

Iron(I) Complexes

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Stable Salts of Heteroleptic Iron Carbonyl/Nitrosyl Cations

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Abstract: The oxidation of $\text{Fe}(\text{CO})_5$ with the $[\text{NO}]^+$ salt of the weakly coordinating perfluoroalkoxyaluminate anion $[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]^-$ ($\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$) leads to stable salts of the 18 valence electron (VE) species $[\text{Fe}(\text{CO})_4(\text{NO})]^+$ and $[\text{Fe}(\text{CO})(\text{NO})_3]^+$ with the Enemark–Feltham numbers of $\{\text{FeNO}\}^8$ and $\{\text{FeNO}\}^{10}$. This finally concludes the triad of heteroleptic iron carbonyl/nitrosyl complexes, since the first discovery of the anionic ($[\text{Fe}(\text{CO})_3(\text{NO})]^-$) and neutral ($[\text{Fe}(\text{CO})_2(\text{NO})_2]$) species over 80 years ago. Both complexes were fully characterized (IR, Raman, NMR, UV/Vis, scXRD, pXRD) and are stable at room temperature under inert conditions over months and may serve as useful starting materials for further investigations.

Iron and its chemistry might be one of the most fascinating amongst all transition metals—not only because of iron's highest abundance in the biosphere or its numerous applications in industry and catalysis, but also due to the crucial role of iron-containing enzymes in biology. All of this while being non-toxic.^[1] Especially in regard to the importance of iron nitrosyl intermediates in biochemistry and biomedicine,^[2] a large variety of model systems has been developed in the recent decades.^[3] However, from a fundamental perspective, the long-known flexible bonding motifs and bonding fashions of the NO ligand^[4] are still under discussion and re-investigation today.^[5] And as much as the chemistry of Fe^{II} and Fe^{III} is well established, as much is yet to learn about the chemistry of iron in the unusual oxidation state of +I. The synthesis of such compounds is mainly achieved by the reduction of Fe^{II} precursors, usually stabilized by bulky strong donor ligands such as $[\text{C}(\text{Si}(\text{CH}_3)_3)_3]^-$,^[6] cyclic (alkyl)-(amino)carbenes^[7] or N-heterocyclic carbenes (NHCs).^[8] But especially in the absence of those strong and sterically demanding ligands, an undisturbed insight to iron(I) systems

is scarce. With that in mind, we made use of the versatility of carbon monoxide (CO) as a ligand by starting from $\text{Fe}(\text{CO})_5$ as a Fe^0 source in combination with an oxidative approach. In order to compensate for the lability of the $\text{Fe}-\text{CO}$ bond in the resulting iron cations, we utilized the weakly coordinating anion (WCA) $[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]^-$ ($\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$)^[9,10] in combination with $[\text{NO}]^+$ as oxidant. The inevitable and (in this case) desirable coordination of the resulting $\text{NO}(\text{g})$ to the iron center led to the formation of the novel heteroleptic 18 valence electron (VE) iron(I) carbonyl/nitrosyl cations $[\text{Fe}(\text{CO})_4(\text{NO})]^+$ and $[\text{Fe}(\text{CO})(\text{NO})_3]^+$ with the respective Enemark–Feltham numbers^[4] $\{\text{FeNO}\}^8$ and $\{\text{FeNO}\}^{10}$. Overall, the reports on homoleptic or heteroleptic transition-metal nitrosyl salts are scarce in literature. Stable salts of homoleptic nitrosyl cations, unlike their carbonyl analogues, were completely unknown until our recent discovery of $[\text{Mn}(\text{NO})_4][\text{WCA}]$.^[11] In regard to ternary carbonyl/nitrosyl cations, the only currently known examples are $[\text{Cr}(\text{CO})_5(\text{NO})][\text{WCA}]$, reported by us^[12] and $[\text{Co}(\text{CO})_2(\text{NO})_2][\text{WCA}]$.^[13] And although the neutral $\text{Fe}(\text{CO})_2(\text{NO})_2$ ^[14] and anionic $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ (the Hieber anion)^[15] shown in Figure 1 were discovered more than half a decade ago and found their applications as useful starting materials or catalysts,^[16] as of yet, their cationic counterparts have been mostly untouched.^[**]

