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CO Cleavage Promoted by Acetylide Addition to Vinyliminium Diiron Complexes

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The vinyliminium complex [Fe_2\{μ-η^1:η^3-C(Me)=C(Me)-C=N(Me)(Xyl)\}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**1**; Xyl = 2,6-$Me_2C_6H_3$) reacts with LiC≡CR [R = C_6H_4Me = Tol, Ph, H, *n*Bu, $SiMe_3$, C(Me)=CH_2] affording the amido-functionalized allylidene complexes [Fe_2\{μ-κ^1(O):η^1(C):η^3(C)-C(C≡CR)-C(Me)C(Me)C(O)N(Me)(Xyl)\}(μ-CO)$(Cp)_2$] [R = C_6H_4Me = Tol, **2**; R = Ph, **3**; R = H, **4**; R = *n*Bu, **5**; R = $SiMe_3$, **6**; R = C(Me)=CH_2, **7**] in good yields. Labelling experiments with ^{13}CO-enriched **1** indicate that formation of **2**–**7** occurs through cleavage of the carbon–oxygen bond of a coordinated CO ligand. The molecular structure of **2** has been determined by an X-ray diffraction study.
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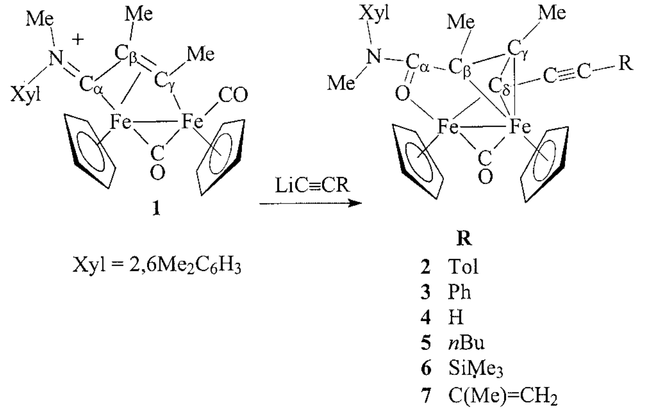
Introduction

Recently, we described the successful preparation of bridging vinyliminium diiron complexes[1] and demonstrated the electrophilic character of the bridging ligand. Regio- and stereoselective additions of hydride ($NaBH_4$) to the μ-vinyliminium have been described in detail.[2] With the aim of extending our investigations to the addition of carbon nucleophiles, we have examined the reaction with lithium acetylides. Here, we report on the rearrangement occurring at the bridging ligand as a consequence of acetylide attack. This involves a terminally coordinated carbonyl, which undergoes CO cleavage and incorporation in the bridging ligand.

Result and Discussion

Complex *cis*-[Fe_2\{μ-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)\}-(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**1**) rapidly reacts with an excess of lithium acetylide (LiC≡CR), affording the air-stable compounds *cis*-[Fe_2\{μ-κ^1(O):η^1(C):η^3(C)-C(C≡CR)C(Me)-C(Me)C(O)N(Me)(Xyl)\}(μ-CO)$(Cp)_2$] (**2**–**7**), in about 60–70% yield (Scheme 1).



Scheme 1.

The molecular structure of **2** has been determined by X-ray diffraction: two different views of the molecule are shown in Figure 1, whereas relevant bond lengths and bond angles are reported in Table 1; the structure of the bridging ligand is also shown in Scheme 2.

