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Probing Redox Non-innocence in Iron-Carbene Complexes ($\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10-11}$) by ^1H and ^{13}C Pulse Electron Paramagnetic Resonance

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Abstract: We report the synthesis and spectroscopic characterization of a series of iron-carbene complexes in redox states $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10-11}$. Pulse EPR studies of the ^1H and ^{13}C isotopologues of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$ reveal the high covalency of the Fe-carbene bonding, leading to a more even spin distribution than commonly observed for reduced Fischer carbenes.

Metal carbene complexes are of interest for their applications in organic methodology and their fundamental bonding properties.^[1] The electronic structure of the $\text{M}=\text{C}$ motifs, typically classified as Fischer and Schrock carbenes, impacts their reactivity pattern, and has been studied extensively.^[2] Variants exhibiting redox non-innocence, wherein the carbene ligand orbitals are substantially involved in the redox process, have emerged as examples of an alternate electronic structure for the metal carbene motif, with distinct physical and chemical properties, prompting detailed spectroscopic characterization.^[3,4] One-electron reduced Fischer-type carbene species have also been implicated as intermediates in a variety of organic transformations, including C-C coupling and olefin cyclopropanation.^[4] These proposals have motivated efforts to correlate the reactivity of open-shell metal carbenoid complexes with their electronic structure. Reactivity studies reveal that reduced Fischer carbenes behave like carbon-centered radicals, engaging in hydrogen atom abstraction, radical-radical coupling and additions to unsaturated substrates.^[4] In accordance with these findings, computational studies indicate that the singly occupied molecular orbitals (SOMOs) of these species are predominantly ligand-centered, with the largest contribution coming from the $2p_\pi$ orbital on the ligating carbon.^[5] To date, however, very few radical metal-carbene complexes have been spectroscopically characterized due to their transient nature. Following reduction of $[(\text{CO})_5\text{M}=\text{C}(\text{OCH}_3)\text{Ar}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) at low temperatures, the CW-EPR spectra of the corresponding metal-carbene radical anions were measured.^[5c] The small deviation of the observed g values ($g_{\text{obs}} = 2.0031\text{--}2.0064$) from the free electron value ($g_e = 2.0023$) as well as the magnitude of the ^1H hyperfine coupling constants provided experimental support for the redox non-innocence of the carbene ligand. More recently, a combined DFT-EPR study on the electronic structure of two porphyrin Co-carbene radical complexes was reported.^[5a] These species can be generated by the reaction of ethyldiazoacetate with a $\text{Co}(\text{II})$ porphyrin and detected by CW-EPR, albeit as part of a mixture with two other species.

Although computational studies uniformly indicate substantial ligand redox non-innocence in radical metal-carbene complexes, it is not yet clear on the basis of experimental data whether this trend is valid or whether there is a broad spectrum of metal vs. carbene-based redox. Pulse EPR spectroscopy has the potential to provide detailed information about the distribution of spin density in open-shell metal carbenoid species, particularly if the ligating carbon can be ^{13}C -enriched.^[6] Herein, we describe the synthesis and spectroscopic characterization of a series of terminal iron-carbene complexes. The ^1H and ^{13}C isotopologues of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$ were studied by pulse EPR spectroscopy which, in combination with DFT calculations, revealed that Fe-carbene bonding is highly covalent, leading to a more even distribution of spin density between the metal and the ligand than is commonly observed for traditional reduced Fischer carbenes.

Exposure of a black-brown solution of the diiron μ -carbyne, μ -hydride complex $(\text{P}_6\text{ArC})\text{Fe}_2(\mu\text{-H})$ ^[7] in tetrahydrofuran to an atmosphere of CO is accompanied by an immediate color change to red. The ^1H NMR spectrum of the reaction mixture indicates clean conversion to a new diamagnetic species identified by X-ray diffraction studies as the diiron carbene, tricarbonyl complex $(\text{P}_6\text{ArCH})\text{Fe}_2(\text{CO})_3$ ($\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10}$ in Enemark-Feltham type notation, with the superscript denoting the sum of the iron $3d$ and carbene $\sigma+\pi$ electrons for the iron-carbene unit). The solid state structure of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10}$ (Figure 1) reveals that, although both iron centers retain a trigonal bipyramidal geometry, only Fe1 remains bound to the central carbon with a short Fe1-C1 distance of 1.922(3) Å. The second iron (Fe2) is no longer bridged, and instead binds two molecules of CO. A single proton can be located in the Fourier difference map attached to C1, consistent with the observation of a diagnostic $\text{Fe}=\text{C}(\text{H})\text{Ar}$ ^1H NMR resonance at $\delta = 10.90$ (d, $J = 4$ Hz, 1H). As further confirmation of this linkage, the ^{13}C resonance associated with the carbene ligand appears at $\delta = 229$ ppm and exhibits coupling to a single proton ($^1J_{\text{C-H}} = 137$ Hz) by gate-decoupled ^{13}C NMR (Figure S4).

