83.4 (s, cp), 108.5 (s, CN), 119.9 (s, C^5), 127.7–140.7 (m, Ph), 141.6 (s, C^4), 230.0 (t, C of carbene)
1b	1.1 (t, 3 H, Me), 2.8, 3.1 (m, 4 H, CH_2P), 4.75 (s, 5 H, cp), 7.15–7.75 (m, 24 H, Ph), 13.8 (s, 1 H, NH), 13.9 (s, Me), 29.9 (t, CH_2P), 60.55 (s, CH_2Me), 82.8 (s, cp), 121.1 (s, C^5), 121.0–139.9 (m, Ph), 138.0 (s, C^4), 155.5 (s, CO_2Et), 224.7 (t, C of carbene)
2a	2.5, 3.1 (m, 4 H, CH_2), 4.3 (s, 5 H, cp), 7.2–7.6 (m, 24 H, Ph), 29.5 (t, CH_2P), 80.9 (s, cp), 114.6 (s, CN), 121.0 (s, C^5), 127.5–147.5 (m, $\text{C}^4 + \text{Ph}$), 213.5 (t, C^2)
2c	2.28 (s, 3 H, Me), 2.5, 3.1 (m, 4 H, CH_2P), 4.28 (s, 5 H, cp), 7.22–7.6 (m, 24 H, Ph), 15.2 (s, Me), 29.4 (t, CH_2P), 80.9 (s, cp), 115.1 (s, CN), 120.2 (s, C^5), 127.0–143.3 (m, Ph), 148.8 (s, C^4), 212.7 (t, C^2)
3a	2.5, 3.2 (m, 4 H, CH_2P), 4.8 (s, 5 H, cp), 7.2–7.7 (m, 24 H, Ph), 28.6 (t, CH_2P), 84.5 (s, cp), 114.6 (s, CN), 118.9 (s, C^5), 127.6–143.3 (m, Ph), 147.9 (s, C^4), 201.3 (t, C^2)
3c	2.3 (s, 3 H, Me), 2.5, 3.1 (m, 4 H, CH_2P), 4.9 (s, 5 H, cp), 7.2–7.65 (m, 24 H, Ph), 21.2 (s, Me), 28.6 (t, CH_2P), 84.4 (s, cp), 114.9 (s, CN), 118.3 (s, C^5), 126.2–143.2 (m, Ph), 149.1 (s, C^4), 200.3 (t, C^2)
4a	2.2 (m, 4 H, CH_2P), 3.55 (s, 3 H, OMe), 4.75 (s, 5 H, cp), 6.9–7.9 (m, 24 H, Ph), 28.7 (t, CH_2P), 59.5 (s, OMe), 83.7 (s, cp), 112.4 (s, CN), 122.5, 127.3 (C=C), 128.5–136.5 (m, Ph), 187.7 (s, C of isocyanide)
4a'	1.25 (t, 3 H, Me), 2.5–2.75 (m, 4 H, CH_2P), 4.0 (q, 2 H, CH_2), 4.75 (s, 5 H, cp), 6.8–7.7 (m, 24 H, Ph), 14.9 (s, Me), 28.7 (t, CH_2P), 68.8 (s, OCH_2), 83.7 (s, cp), 112.7 (s, CN), 122.8, 127.5 (C=C), 128.2–136.4 (m, Ph), 187.0 (t, C of isocyanide)
5a	2.6 (m, 4 H, CH_2P), 3.55 (s, 3 H, OMe), 5.35 (s, 5 H, cp), 6.8–7.8 (m, 24 H, Ph), 27.6 (t, CH_2P), 59.5 (s, OMe), 86.9 (s, cp), 112.3 (s, CN), 121.2, 125.2 (C=C), 127.3–136.6 (m, Ph), 175.5 (s, C of isocyanide)
5a'	1.3 (t, 3 H, Me), 2.5–2.75 (m, 4 H, CH_2P), 4.0 (q, 2 H, CH_2Me), 5.2 (s, 5 H, cp), 6.75–7.7 (m, 24 H, Ph), 15.0 (s, Me), 28.6 (s, CH_2P), 68.8 (s, OCH_2), 86.8 (s, cp), 112.5 (s, CN), 122.2, 127.2 (C=C), 127.5–136.9 (m, Ph), 173.7 (s, C of isocyanide)
5c	2.4 (s, 3 H, Me), 2.6–3.2 (m, 4 H, CH_2P), 5.1 (s, 5 H, cp), 7.2–7.8 (m, 24 H, Ph), 21.4 (s, Me), 59.3 (s, OMe), 86.4 (s, cp), 108.8 (s, CN), 118.4, 126.8 (C=C), 128.6–142.3 (m, Ph)



- 4a** R' = Me, R = 4-ClC₆H₄, M = Fe
4a' R' = Et, R = 4-ClC₆H₄, M = Fe
5a R' = Me, R = 4-ClC₆H₄, M = Ru
5a' R' = Et, R = 4-ClC₆H₄, M = Ru
5c R' = Me, R = 4-MeC₆H₄, M = Ru