The molecule is composed by a Fe_2(μ-CO)$(Cp)_2$ core with a bridging amido-functionalized allylidene μ-κ^1-(O):η^1(C):η^3(C)-\{C(C≡CR)C(Me)C(Me)C(O)N(Me)(Xyl)\} ligand, which is σ-coordinated to Fe(1) [Fe(1)–C(12) 1.923(4) Å] and η^3-coordinated to Fe(2) [Fe(2)–C(12) 2.004(4) Å; Fe(2)–C(21) 2.030(4) Å; Fe(2)–C(23)– 2.157(4) Å], in an allyl-like fashion (see structure **A** in Scheme 2). The Fe(2)–C(23) interaction is significantly longer than that of Fe(2)–C(12) and Fe(2)–C(21), suggesting that an alternative description of the bridging ligand is possible (Scheme 2, **B**). The C_β–C_γ–C_δ sequence [C(23)–C(21)–C(12)] can be considered as a vinyl-substituted μ-alkylidene, which corresponds to a coordination mode commonly found in diiron[2] and diruthenium[3] complexes. However, because the C(12)–C(21) interaction [1.417(5) Å] is shorter than in C(21)–C(23) [1.455(6) Å] a description of the ligand as η^1:η^2-vinyl connected to an alkynyl and an amido-functionality also appears possible (structure **C**). The coordination of the amido group to Fe(1) is presumably crucial in determining the observed geometry of the bridging ligand. The oxygen atom O(2) coordinates to Fe(1) forming a five-membered oxadimetallacycle with a Fe–O

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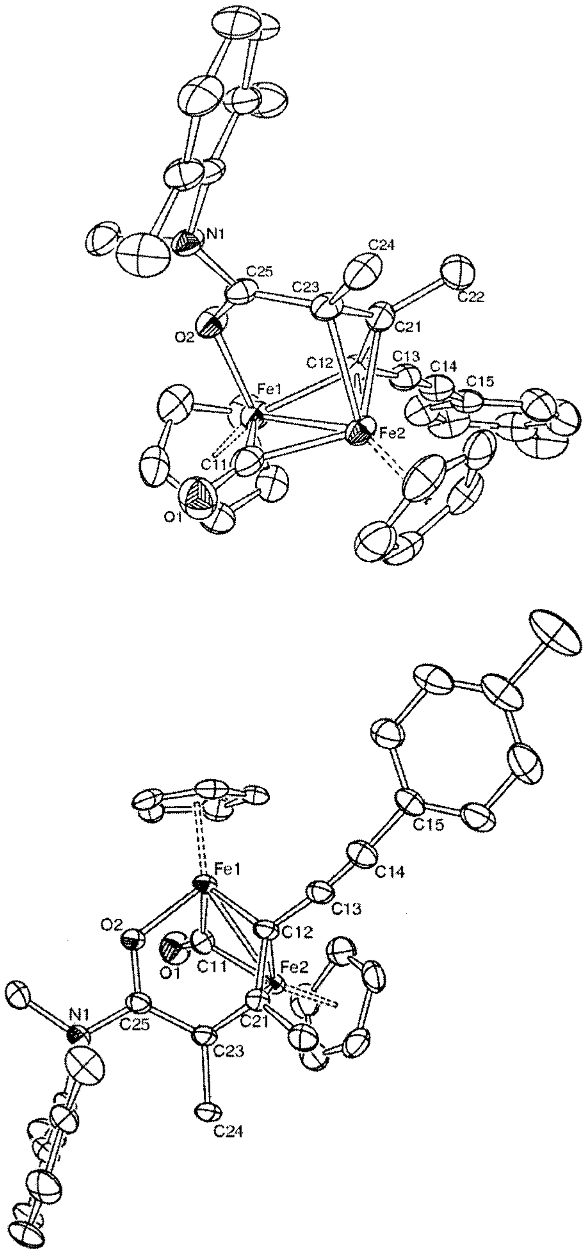
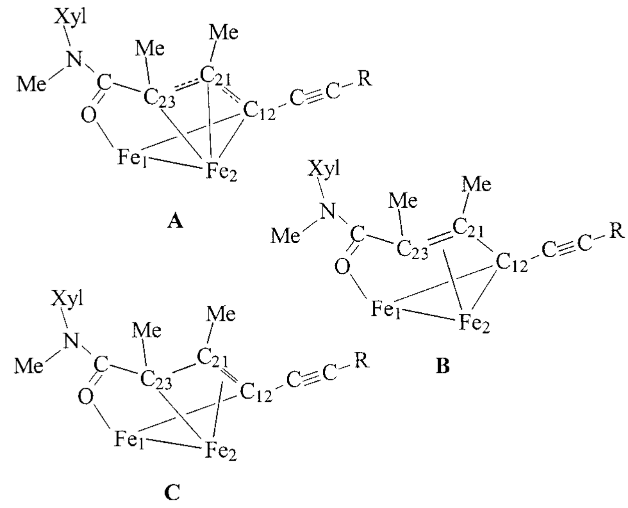


Figure 1. Different views of the molecular structure of **2** (hydrogen atoms are omitted for clarity). Displacement ellipsoids are at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2**.