COMMUNICATION

Figure 1. Synthesis and solid state structure of $(P_6ArCH)Fe_2(CO)_3$ ($\{Fe=C(H)Ar\}^{10}$).

When *c.a.* 50% 2H -enriched $(P_6ArC)Fe_2(\mu-H)$ is reacted with CO, the intensity of the 1H resonance at $\delta = 10.90$ resonance is halved, indicating that the μ -hydride ligand is the source of the $Fe=C(H)Ar$ proton (Figure S5). We previously reported that hydrogenation of $(P_6ArC)Fe_2(\mu-H)$ proceeds through an isolable diiron carbene, dihydride species $(P_6ArCH)Fe_2(N_2)_2(H)_2$,^[4] which is structurally related to $\{Fe=C(H)Ar\}^{10}$. In that study, however, deuterium labelling experiments revealed that the μ -hydride ligand is *not* incorporated into the central carbon, distinct from what is observed here. Whereas H_2 activation by $(P_6ArC)Fe_2(\mu-H)$ proceeds via proton transfer or σ -bond metathesis, coordination of CO by $(P_6ArC)Fe_2(\mu-H)$ is evidently accommodated by direct C-H reductive elimination. To the best of our knowledge, this mode of reactivity has not been reported previously for diiron μ -carbyne complexes.^[8]

Insight into the electronic structure of $\{Fe=C(H)Ar\}^{10}$ was obtained by ^{57}Fe Mössbauer spectroscopy in combination with DFT calculations. Three limiting electronic structure descriptions can be envisioned for $\{Fe=C(H)Ar\}^{10}$. Formally, at least, the ligand is dianionic, which would result in the metal oxidation states being either $2Fe(I)$ or $Fe(II)Fe(0)$. Alternatively, however, the arylcarbene ligand may be considered as a neutral *L*-type donor (i.e. a Fischer carbene),^[2] leading to an oxidation state assignment of $2Fe(0)$. The ^{57}Fe Mössbauer spectrum of $\{Fe=C(H)Ar\}^{10}$ (Figure 2) is composed of two sharp quadrupole doublets with $\delta_1 = -0.03$ mm s⁻¹, $|\Delta E_Q|_1 = 2.01$ mm s⁻¹ (orange) and $\delta_2 = -0.11$ mm s⁻¹, $|\Delta E_Q|_2 = 0.94$ mm s⁻¹ (blue). DFT calculations on the *mononuclear* fragments $(P_3)Fe^0(CO)_2$ ($\delta_{calc} = -0.00$ mm s⁻¹, $|\Delta E_Q|_{calc} = 2.04$ mm s⁻¹) and $(P_3)Fe=C(H)Ar$ ($\delta_{calc} = -0.11$ mm s⁻¹, $|\Delta E_Q|_{calc} = 0.77$ mm s⁻¹) accurately reproduce the experimental parameters, inconsistent with a $2Fe(I)$ oxidation state assignment.

Figure 2. Zero-field ^{57}Fe Mössbauer spectrum of $(P_6ArCH)Fe_2(CO)_3$ ($\{Fe=C(H)Ar\}^{10}$) collected at 80 K.

Ambiguity remains, however, regarding the *d* electron count of the iron-carbene motif. The calculated frontier molecular orbitals of the $(P_3)Fe=C(H)Ar$ fragment (Figure 3) include three filled orbitals with predominant Fe character (53-70%). These include orbitals of $3d_{xz,yz}$ parentage (HOMO-2 and HOMO-3) that engage in π -backbonding with the axial CO ligand as well as an orbital derived from $Fe\ 3d_{x^2-y^2}$ (HOMO) which is largely non-bonding due to *d/p* mixing. In addition to these, the $Fe=C(H)Ar$ π -bonding orbital (HOMO-1) appears just below the HOMO in energy and also has substantial Fe character (30%). The lowest unoccupied orbital (LUMO) associated with the $(P_3)Fe=C(H)Ar$ motif is the iron-carbene π -antibonding orbital. In contrast to most Fischer-type carbene complexes, this orbital is not predominantly localized on the ligating carbon, but is more evenly distributed between Fe (24%), C1 (14%) and the aryl substituent (54%). These calculations indicate that the bonding within the $Fe=C(H)Ar$ fragment of $\{Fe=C(H)Ar\}^{10}$ is considerably more covalent than that in traditional Fischer-type carbene complexes, suggesting that both $d^6\ Fe^{II}=C(H)Ar$ and $d^8\ Fe^0 \leftarrow C(H)Ar$ are significant resonance contributors.