Our oxidative syntheses started from $\text{NO}[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]$ and $\text{Fe}(\text{CO})_5$ in dichloromethane (CH_2Cl_2). Conveniently, this reaction can be done with an excess of $\text{Fe}(\text{CO})_5$ or even with impure $\text{NO}[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]$, since $[\text{Fe}(\text{CO})_4(\text{NO})][\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]$ (**1**) is only poorly soluble in CH_2Cl_2 (Scheme 1a). Subsequent washings of the crude product with CH_2Cl_2 or *n*-pentane and a crystallization by vapor diffusion of *n*-pentane into an *ortho*-difluorobenzene (*o*DFB) or 1,2,3,4-tetrafluorobenzene (TFB) solution led to pure brown crystals of **1** in 49% yield. If starting from pure $\text{NO}[\text{WCA}]$, usually about 80% yield of crystalline **1**, $\lambda_{\text{max}} = 450$ and 330 nm in *o*DFB solution (see Supporting Information Figure S23), was obtained. For the synthesis of **2**, the stoichiometry is more important. Therefore, the use of solid $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ as the iron source is more practicable. The reaction is best carried out in solution (*o*DFB, TFB) to promote the CO/NO exchange of the NO atmosphere with the initially formed **1**. After several minutes of stirring at room temperature, the brown solution of **1** turned dark green, indicating a complete transformation to **2**. Filtration and crystallization by slow vapor diffusion of *n*-pentane into the reaction solution led to

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Supporting information (a complete analysis of all bands in IR and Raman spectroscopy (section 4) as well as powder-XRD diffractograms (section 5), NMR spectra (section 2), UV/VIS spectra (section 6) and additional details on the crystal structures (section 8) and DFT calculations (section 9)) and the ORCID identification number(s) for the author(s) of this article can be found under: <https://doi.org/10.1002/anie.201915942>.

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[**] The formal Fe^{II} cation $[\text{Fe}(\text{CO})_5(\text{NO})]\text{Cl}$ was postulated and assigned in 1968 (IR-, UV/Vis-spectroscopy and elemental analysis).^[17] See the Supporting Information section 7 for a detailed discussion, why we doubt its existence.

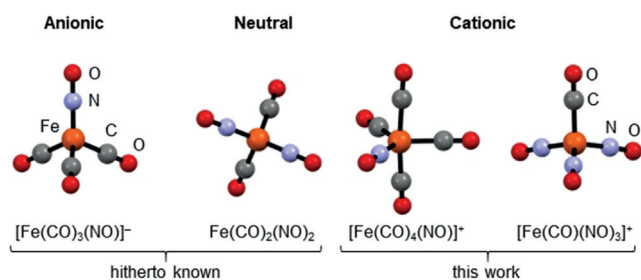


Figure 1. Calculated structures (BP86/def2-TZVPP-D3BJ) of the currently known iron carbonyl/nitrosyl complexes.* Only the *Hieber* anion $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ was hitherto structurally characterized.

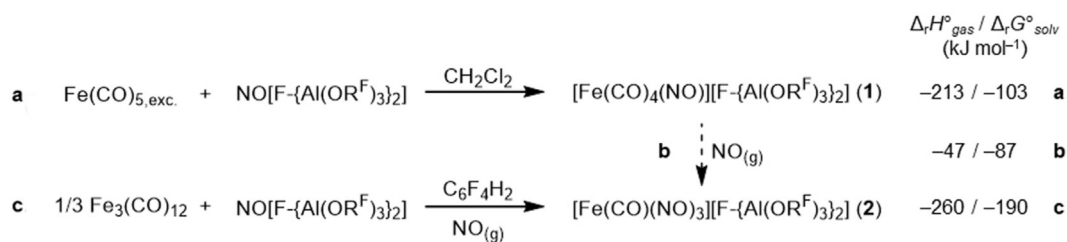
dark green crystals of pure **2** (80% yield, $\lambda_{\text{max}} = 610, 420$ and 310 nm in *o*DFB solution (see Figure S24), Scheme 1c).