Fe(1)–Fe(2)	2.5131(8)	C(13)–C(14)	1.191(6)
Fe(1)–C(11)	1.858(5)	C(14)–C(15)	1.443(6)
Fe(2)–C(11)	1.938(5)	C(12)–C(21)	1.417(5)
Fe(1)–C(12)	1.923(4)	C(21)–C(22)	1.506(6)
Fe(2)–C(12)	2.004(4)	C(21)–C(23)	1.455(6)
Fe(2)–C(21)	2.030(4)	C(23)–C(24)	1.529(5)
Fe(2)–C(23)	2.157(4)	C(23)–C(25)	1.464(6)
Fe(1)–O(2)	1.941(3)	C(25)–O(2)	1.267(4)
C(11)–O(1)	1.205(5)	C(25)–N(1)	1.363(5)
C(12)–C(13)	1.440(6)	C(26)–N(1)	1.477(5)
Fe(1)–C(11)–Fe(2)	82.9(2)	C(22)–C(21)–C(23)	120.7(4)
Fe(1)–C(12)–Fe(2)	79.56(16)	C(21)–C(23)–C(24)	118.8(4)
Fe(1)–C(12)–C(21)	121.1(3)	C(21)–C(23)–C(25)	115.7(4)
C(13)–C(12)–C(21)	119.0(4)	C(24)–C(23)–C(25)	119.1(4)
C(12)–C(13)–C(14)	172.9(5)	C(23)–C(25)–O(2)	121.6(4)
C(13)–C(14)–C(15)	174.9(5)	C(23)–C(25)–N(1)	124.4(4)
C(12)–C(21)–C(23)	118.1(4)	O(2)–C(25)–N(1)	114.0(4)
C(12)–C(21)–C(22)	121.1(4)	C(25)–O(2)–Fe(1)	121.1(3)



Scheme 2.

bond length [Fe(1)–O(2) 1.941(3) Å] slightly shorter than in $[Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}\eta^1(O):\eta^1(C):\eta^2(C)\text{-}\{O=C(N\textit{t}BuH)\text{-}CH_2\}C=CH_2)]$ [2.017(5) Å][4] and $[Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}dppm)\{C(CO_2\text{–}Me)=CHC(OMe)=O\}]$ [2.024(3) Å],[5] which contain a diiron five-membered oxametallacycle.

The spectroscopic data of **2** are in agreement with its structure: the IR spectrum (in CH_2Cl_2 solution) exhibits one band for the bridging carbonyl group, at 1753 cm^{-1}, whereas weaker absorptions at 2169 cm^{-1} and 1511 cm^{-1} are attributable to the C≡C and to the amide C–O interactions, respectively. NMR assignments, based on gs-HSQC, gs-HMBC and NOE experiments evidence a single ^1H NMR resonance for each of the six different Me groups present in **2** (at δ = 2.75, 2.42, 2.40, 2.30, 1.55 and 0.47 ppm, assigned to $C_\gamma Me$, NMe, C_6H_4Me, $Me_2C_6H_3$, $C_\beta Me$, respectively). In particular, assignments of the $C_\gamma Me$ and $C_\beta Me$ resonances are based on observed NOE effects between $C_6H_3Me_2$ (Xyl) and $C_\beta Me$. ^{13}C NMR resonances at δ = 179.7 and 155.5 ppm, are assigned to C_α and C_δ, respectively. The attribution of these two signals is crucial in the later described experiment and deserves some comments: the gs-HMBC spectrum evidences correlation between the ^1H NMR resonance at δ = 2.42 ppm (NMe) and the ^{13}C resonance at δ = 179.7 ppm, while the ^{13}C NMR signal falling at δ = 155.5 ppm presents only one correlation, i.e. with the ^1H NMR resonance at δ = 2.75 ppm ($C_\gamma Me$). It is worth noting that the *C*O resonance, in other analogous iron-coordinated amido functionalities, is reported at ca. 182 ppm.[4] Moreover, the C_γ and C_β carbon atoms give raise to signals at δ = 96.6 and 52.3 ppm, whereas the *sp* carbon atoms of the acetylenic group typically fall at δ = 104.5 and 101.6 ppm.