Figure 3. Qualitative molecular orbital diagram for $(P_6ArCH)Fe_2(CO)_3$ ($\{Fe=C(H)Ar\}^{10}$, black) and $[Na(THF)_n]([P_6ArCH)Fe_2(CO)_3]$ ($\{Fe=C(H)Ar\}^{11}$, red). Reduction to $\{Fe=C(H)Ar\}^{11}$ places an additional electron (red) in the $Fe-C\ \pi^*$ orbital.

COMMUNICATION

C π^* orbital. Orbital plots (isovalue = 0.05) and population analysis are shown for key Fe-C interactions.

The accessibility of the low-lying $\text{Fe}=\text{C}(\text{H})\text{Ar} \pi^*$ orbital motivated us to target the radical anion $[(\text{P}_3\text{ArCH})\text{Fe}_2(\text{CO})_3]^-$ ($\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$). The cyclic voltammogram of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10}$ in tetrahydrofuran (0.1 M $[n\text{Bu}_4\text{N}][\text{PF}_6]$, Figure S11) exhibits three reversible redox events, including two oxidative features at -0.64 V and -0.99 V (vs. Fc/Fc^+), respectively, and one reductive feature at -2.70 V (vs. Fc/Fc^+). Reduction of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{10}$ on preparative scale with sodium naphthalenide ($\text{Na}[\text{Np}]$) leads to a shift in the vibrational frequency associated with only one of the coordinated CO ligands (Figure S30), suggesting that reduction is localized on the $(\text{P}_3)\text{Fe}=\text{C}(\text{H})\text{Ar}$ fragment. Although the presumed product $[\text{Na}(\text{THF})_n][(\text{P}_3\text{ArCH})\text{Fe}_2(\text{CO})_3]$ ($\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$) is NMR-silent, it exhibits a characteristic EPR signal (Figure 4) with $g = [2.048, 2.015, 2.015] \pm 0.001$, as determined by simulation of both X- and Q-band data.

Figure 4. X-band CW-EPR (top panel) and pseudomodulated^[12] Q-band ESE-EPR (bottom panel) of $[\text{Na}(\text{THF})_n][(\text{P}_3\text{ArCH})\text{Fe}_2(\text{CO})_3]$ ($\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$), in 2-MeTHF (2 mM). Experimental data shown in black and simulations are shown in red. Simulation parameters: $S = 1/2$, $g = [2.048, 2.015, 2.015]$, ^{31}P and ^1H hyperfine parameters in main text and tabulated in Table S5, with broadening parameters: $\text{HStrain} = [80, 10, 10]$ MHz, $\text{gStrain} = [0.006, 0.0035, 0.0035]$.

X-band CW-EPR acquisition parameters: temperature = 7 K; MW frequency = 9.639 GHz; MW power = 2 mW; modulation frequency = 100 kHz; modulation amplitude = 0.4 mT; conversion time = 82 ms. Q-band ESE-EPR acquisition parameters: temperature = 25 K; MW frequency = 33.960 GHz; MW pulse length ($\pi/2$, π) = 40 ns, 80 ns; τ = 240 ns; shot repetition time = 5 ms.

This species proved challenging to crystallize and does not appear to be indefinitely stable, so further characterization was conducted on samples prepared *in situ* at low temperatures. The g tensor associated with $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$ exhibits anisotropy indicative of substantial metal-based spin. To directly evaluate the degree of metal vs. ligand radical character, EPR studies were conducted on the ^2H and ^{13}C isotopologues $\{\text{Fe}=\text{C}(^2\text{H})\text{Ar}\}^{11}$ (^2H -enriched at the carbene C-H) and $\{\text{Fe}=\text{C}(^13\text{C})\text{Ar}\}^{11}$ (^{13}C -labelled at the carbene $\text{Fe}=\text{C}$), respectively. The continuous-wave (CW) EPR spectra of the natural abundance, ^2H -enriched and ^{13}C -labelled samples are nearly identical (Figure 4), indicating that the observed splitting is due to ^{31}P hyperfine coupling alone. Instead, the smaller ^2H and ^{13}C couplings were determined by Q-band electron nuclear double resonance (ENDOR) and hyperfine sublevel correlation (HYSCORE) measurements.^[13,14] These spectroscopies, in combination with the field swept spectra, also allowed for direct detection of couplings to three distinct ^{31}P nuclei, with $A(^{31}\text{P}) = [9.6, 6.5, 9.6]$ MHz, $A(^{31}\text{Pb}) = [28, 20, 36]$ MHz, and $A(^{31}\text{Pc}) = [34, 21, 84]$ MHz.