Both reactions shown in Scheme 1 work with either combinations of the iron carbonyl source ($\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$) and solvents (CH_2Cl_2 , *o*DFB, TFB or perfluorohexane C_6F_{14}), only reaction times and overall yields may vary. The thermodynamics underlying equations in Scheme 1 were determined as $\Delta_r G^\circ_{\text{soln}}$ in CH_2Cl_2 starting from $\text{Fe}(\text{CO})_5$ at the BP86/def2-TZVPP-D3BJ/COSMO level and are in agreement with the experimental findings. Also the colors of the complexes are in good qualitative agreement to TD-DFT calculations (cf. section S6). However, similar reactions showed that the more accessible alternative $[\text{Al}(\text{OR}^F)_4]^-$ anion is not suitable for this system: although the $[\text{Fe}(\text{CO})_4(\text{NO})][\text{Al}(\text{OR}^F)_4]$ salt immediately precipitates as a powder in CH_2Cl_2 , upon dissolution in *o*DFB it readily reacts by anion decomposition to give the thermodynamically favored $[\text{Fe}(\text{CO})(\text{NO})_3][\text{F}-\{\text{Al}(\text{OR}^F)_3\}_2]$ salt and an unidentifiable precipitate. In addition, the crystal structure of $[\text{Fe}(\text{CO})(\text{NO})_3][\text{Al}(\text{OR}^F)_4]$ exhibits the typical overstructure and twinning problems observed for several $[\text{Al}(\text{OR}^F)_4]^-$ salts with (pseudo-)tetrahedral cations such as $[\text{Mn}(\text{NO})_4][\text{Al}(\text{OR}^F)_4]$.^[11] Therefore, we limit our report to the use of the more stable and less-symmetric $[\text{F}-\{\text{Al}(\text{OR}^F)_3\}_2]^-$ anion. With this anion, the reactions in Scheme 1 led to phase-pure crystals of **1** and **2** (cf. section S5 powder XRD; note that **1** crystallizes from CH_2Cl_2 in space group $P2_1/c$ and from *o*DFB/TFB in $P-1$). In their molecular structures, a differentiation between CO and NO ligands is not possible. The NO ligands were only refined and displayed for visual clarity (Figure 2c). However, their presence is evident from the averaged Fe–N/C bond lengths **1** (183.2(3) pm; cf. $\text{Fe}(\text{CO})_5$: 181.4 pm^[18]/ $[\text{Fe}(\text{CO})_6]^{2+}$: 191.1 pm^[19]) and **2** (176.4(3) pm, Table 1) that agree within 2 pm to the DFT calculations

(Table 1). All bond angles Fe–N/C–O are close to linear and range from 178 to 180° for **1** and from 176 to 177° for **2** (see section S8). This was also observed for the homoleptic $[\text{Mn}(\text{NO})_4]^+$ cation, the $[\text{F}-\{\text{Al}(\text{OR}^F)_3\}_2]^-$ salt of which is isomorphous to **2**.

A differentiation between both ligands and an unambiguous characterization of **1** and **2** is possible by IR and Raman spectroscopy. In both cases, the agreement between the simulated (@BP86def2/TZVPP-D3BJ) and experimental spectra is excellent (Figure 2a). Generally, the BP86 method is a good compromise between computational demand and the quality of the resulting data (structures, vibrations and NMR parameters, see Table 1) for these systems. The vibrational frequencies of the CO and NO bands of **1** and **2** are surprisingly similar to those of $[\text{Co}(\text{CO})_2(\text{NO})_2]^+$,^[13] indicating comparable bond strengths and a similar electronic situation. The $\nu(\text{CO})$ stretching vibrations of **1** are also very similar to those of the isoelectronic and pseudo-isostructural $[\text{Co}(\text{CO})_5]^+$ (2197/2155/2146/2120 cm^{-1})^[13] and are in the typical range for monocationic homoleptic carbonyl cations.^[12,20] In addition, the four observed CO bands of **1**, including the 2144 cm^{-1} shoulder (Raman: 2145 cm^{-1}) of the A_1/B_1 vibration at 2137 cm^{-1} (Figure 2a), indicate that the NO ligand resides in the equatorial plane. This is in agreement with BP86def2/TZVPP-D3BJ calculations that give the A_1 and B_1 stretches as isoenergetic and resonating at 2114 cm^{-1} (Table 1). In addition, DFT supports the equatorial isomer as the global minimum and reveals the axial isomer as being 43 kJ mol^{-1} higher in energy. Moreover, the C_{3v} -symmetric axial isomer would have only three independent CO stretches (calcd at 2158 (A_1), 2113 (A_1), and 2098 (E) cm^{-1}) (see Figure S27). The $\nu(\text{NO})$ stretching vibrations of **1** (1905 cm^{-1}) and **2** (1972/1881 cm^{-1}) are in part significantly blue-shifted compared to those of free $\text{NO}_{(\text{g})}$ (cf. 1876 cm^{-1})^[12] and similar to $[\text{Mn}(\text{NO})_4]^+$ (1978/1866/1855 cm^{-1}). Furthermore, the close agreement between the experimental vibrations in the solid state and the ideal, non-distorted calculated frequencies of $[\text{Fe}(\text{CO})_4(\text{NO})]^+$ (C_{2v}) and $[\text{Fe}(\text{CO})(\text{NO})_3]^+$ (C_{3v}), indicate that the $[\text{F}-\{\text{Al}(\text{OR}^F)_3\}_2]^-$ anion truly induces pseudo-gas-phase conditions in condensed phases.^[10]