The reaction sequence leading to **2**–**7** is far from being obvious. One possibility is that the reaction proceeds through initial attack of the acetylide to the terminal carbonyl group of **1**, originating an acyl intermediate, which further rearrange involving the μ-vinyliminium ligand. Support for this hypothesis comes from the observation that acetylides selectively attack the terminal CO in the related complexes $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$.[6] Moreover, nucleophilic attack to CO is often followed by coupling with the bridging ligands. For instance, $LiC{\equiv}CPh$ addition to the CO in the thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ is followed by the migration of the acyl ligand, leading to the formation of the μ-carbene complexes $[Fe_2\{\mu\text{-}C(SMe)C(O)CCPh\}(\mu\text{-}CO)(CO)(Cp)_2]$.[7] Similarly, the allenyl $[Fe_2\{\mu\text{-}PPh_2\}(\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C{=}C{=}CH_2)(CO)_6]$ undergoes amine addition to the terminal CO, with consequent migration of the resulting amide to the allenyl moiety.[4] The unexpected formation of **2**–**7** does not simply concern the coupling between acyl- and vinyliminium ligands: if we assume that the $C_{\delta}{-}C{\equiv}C{-}R$ moiety in the bridging ligand of **2**–**7** originates from an acyl intermediate $[C(O)C{\equiv}C{-}R]$, this implies the cleavage of the C=O.

Alternatively, the $C_{\alpha}{=}O$ moiety in the bridging ligand of **2**–**7** could be originated from a migration of the terminal CO group, and acetylide addition at the C_{α} of the vinyliminium ligand. This, in turn, would require a considerable rearrangement of the iminium moiety, with 1,2 shifts of the Me and NR_2 groups, in order to explain the formation of **2**–**7**.

With the aim of obtaining more evidence for the reaction mechanism, we have prepared a ^{13}CO-enriched sample of **1**, which has been reacted with $Li{-}C{\equiv}C{-}Tol$ (see Exp. Section). The reaction yielded compound **2**, as expected, and the corresponding ^{13}C NMR spectrum exhibited two clearly enhanced signals at δ = 291.6 (μ-CO) and 155.8 ppm (C_{δ}), and doublets at δ = 96.1 ($^1J_{CC}$, 50.7 Hz, C_{γ}), 52.4 ($^2J_{CC}$, 11.9 Hz, C_{β}), and 20.9 ppm ($^2J_{CC}$, 4.5 Hz, $C_{\gamma}Me$). Moreover, the IR spectra showed an isotopic effect for the bridging CO group and not for the $C_{\alpha}{=}O$ of the bridging ligand. The above mentioned experiment indicates that the C_{δ} in **2** is originated from a carbonyl ligand, and implies that CO cleavage must occur at some stage of the reaction, as suggested in the former hypothesis. Interestingly, in the conversion of **1** to **2**, the three-carbon-atom chain of the bridging ligand grows by several units as a consequence of the inclusion of both the alkynyl ($C{\equiv}C{-}Tol$) group and the C_{δ} carbon atom, the latter originating from a CO.