Simulation of the ^2H - ^1H difference HYSCORE spectra of $\{\text{Fe}=\text{C}(^2\text{H})\text{Ar}\}^{11}$ (Figures S17-19) affords an anisotropic deuterium hyperfine tensor $A(^2\text{H}) = \pm[0.84, 2.15, 2.15]$ MHz, rotated by $(\alpha, \beta, \gamma)^\circ = (40, 30, 0)^\circ$ relative to the coordinate frame of the g tensor. Variable mixing time (VMT) Mims ^2H ENDOR indicates that the absolute sign of $A(^2\text{H})$ is negative, thus $A(^2\text{H}) = [-0.84, -2.15, -2.15]$. Scaling the ^2H hyperfine tensor by the proportion of the $^1\text{H}/^2\text{H}$ gyromagnetic ratios ($^1\text{H}\gamma/^2\text{H}\gamma = 6.514/1$) provides the ^1H hyperfine tensor $A(^1\text{H}) = [-5.5, -14, -14]$ MHz for $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$, which is consistent with simulations of the ^1H - ^2H difference ENDOR spectra (Figure S14).

The proton hyperfine tensor of $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$ can be decomposed into an isotropic contribution $a_{\text{iso}}(^1\text{H}) = -11.2$ MHz and a nearly axial anisotropic component $T(^1\text{H}) = [5.7, -2.8, -2.8]$ MHz. The isotropic coupling arises from spin polarization of the core H 1s electrons and, compared to the expected value for a hydrogen atom ($a_{\text{iso}}^0 = 1420$ MHz),^[9] corresponds to a H 1s spin density of only *c.a.* 0.008 e^- . On the other hand, the anisotropic ^1H hyperfine is attributable to dipolar interactions with the metal- and ligand-based spin. In the principal axis system of the proton hyperfine interaction, the through-space coupling can be calculated according to equation (1)-(2):

$$T(^1\text{H})_{\text{calc}} = t_{\text{dipolar}}[2 \ -1 \ -1] \quad (1)$$

$$t_{\text{dipolar}} = K\mu_0\mu_B\mu_N g_e g_N / 4\pi r^3 \quad (2)$$

Where K is the spin projection factor of the spin-bearing atom, μ_0 is the vacuum permeability, μ_B is the Bohr magneton, μ_N is the nuclear magneton, g_e is the electronic g -factor, g_N is the nuclear g -factor and r is the distance between the proton and the spin-bearing atom.

Thus, in combination with DFT calculations, simulation of $T(^1\text{H})$ using a point dipole model provides a means to validate structural and electronic assignments for $\{\text{Fe}=\text{C}(\text{H})\text{Ar}\}^{11}$. Geometry optimization of the *mononuclear* fragment $[(\text{P}_3)\text{Fe}=\text{C}(\text{H})\text{Ar}]$ provides an estimate for the Fe-H distance of 2.7 Å, from which $T(^1\text{H})_{\text{calc}} = [16, -8, -8]$ MHz can be determined assuming Fe1 bears all of the α spin. However, Löwdin population analysis for the

COMMUNICATION

truncated model $[(P_3)Fe=C(H)Ar]^-$ suggests that the spin density of Fe1 is only c.a. $0.40 e^-$. This infers that $K_{Fe} = 0.4$ and, neglecting all other spin-carrying atoms, reduces the magnitude of the principal components of $T(^1H)_{calc}$ to [6.6, -3.3, -3.3] MHz, which is in reasonable agreement with the experimental tensor $T(^1H) = [5.7, -2.8, -2.8]$ MHz.

Simulations of the HYSCORE spectra (Figure 5) of the ^{13}C -labelled compound $\{Fe=^{13}C(H)Ar\}^{11}$ provide an anisotropic hyperfine tensor $A(^{13}C) = \pm[14, -2, -12]$ MHz for the ligating carbon.

Figure 5. Q-band HYSCORE spectrum of $[Na(THF)_n][(P_6Ar^{13}CH)Fe_2(CO)_3] (\{Fe=^{13}C(H)Ar\}^{11})$ acquired at 1185 mT ($g = 2.047$). Bottom: Monochromatic representation of the HYSCORE data (grey) with simulations of ^{13}C (red), $^{31}P_a$ (blue) and $^{31}P_b$ (green) overlaid using parameters given in the text. Acquisition parameters: temperature = 35 K; microwave frequency = 33.954 GHz; MW pulse length ($\pi/2$, π) = 12 ns, 24 ns; $\tau = 100$ ns, $t_1 = t_2 = 100$ ns; $\Delta t_1 = \Delta t_2 = 12$ ns; shot repetition time (srt) = 1 ms.

