

[Fe(CNXyl)₄]^{2−}: An Isolable and Structurally Characterized Homoleptic Isocyanidemetalate Dianion**

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Dedicated to Professor Robert G. Bergman on the occasion of his 65th birthday

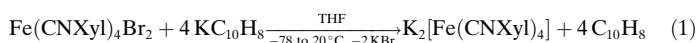
Malatesta noted nearly 50 years ago that homoleptic isocyanidemetalates were unknown but potentially very interesting species^[1] as a result of their formal similarity to the long-established carbonylmatalates.^[2] Almost 30 years later, Warkock and Cooper announced the synthesis and full characterization of the first example, [Co(CNXyl)₄][−] (Xyl = 2,6-dimethylphenyl).^[3] Subsequently, related monoanionic complexes were established, including [Mn(CNXyl)₅][−],^[4] [V(CNXyl)₆][−],^[5] and [Ta(CNXyl)₆][−].^[6] Cooper and co-workers also reported on quite thermally unstable isocyanideruthenates, and provisionally formulated these species as the first dianions of this class, [Ru(CNR)₄]^{2−} (R = Xyl and *t*Bu).^[7] Neither salt could be isolated, and their characterizations were mainly based on their reactions with suitable main-group halides, E-X, to afford appropriate products, that is, Ru(CNR)₄E₂.^[8] However, because derivative data can be unreliable indicators of the true nature of a highly reduced metalate precursor,^[9] we report herein the first proof for the existence of a homoleptic isocyanide dianion. This work involves the synthesis, isolation, and structural characterization of [Fe(CNXyl)₄]^{2−}, an unprecedented iron isocyanide analogue of the first metal carbonyl anion, [Fe(CO)₄]^{2−}.^[2,10]

Reduction of iron(II) bromide in the presence of four equivalents of CNXyl by four equivalents of potassium naphthalene in tetrahydrofuran (THF) at −78 °C afforded an intensely bright red reaction mixture, from which thermally stable but quite air-sensitive unsolvated K₂[Fe(CNXyl)₄] (**1**) was isolated in about 70 % yield as a satisfactorily pure brick red powder (Equation (1); see the

gave a product that was too thermally unstable to isolate or spectroscopically characterize. However, this species reacted with triphenyltin chloride to provide a product consistent with its formulation as a dipotassium salt of [Fe(CN*t*Bu)₄]^{2−} (**2**; see below).

¹H and ¹³C NMR spectra of **1** in solution showed unexceptional resonances characteristic of the aromatic and aliphatic groups present in the coordinated xylyl isocyanide ligands. In addition, a ¹³C NMR resonance at δ = 238.7 ppm was observed and assigned to the ligated isocyanide carbon. Interestingly, this δ_C value is the most downfield carbon resonance previously observed for a terminal isocyanide ligand in a diamagnetic compound. Because ligated carbon ¹³C NMR resonances of isocyanides tend to shift downfield as metal centers assume lower oxidation states,^[11] it is reasonable that **1**, formally containing Fe^{II−}, should have a more downfield (positive) isocyanide carbon resonance position than the previous “record” value of δ = 210.4 ppm reported for the Ta^{I−} complex, [Ta(CNXyl)₆][−].^[6] Carbonyl ¹³C NMR resonances of homoleptic metal carbonyls also move downfield as the formal oxidation state of the metal decreases,^[12] and it is interesting that the previously unreported carbonyl carbon shift of K₂[Fe(CO)₄] at 20 °C in [D₆]DMSO (δ_C = 234.6 ppm)^[13] is not greatly different from that observed for **1**. More evidence for the electron-rich character of **1** is its IR spectrum in THF that exhibits a broad intense absorption at very low energy, 1670 cm^{−1}, which is assigned to the isocyanide CN stretching frequency. In contrast, homoleptic isocyanidemetalate monoanions have infrared ν(CN) bands at appreciably higher energies; for example, for [Ta(CNXyl)₆][−] the value is 1812 cm^{−1},^[6] indicative of significantly less metal-to-isocyanide back-bonding in this higher-valent species, relative to that in **1**.