Finally, it is to be remarked that reactions of organometallic complexes involving CO cleavage are of great interest, because this is considered an early and fundamental step in the heterogeneous conversion of carbon monoxide to hydrocarbons (Fischer–Tropsch process).[8] Examples, so far reported, mainly concerns: carbonyl clusters, which generally provide metal carbides,[9] polynuclear early transition-metal complexes, that take advantage of the oxophilic character of these metals for promoting CO dissociation,[10] and dinuclear tungsten complexes, with multiple metal–metal bonds.[11] Our results further support the conviction[8b] that dinuclear complexes are effective organometallic models for studying CO cleavage and C–C bond formation.

Experimental Section

General Remarks: All reactions were routinely carried out under nitrogen, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded at 298 K with a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed with a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K with a Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned by $^1H,^{13}C$ correlation measured by means of gs-HSQC and gs-HMBC experiments.[12] NOE measurements were recorded using the DPFGSE-NOE sequence.[13] All the reagents, included ^{13}CO, were commercial products (Aldrich) of the highest purity available and used as received. Compound **1** was prepared by published methods.[1a]

Synthesis of $[Fe_2\{\mu\text{-}\kappa^1(O){:}\eta^1(C){:}\eta^3(C)\text{-}C(C{\equiv}CR)C(Me)C(Me)C(O)N(Me)(Xyl)\}(\mu\text{-}CO)(Cp)_2]$ [R = C_6H_4Me = Tol, 2; R = Ph, 3; R = H, 4; R = *n*Bu, 5; R = $SiMe_3$, 6; R = $C(Me){=}CH_2$, 7]. General Procedure: A solution of *cis*-$[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me){=}C(Me)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1**) (0.150 mmol), in THF (10 mL) was treated with $LiC{\equiv}CR$ (0.350 mmol), freshly prepared from *n*BuLi and $HC{\equiv}CR$. The mixture was stirred for 30 min, and then it was filtered through a Celite pad. The solvent was removed under reduced pressure; hence the residue was dissolved in diethyl ether and filtered through alumina. The final product was obtained as a red powder upon removal of the solvent. Crystals of **2** suitable for X ray analysis were obtained from a hexane solution at –20 °C.

2: $C_{35}H_{35}Fe_2NO_2$ (613.35): calcd. C 68.54, H 5.75, N 2.28; found: C 68.46, H 5.64, N 2.33. Yield: 57 mg, 62%. ^1H NMR ($CDCl_3$): δ = 7.61–6.81 (m, 7 H, $Me_2C_6\mathit{H}_3$ and $C_6\mathit{H}_4Me$), 4.55, 4.08 (s, 10 H, Cp), 2.75 (s, 3 H, $C_{\gamma}Me$), 2.42 (s, 3 H, NMe), 2.40 (s, 3 H, $C_6H_4\mathit{Me}$), 2.30, 1.55 (s, 6 H, $\mathit{Me}_2C_6H_3$), 0.47 (s, 3 H, $C_{\beta}Me$) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 291.3 (μ-CO), 179.7 (C_{α}), 155.5 (C_{δ}), 143.1 (*ipso*-$Me_2\mathit{C}_6H_3$), 136.8–123.5 ($Me_2\mathit{C}_6H_3$ and C_6H_4Me), 104.5, 101.6 ($C{\equiv}C$), 96.6 (C_{γ}), 85.1, 83.5 (Cp), 52.3 (C_{β}), 39.5 (NMe), 22.2 ($C_{\beta}\mathit{Me}$), 21.5 ($C_6H_4\mathit{Me}$), 20.9 ($C_{\gamma}\mathit{Me}$), 18.2, 17.3 ($\mathit{Me}_2C_6H_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2169 w ($C{\equiv}C$), 1753 vs. (μ-CO), 1511 w ($C_{\alpha}O$) cm^{-1}.