Considerable overlap between ^{13}C and ^{31}P ENDOR signals prevented unambiguous determination of the sign of the ^{13}C hyperfine, though DFT calculations predict that both $A(^1H/2H)$ and $A(^{13}C)$ are negative.

From $A(^{13}C)$, it can be inferred that the isotropic coupling to the carbene ligand in $\{Fe=^{13}C(H)Ar\}^{11}$ is negligible ($a_{iso}(^{13}C) \approx 0$ MHz). Although ^{13}C hyperfine couplings have not been reported for any metal-carbene species, comparison can be made to the benzyl radical, for which a proton replaces iron. Room temperature CW-EPR studies of the 90% $^{13}C_7$ -enriched benzyl radical revealed a significantly larger isotropic coupling ($a_{iso}(^{13}C_7) \approx 68.7$ MHz) to the tolyl carbon.^[10] Two synthetic iron-carbyne complexes have also been ^{13}C enriched and exhibit non-negligible isotropic couplings of c.a. 32 MHz.^[6] Evidently, spin polarization of the C 2s electrons in $\{Fe=^{13}C(H)Ar\}^{11}$ is minimal, perhaps due to the relatively small C $2p_\pi$ spin density (*vide infra*).

The anisotropic contribution to the ^{13}C hyperfine in $\{Fe=^{13}C(H)Ar\}^{11}$ $T(^{13}C) = \pm[14, -2, -12]$ MHz arises from local $2p$

contributions, in addition to dipolar interactions with the spin localized at the adjacent atoms.^[9a] The anisotropic tensor $T(^{13}C)$ can be decomposed into two axial terms,^[6a, 11] affording $b_\pi(^{13}C) = -8.7$ MHz and $t_{dipolar}(^{13}C) = 3.3$ MHz. The latter term reflects the strength of the through-space interactions with iron-based spin and is in reasonable agreement with a value of 2.2 MHz predicted using the point dipole model assuming $K_{Fe} = 0.4$. On the other hand, the magnitude of $b_\pi(^{13}C) = -8.7$ MHz reflects the local C $2p_\pi$ spin density at the ligating carbon, which can be estimated at c.a. $0.1 e^-$ by comparison to the intrinsic coupling expected for an electron localized in a C $2p$ orbital ($b_\pi^0 = 90.8$ MHz)^[9a].

Consistent with our interpretation of the ^{13}C EPR data, DFT calculations predict an isotropic ^{13}C coupling of only 2 MHz and a total C1 spin density of only $0.15 e^-$ for the mononuclear model $[(P_3)Fe=C(H)Ar]^-$. Instead, DFT indicates that there is substantial spin density localized at the carbene-bound Fe center (c.a. $0.4 e^-$), in line with simulations of $T(^1H)$. These findings are in contrast with what has been reported for radical metal-carbenoid species to date.^[4a, 5] For example, calculations on the radical anion $[(CO)_5Cr=C(OCH_3)Ar]^-$ indicate that the spin density is biased toward the ligating carbon (65%), with little accumulated at the metal center (c.a. 4% on Cr).^[5c] This description is validated by the fact that the experimental 1H couplings in $[(CO)_5Cr=C(OCH_3)Ar]^-$ are nearly identical to those observed in the benzylic radical $[HC(OCH_3)Ar]^\cdot$, as well as the lack of large ^{53}Cr coupling in $[(CO)_5Cr=C(OCH_3)Ar]^-$. This dichotomy highlights the enhanced Fe-C covalency in $\{Fe=C(H)Ar\}^{10/11}$ compared to more traditional Fischer-type carbenes. The $\{Fe=C(H)Ar\}^{11}$ species discussed herein serves as a rare but well-defined reference compound for comparison to data reported for *in situ* trapped-intermediates.

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Keywords: metal-carbene • open-shell complexes • pulse EPR • organometallics • redox non-innocence

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COMMUNICATION

Entry for the Table of Contents

Presented herein are detailed $1/2H$ and ^{13}C pulse EPR and DFT investigations of an $S = 1/2$ terminal iron-carbene species. These studies reveal substantial spin density localized at the carbene-bound Fe center, in contrast with what has been reported to date for radical metal-carbenoid species. The $\{Fe=C(H)Ar\}^{11}$ complex serves as a rare but well-defined reference compound for comparison to data reported for *in situ* trapped-intermediates.