The broad signal in the ^{14}N NMR spectrum (Figure 2b, left) and the appearance of only one signal in the ^{13}C NMR spectrum (see section S2) for **1** indicate a Berry pseudorotation^[21] in solution, equilibrating the expected two different sets of CO ligands (Table 1), similar to the related $[\text{Co}(\text{CO})_5]^+$.^[22] For **2**, the ^{14}N NMR signal is sharper, hinting at a more static structure in solution (Figure 2b, right).



Scheme 1. Synthesis of the desired heteroleptic iron carbonyl/nitrosyl cations $[\text{Fe}(\text{CO})_4(\text{NO})]^+$ and $[\text{Fe}(\text{CO})(\text{NO})_3]^+$ as $[\text{F}-\{\text{Al}(\text{OR}^F)_3\}_2]^-$ salts **1** and **2**. Reactions (a) and (c) give 80% yield, if starting from pure materials.

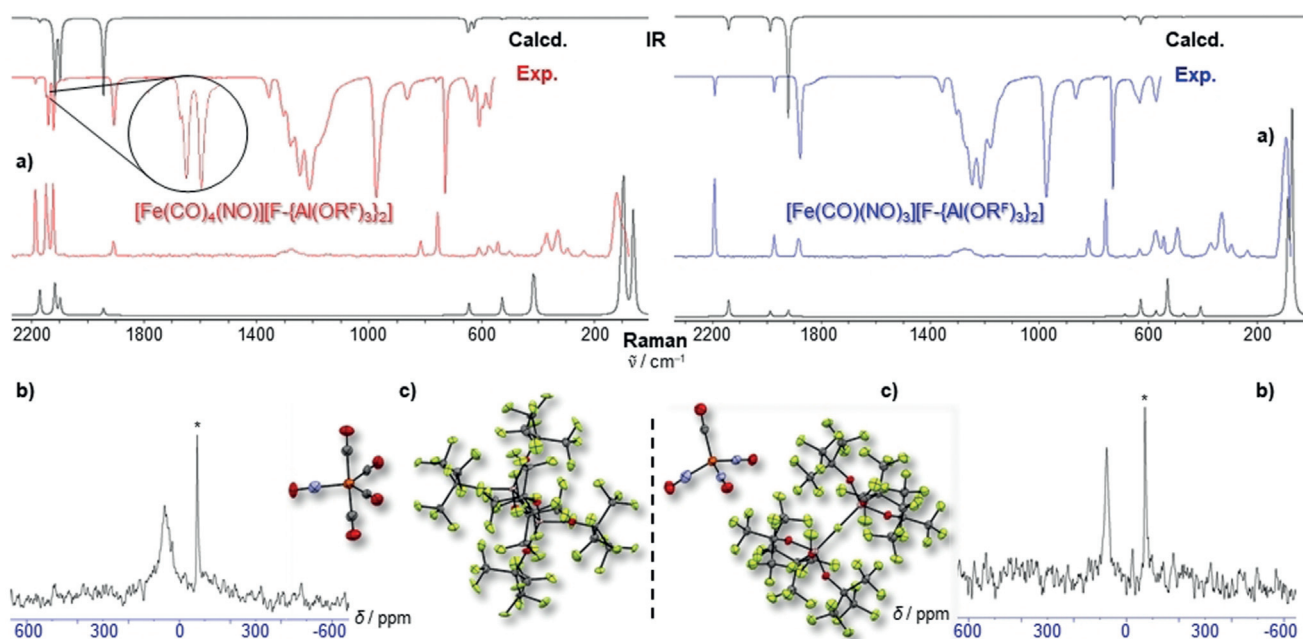


Figure 2. a) Experimental (Exp., red or blue) and calculated (Calcd, black, cations only, C_{2v}/C_{3v} symmetry @BP86def2/TZVPP-D3B), no scaling factor was applied) vibrational spectra of **1** and **2**, note the 2144 cm^{-1} shoulder in the expanded CO region of the IR spectrum of **1**; b) ^{14}N NMR spectra (21.69 MHz, oDFB, 298 K), * signal from N_2 atmosphere; c) molecular structures of **1** ($P2_1/c$, $R1 = 4.2\%$, $wR2 = 11.9\%$) and **2** ($P-1$, $R1 = 4.3\%$, $wR2 = 10.7\%$). Note that the NO ligands are crystallographically indistinguishable from CO and were only colored for visual purposes; thermal ellipsoids set at 50% probability.