Scheme 2



Scheme 3 (i) LiBu^+ ; (ii) SiMe_3Cl ; (iii) heat

Table 5 Crystallographic and data collection parameters

Molecular formula	$C_{43}H_{38}BClF_4FeN_2OP_2 + \frac{1}{2}C_6H_5CH_3$
<i>M</i>	838.89
Colour and habit	Orange prisms
Crystal system	Monoclinic
Space group	<i>C2/c</i> (no. 15)
<i>a</i> /Å	28.446(3)
<i>b</i> /Å	15.909(2)
<i>c</i> /Å	26.534(3)
β /°	134.09(1)
<i>U</i> /Å ³	8624.47
<i>Z</i>	8
<i>D_c</i> /g cm ⁻³	1.321
μ (Mo-K α)/cm ⁻¹	5.54
Minimum, maximum absorption correction	0.746, 1.104
Crystal size/mm	0.625 × 0.250 × 0.170
Total collected data	5285
Observed data ($ F \geq 2\sigma F_o $)	3812
No. variables	644
<i>R</i>	0.078
<i>R'</i>	0.047
Highest residual electron-density peaks/e Å ⁻³	0.757

(4-Aryl-5-cyanooxazol-2-yl)[1,2-bis(diphenylphosphino)ethane]cyclopentadienyl-iron and -ruthenium complexes 2 and 3. In a typical experiment [Fe(CN)(cp)(dppe)] (2.00 g, 3.7 mmol) and epoxide **1a** (1.13 g, 5.55 mmol) were heated under reflux in CH₂Cl₂ (40 cm³) for ca. 20 h, after which time the solvent was removed. The brown residue was stirred in ice-cold acetone and filtered off. The remaining orange solid was washed several times with ice-cold acetone and dried *in vacuo* to give 1.6 g (60%) of complex **3a**. For the preparation of complexes **2c**, **3a** and **3c** the following quantities were used: **2c**, [Fe(CN)(cp)(dppe)] (2.72 g, 5.0 mmol) and epoxide **1c** (1.38 g, 7.5 mmol), yield 52%; **3a**, [Ru(CN)(cp)(dppe)] (2.95 g, 5.0 mmol) and epoxide **1a** (1.53 g, 7.5 mmol), yield 55%; **3c**, [Ru(CN)(cp)(dppe)] (2.95 g, 5.0 mmol) and epoxide **1c** (1.38 g, 7.5 mmol), yield 46%.

[(*Z*)(1-Aryl-2-alkoxy-2-cyanovinyl isocyanide)[1,2-bis(diphenylphosphino)ethane](cyclopentadienyl)-iron and -ruthenium complexes 4 and 5. In a typical experiment, compound **2a** (2.9 g, 4.0 mmol) and Et₃O⁺BF₄⁻ (0.76 g, 4.0 mmol) were stirred in CH₂Cl₂ (40 cm³) for 2 h at room temperature. Filtration and removal of the solvent led to a yellow powder which was recrystallized from toluene–ethyl methyl ketone (5:1) to give 2.3 g (79%) of **4a'** as orange crystals. The remaining complexes **4** and **5** were prepared using the following quantities: **4a**, **2a** (2.89 g, 4.0 mmol) and Me₃O⁺BF₄⁻ (0.59 g, 4.0 mmol), yield 71%; **5a**, **3a** (3.07 g, 4.0 mmol) and Me₃O⁺BF₄⁻ (0.59 g, 4.0 mmol), yield 75%; **5c**, **3c** (2.81 g, 4.0 mmol) and Me₃O⁺BF₄⁻ (0.59 g, 4.0 mmol), yield 68%; **5a'**, **3a** (3.07 g, 4.0 mmol) and Et₃O⁺BF₄⁻ (0.76 g, 4.0 mmol), yield 65%.

Crystallography

Single crystals of complex **4a'** were grown from toluene–ethyl methyl ketone. One crystal of suitable quality for X-ray diffraction was placed on a goniometer head. The crystal symmetry and approximate cell parameters were obtained from Weissenberg photographs. Intensity data in ω -2 θ scan mode were collected at 298 K on a Nonius CAD 4 diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) over the range 2 θ 4–50°. During the structure refinement by full-matrix least squares [based on $\Sigma w(|F_o| - |F_c|)^2$] the BF₄⁻ anion turned out to be rotationally disordered;

still, anisotropic refinement in two orientations with fluorine populations of 0.5 proved possible. A second problem arose from the presence in the crystal lattice of a molecule of toluene. Owing to complete rotational disorder about the pseudo-C₆ axis of its aromatic ring only an isotropic refinement was carried out. All other non-hydrogen atoms were refined anisotropically in the last cycle of refinement; most of the hydrogen atoms were found and refined isotropically. The final *R'* was 0.047, with a conventional *R* value of 0.078 based on *F*, for a total of 644 refined parameters; the highest residual electron-density peak was 0.757 e Å⁻³.

Table 5 lists the crystallographic and data-collection parameters. All data processing and calculations were performed on a VAX computer with a combination of direct methods (SHELXS 86⁴⁰) and Fourier-difference syntheses (XTAL 3.0⁴¹). An absorption correction (DIFABS⁴²) was carried out.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/139.

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