A single-crystal X-ray study on **1**, as the [K-([2.2.2]cryptand)]⁺ salt, revealed undistorted cations that were well-separated from the anion.^[14] The latter contained four discrete CNXyl ligands and was only marginally perturbed by the roughly spherical counterions. Essentially linear Fe-C-N units (av 173(1)°) and a nearly tetrahedral FeC₄ core were present in **1**, appropriate for a d¹⁰-iron(II−) complex (Figure 1). Despite the rather bulky character of the isocyanide ligand, the average Fe-C bond length in **1** of 1.765(3) Å was only slightly longer than the corresponding value of 1.742(6) Å reported for Na₂[Fe(CO)₄]·3/2(dioxane).^[15] These data suggest that CNXyl and CO have similar acceptor abilities in the two subvalent iron complexes.^[16,17] Another measure of metal-to-ligand back-bonding in **1** is the average isocyanide C-N bond length of 1.237(7) Å, which is appreciably longer than analogous bond lengths found in homoleptic



Experimental Section for details). In contrast, analogous reductions of FeBr₂ in the presence of *tert*-butylisocyanide

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

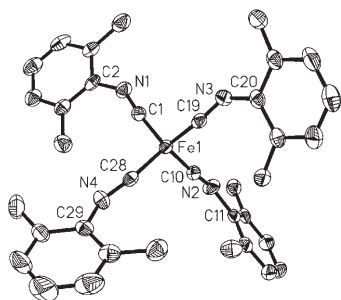


Figure 1. Molecular structure of **1** (cations not shown). Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 1.761(3), Fe–C10 1.766(3), Fe–C19 1.763(3), Fe–C28 1.768(3), C1–N1 1.230(4), C10–N2 1.233(4), C19–N3 1.246(4), C28–N4 1.237(4); C1–N1–C2 143.3(3), C10–N2–C11 144.6(3), C19–N3–C20 139.9(3), C28–N4–C29 147.3(3), av Fe–C–N 173(1), av C–Fe–C 109(5).

isocyanidemetalate monoanions,^[18] such as $[\text{V}(\text{CNXyl})_6]^-$ (av 1.20(2) Å),^[5] or free CNXyl (1.160(3) Å).^[19] Finally, the substantially electron-rich character of anion **1** is evident by its unusually nonlinear isocyanide C–N–C units, which have an average angle of 144(3)°. Thus, both structural and spectroscopic data point to a high degree of metal-to-isocyanide back-bonding in **1** and these correlate with significant bending at the nitrogen atoms in the coordinated isocyanides.^[20,21]

Because $[\text{Fe}(\text{CO})_4]^{2-}$ was reported to react with triphenyltin chloride to provide an unusually robust and well-characterized product, *cis*- $[\text{Fe}(\text{CO})_4(\text{SnPh}_3)_2]$,^[22] corresponding reactions of **1**, and the unstable intermediate postulated to be **2**, were carried out and these gave the analogous air-stable products, $[\text{Fe}(\text{CNR})_4(\text{SnPh}_3)_2]$ (R = Xyl: **3**; R = *t*Bu: **4**) in about 60% isolated yields.^[23] In contrast to the carbonyl complex, IR and NMR spectral data indicated that **3** and **4** were only present as *trans* isomers, likely because the isocyanides are poorer acceptors and bulkier ligands than carbon monoxide. Because no complexes of the general formula $[\text{M}(\text{CNR})_4\text{L}_2]^{2-}$, for L = SnR_3' and related Group 14 based ligands, had been structurally characterized previously, single-crystal X-ray studies were carried out on **3** and **4** to verify their structures (Figure 2).^[24] Both compounds show essentially identical $\text{Fe}(\text{CN})_4\text{Sn}_2$ core structures of nearly D_{4h} symmetry, with experimentally indistinguishable average Fe–C and isocyanide C–N bond lengths of 1.851(6) and 1.162(5) Å, respectively. Corresponding Fe–C and C–N bond lengths in **1** are about 0.09-Å shorter and 0.08-Å longer, respectively, than those in **3** and **4** as a result of the much greater degree of $d\pi(\text{Fe})$ -to- $p\pi^*(\text{CN})$ back-bonding present in **1**. Changes in the isocyanide stretching frequencies, $\nu(\text{CN})$, and ^{13}C NMR shifts for ligated carbon atoms, δ_{C} , in moving from subvalent iron complex **1** to formally divalent iron complexes **3** and **4** are also in accord with expectations based on the classic Chatt–Dewar–Duncanson model for back-bonding.^[25] Other interatomic data of the structures for **3** and **4** are unexceptional, including the average Fe–Sn bond lengths of 2.565(1) and 2.529(3) Å, respectively, which are within the range of values of 2.526(3)^[26] to 2.661(7) Å^[22] previously reported for triphenylstannyliron complexes.