Table 1: Experimental and calculated (calcd) data of crystalline $[\text{Fe}(\text{CO})_4(\text{NO})][\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]$ **1** and $[\text{Fe}(\text{CO})(\text{NO})_3][\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]$ **2** as well as selected literature-known compounds; v: very, s: strong, m: medium, w: weak, sh: shoulder.

	$[\text{Fe}(\text{CO})_4(\text{NO})]^+$ $[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]^-$	$[\text{Fe}(\text{CO})_4(\text{NO})]^+$ calcd. ^[a]	$[\text{Fe}(\text{CO})(\text{NO})_3]^+$ $[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]^-$	$[\text{Fe}(\text{CO})(\text{NO})_3]^+$ calcd. ^[a]	$[\text{Mn}(\text{NO})_4]^+$ $[\text{F}-\{\text{Al}(\text{OR}^{\text{F}})_3\}_2]^{-(11)}$	$[\text{Co}(\text{CO})_2(\text{NO})_2]^+$ $[\text{B}(\text{CF}_3)_4]^{-(13)}$		
$\tilde{\nu}(\text{CO}/\text{NO})$	2183 (vww)	2168 (vww)	v(CO) (A_1)	2189 (vw)	v(CO) (A_1)	1855 (vvs)	2183 (s)	
IR [cm^{-1}]	2144 (sh) ^[b]	2114 (vvs)	v(CO) (A_1) ^[b]	1971 (vw)	1986 (vww)	v(NO) (A_1)	2165 (s)	
	2137 (mw) ^[b]	2114 (vvs)	v(CO) (B_1) ^[b]	1876 (s)	1919 (vww)	v(NO) (E)	1960 (m)	
	2119 (m)	2096 (vvs)	v(CO) (B_2)				1886 (m)	
	1904 (m)	1905 (w)	v(NO) (A_1)					
$\tilde{\nu}(\text{CO}/\text{NO})$	2183 (vvs)	2169 (vww)	v(CO) (A_1)	2190 (s)	2139 (vw)	v(CO) (A_1)	1978 (mw)	2183 (s)
Raman [cm^{-1}]	2145 (vvs)	2114 (vvs)	v(CO) (B_1)	1972 (vw)	1986 (vw)	v(NO) (A_1)	1866 (ms)	2167 (s)
	2121 (vvs)	2096 (vvs)	v(CO) (B_2)	1881 (vw)	1919 (vww)	v(NO) (E)	1962 (m)	
	1905 (w)	1905 (w)	v(NO) (A_1)				1893 (m)	
$d(\text{M}-\text{NO}/\text{CO})$ [pm] ^[c]	183.2(3) ($P2_1/c$) 183.8(4) ($P-1$)	181.9		176.5(3)	174.6	173.4(5)	— ^[d]	
α (M-N/C-O) [°] ^[c]	179(1) ($P2_1/c$) 178(1) ($P-1$)	179		177(1)	178	178(1)	— ^[d]	
^{13}C NMR Shift [ppm] ^[e]	191.8	196.2 205.7		184.1	200.3	—	— ^[d]	
^{14}N NMR Shift [ppm] ^[e]	56	43		73	65	107	— ^[d]	

[a] C_{2v}/C_{3v} symmetry @BP86def2/TZVPP-D3B, no scaling factor was applied. For comparison, the experimental d_{FeC} in $\text{Fe}(\text{CO})_5$ is $181.4\text{ pm}^{[18]}$ and the calculation at the same level of theory gives 180.4 pm ; [b] the assignment of the shoulder is ambiguous; [c] distances and angles averaged over all positions (CO and NO); [d] no data are available; [e] oDFB solution, 298 K, calculated shifts referenced to CH_3NO_2 (^{14}N) and $\text{CH}_3\text{NO}_2/\text{Si}(\text{CH}_3)_4$ (^{13}C).

From the preceding the question arose, where the “electronic truth” in between the two limiting descriptions as M^0/NO^+ and M^+/NO^0 (M: metal) might lie. Owing to the linearity of the NO ligands, combined with the $\nu(\text{NO})$

vibrational frequencies of complexes **1** and **2** close to that of gaseous NO, the oxidation state of the iron atom appears to be +I, incorporating neutral $3e^-$ NO donors as ligands. To further evaluate the possible (non-)innocence of the NO

Table 2: The AIM charges for the isoelectronic and pseudo-isoelectronic couples $[\text{Fe}(\text{CO})_4(\text{NO})]^+ / [\text{Co}(\text{CO})_5]^+$ and $[\text{Fe}(\text{CO})(\text{NO})_3]^+ / [\text{Mn}(\text{NO})_4]^+ / [\text{Co}(\text{CO})_2(\text{NO})_2]^+$.^[a]

AIM charges at:	$[\text{Fe}(\text{CO})_4(\text{NO})]^+ (C_{2v})$	$[\text{Fe}(\text{CO})_4(\text{NO})]^+ (C_{3v})$	$[\text{Co}(\text{CO})_5]^+$	$[\text{Fe}(\text{CO})(\text{NO})_3]^+$	$[\text{Mn}(\text{NO})_4]^+$	$[\text{Co}(\text{CO})_2(\text{NO})_2]^+$
M (= Fe, Co, or Mn)	+0.93	+0.89	+0.74	+1.05	+1.23	+0.87
C	ax: +1.05 equiv: -1.02	ax: +1.06 equiv: -1.03	ax: +1.08 equiv: +1.06	+1.03	-	+1.06
O(-C)	ax: -1.01 equiv: -1.02	ax: -1.01 equiv: -1.02	ax: -1.01 equiv: -1.02	-1.02	-	-1.02
N	+0.24	+0.24	-	+0.22	+0.18	+0.26
O(-N)	-0.26	-0.20	-	-0.23	-0.24	-0.23

[a] ax/eq refers to axial and equatorial ligands in a trigonal bipyramid.

ligand, we conducted AIM charge analyses on the cations of compounds **1** and **2** and compared them to the fully characterized isoelectronic and pseudo-isoelectronic analogues $[\text{Co}(\text{CO})_5]^+$,^[13] $[\text{Mn}(\text{NO})_4]^{+11}$ as well as $[\text{Co}(\text{CO})_2(\text{NO})_2]^{+13}$ (Table 2). Based on their AIM charges, all three metal nitrosyl species appear to be true Fe^I and Mn^I complexes with neutral NO ligands and calculated positive charges of about +1 on the metal atoms. Thus, the formal oxidation state and the partial charge on the metal appear to coincide here. The commonly as Co^I regarded homoleptic carbonyl cation $[\text{Co}(\text{CO})_5]^+$ with the stronger CO donor exhibits, as expected, a lower charge of only +0.74 residing on the cobalt atom.

Therefore, the AIM analyses and the linearity of the NO ligands in complexes **1** and **2**, combined with the $\nu(\text{NO})$ vibrational frequencies close to gaseous NO would assign those as true iron(I) complexes.^[*]

In conclusion, we discovered a simple pathway to two novel heteroleptic iron carbonyl/nitrosyl cations, stabilized by a weakly coordinating anion. Both complexes are the first of their kind, exhibit the unusual oxidation state +I, were fully characterized and are accessible as phase pure materials in good to excellent yields. Owing to their simplicity, they may serve as model compounds for further investigations to yield insights into metal NO complexes. We encourage other groups to take over from here on, to pick up on this report not only from a fundamental point of view—but also to apply this knowledge in biochemistry or catalysis in order to allow for a better understanding of the role and nature of the NO ligand.

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[*] Experimental verification of the oxidation state by X-ray photoelectron spectroscopy (XPS) were deemed unreliable after explicit discussion with experts at the KIT XPS-site. The problems arise from the difficulty in determining the weak iron peak in XPS at about 706–710 eV in the presence of the intense fluorine peak of the anion with 55 F-atoms at 688–89 eV. For Mössbauer spectroscopy—to our knowledge—the nonexistence of true and stable iron(I) reference complexes greatly limits its usefulness.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbonyl ligands · iron(I) · nitrogen oxides · vibrational spectroscopy · weakly coordinating anions (WCAs)

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