In summary, we have isolated and structurally characterized a homoleptic isocyanidemetalate dianion, $[\text{Fe}(\text{CNXyl})_4]^{2-}$, for the first time. Data from IR and NMR spectroscopy and X-ray studies show that the formal d^{10} -iron(II-) center participates in back-bonding to the isocyanides to the greatest extent previously observed for isolable homoleptic isocyanide complexes containing only terminally bound ligands. Thus, among these homoleptic species, $[\text{Fe}(\text{CNXyl})_4]^{2-}$ has the lowest known isocyanide stretching frequency of 1670 cm^{-1} , the most downfield isocyanide ligated carbon ^{13}C NMR resonance ($\delta = 238.7$ ppm), the longest isocyanide C–N bond length of 1.237(7) Å, and the greatest degree of bending at the isocyanide nitrogen atoms (average C–N–C angle of 144(3)°). Here we have emphasized qualitative similarities between $[\text{Fe}(\text{CNXyl})_4]^{2-}$ and $[\text{Fe}(\text{CO})_4]^{2-}$. In metal carbonyl chemistry, more highly reduced species are known, such as $[\text{Mn}(\text{CO})_4]^{3-}$ and $[\text{Cr}(\text{CO})_4]^{4-}$,^[2,27] so it will be of considerable interest to determine whether analogous isocyanide complexes are accessible.

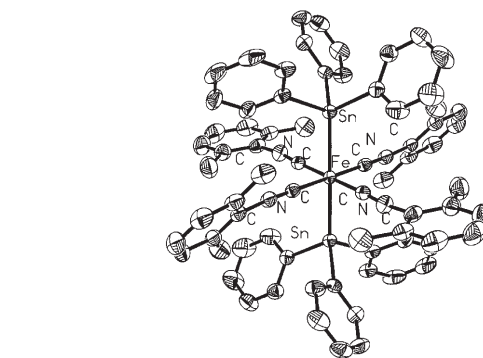


Figure 2. Molecular structure of **3**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–Sn 2.5663(5), av Fe–C 1.850(4), av isocyanide C–N 1.165(5), av C–N–C 174(1), av Fe–C–N 178(1), av *cis* C–Fe–C 90(1), av *trans* C–Fe–C 180.0(2), Sn–Fe–Sn 180.0.

Experimental Section

1: Treatment of an orange solution of anhydrous FeBr_2 (0.500 g, 2.32 mmol) in THF (50 mL) with CNXyl (1.247 g, 9.51 mmol) provided a clear red-violet solution of *cis*- and *trans*- $\text{Fe}(\text{CNXyl})_4\text{Br}_2$.^[13] This solution was cooled to -78°C and added to a deep green solution of potassium naphthalene ($[\text{K}][\text{C}_{10}\text{H}_8]$, 9.27 mmol) in THF (50 mL) at -78°C . The resulting bright red reaction mixture was slowly warmed to room temperature over a period of about 12 h, filtered to remove KBr, and evaporated under vacuum to dryness. Trituration of the residue with diethyl ether (1 \times 50 mL, 1 \times 20 mL), followed by drying in vacuo, afforded a brick red powder (1.084 g, 71% yield based on FeBr_2), which proved to be satisfactorily pure, unsolvated $\text{K}_2[\text{Fe}(\text{CNXyl})_4]$ (**1**). Elemental analysis (%) calcd for $\text{C}_{36}\text{H}_{36}\text{FeK}_2\text{N}_4$: C 65.64, H 5.51, N 8.51; found: C 65.60, H 5.59, N 8.83; m.p. 148–155 $^\circ\text{C}$ (decomp); IR (THF): $\tilde{\nu} = 1675$ cm^{-1} (vs br; CN); ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta = 2.45$ (s, 6H, CH_3), 6.48 (t, 1H, *p*-CNXyl), 6.73 ppm (d, 2H, *m*-CNXyl); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta = 21.2$ (s, CH_3), 119.6 (s, *p*-CNXyl), 127.9 (s, *m*-CNXyl), 131.5 (s, *o*-CNXyl), 141.1 (s, *ipso*-CNXyl), 238.7 ppm (s, CNXyl). Assignments were confirmed by HMQC 2D NMR spectroscopy. Attempts to grow X-ray quality crystals of **1** from several solvents failed. However, addition of [2.2.2]cryptand (0.090 g) to a solution of **1** (0.075 g) in hexamethylphosphoramide (HMPA, 10 mL), followed by layering with excess THF at 0°C , resulted in growth of suitable single crystals of $[\text{K}][2.2.2]\text{cryptand}][\text{Fe}(\text{CNXyl})_4]$ in about 24 h. These revealed identical spectroscopic properties to **1**, without cation.

3: Preparation was identical to that shown in detail for **4** below, except pure **1** was combined with two equivalents of Ph_3SnCl in THF. The isolated yield of satisfactorily pure **3** was 60% based on **1**. Elemental analysis (C, H, N) results were satisfactory; m.p. 250–252 °C (decomp). Selected spectral data: IR (THF): $\tilde{\nu}$ = 2055 (vs), 2008 cm^{-1} (sh, CN); ^{13}C NMR (75 MHz, CDCl_3 , 20 °C): δ = 179.3 (s, CNXyl); normal carbon resonances due to Ph_3Sn and xyllyl groups were also observed; ^{119}Sn NMR (186 MHz, CDCl_3 , 20 °C, ext. ref. SnMe_4): δ = 14.4 ppm (s). Pale yellow plates of **3** were grown from a pentane-layered THF solution at 0 °C for the X-ray study.^[24]

4: Addition of $t\text{BuNC}$ (1.0 mL, 9.6 mmol) to FeBr_2 (0.500 g, 2.32 mmol) in THF (50 mL) produced a red-violet solution, which was cooled to –78 °C and added to KC_{10}H_8 (9.27 mmol) in THF (50 mL) at –78 °C. Ph_3SnCl (1.787 g, 4.64 mmol) in THF (30 mL, –78 °C) was rapidly added to the resulting dark solution to afford a dark reddish yellow reaction mixture, which was warmed to 20 °C over a period of 12 h. Following filtration, solvent was removed in vacuo and the product was vigorously washed with heptane, then pentane, and dried in vacuo to afford **4** as a satisfactorily pure light yellow powder (1.511 g, 60% based on FeBr_2). Elemental analysis (C, H, N) results were satisfactory; m.p. 198 °C. Selected spectral data: IR (oil mull): $\tilde{\nu}$ = 2098 (s), 2065 cm^{-1} (s); ^{13}C NMR (75 MHz, CDCl_3 , 20 °C): δ = 166.3 (s, $\text{CN}t\text{Bu}$), normal carbon resonances due to $t\text{BuNC}$ and Ph_3Sn groups were also observed; ^{119}Sn NMR (186 MHz, CDCl_3 , 20 °C, ext. ref. SnMe_4): δ = 41.7 ppm (s). Colorless blocks of **4** were grown from a pentane-layered THF solution at 0 °C for the X-ray study.^[24]

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