3: $C_{34}H_{33}Fe_2NO_2$ (599.32): calcd. C 68.14, H 5.55, N 2.34; found C 68.19, H 5.57, N 2.39. Yield: 68 mg, 76%. ^1H NMR ($CDCl_3$): δ = 7.71–6.82 (m, 8 H, $Me_2C_6\mathit{H}_3$ and C_6H_5), 4.56, 4.09 (s, 10 H, Cp), 2.76 (s, 3 H, $C_{\gamma}Me$), 2.43 (s, 3 H, NMe), 2.30, 1.56 (s, 6 H, $\mathit{Me}_2C_6H_3$), 0.48 (s, 3 H, $C_{\beta}Me$) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 291.0 (μ-CO), 179.7 (C_{α}), 154.9 (C_{δ}), 143.1 (*ipso*-$Me_2\mathit{C}_6H_3$), 135.4–126.6 ($Me_2\mathit{C}_6H_3$ and C_6H_5), 105.2, 101.4 ($C{\equiv}C$), 96.8 (C_{γ}), 85.1, 83.5 (Cp), 52.4 (C_{β}), 39.5 (NMe), 22.2 ($C_{\beta}\mathit{Me}$), 20.9 ($C_{\gamma}\mathit{Me}$), 18.2, 17.3 ($\mathit{Me}_2C_6H_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2170 w ($C{\equiv}C$), 1751 vs. (μ-CO), 1511 w ($C_{\alpha}O$) cm^{-1}.

4: $C_{28}H_{29}Fe_2NO_2$ (523.23): calcd. C 64.27, H 5.59, N 2.68; found C 64.19, H 5.57, N 2.62. Yield: 56 mg, 71%. ^1H NMR ($CDCl_3$): δ = 7.55–6.77 (m, 3 H, $Me_2C_6\mathit{H}_3$), 4.48, 4.05 (s, 10 H, Cp), 3.15 (s, 1 H, $C{\equiv}CH$), 2.70 (s, 3 H, $C_{\gamma}Me$), 2.41 (s, 3 H, NMe), 2.28, 1.53 (s, 6 H, $\mathit{Me}_2C_6H_3$), 0.46 (s, 3 H, $C_{\beta}Me$) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1762 vs. (μ-CO) cm^{-1}.

5: $C_{32}H_{37}Fe_2NO_2$ (579.33): calcd. C 66.34, H 6.44, N 2.42; found C 66.30, H 6.52, N 2.36. Yield: 49 mg, 56%. ^1H NMR ($CDCl_3$): δ = 7.20–6.82 (m, 3 H, $Me_2C_6\mathit{H}_3$), 4.47, 4.02 (s, 10 H, Cp), 2.65 (s, 3 H, $C_{\gamma}Me$), 2.41 (s, 3 H, NMe), 2.33 (m, 2 H, $C{\equiv}C\mathit{CH}_2$), 2.29, 1.53 (s, 6 H, $\mathit{Me}_2C_6H_3$), 1.68 (m, 2 H, $C{\equiv}CCH_2\mathit{CH}_2$), 1.51–1.35

(m, 2 H, $C\equiv CCH_2CH_2CH_2$), 1.03 (t, 3 H, $^3J_{HH}$ = 7 Hz, $C\equiv CCH_2CH_2CH_2CH_3$), 0.44 (s, 3 H, $C_\beta Me$) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 291.5 (μ-CO), 179.2 (C_α), 155.8 (C_δ), 143.1 (*ipso*-$Me_2C_6H_3$), 136.8–124.3 ($Me_2C_6H_3$ and C_6H_4Me), 110.5, 105.7 ($C\equiv C$), 96.5 (C_γ), 85.2, 83.5 (Cp), 52.4 (C_β), 39.5 (NMe), 32.5 ($C\equiv CCH_2$), 23.0 ($C\equiv CCH_2CH_2$), 22.2 ($C_\beta Me$), 20.8 ($C_\gamma Me$), 19.2 ($C\equiv CCH_2CH_2CH_2$), 18.3, 17.4 ($Me_2C_6H_3$), 14.2 ($C\equiv CCH_2CH_2CH_2CH_3$) ppm. IR ($CH_2Cl_2$): ṽ = 2206 w ($C\equiv C$), 1754 vs. (μ-CO) cm^{-1}.

6: $C_{31}H_{37}Fe_2NO_2Si$ (595.41): calcd. C 62.53, H 6.26, N 2.35; found C 62.48, H 6.39, N 2.44. Yield: 63 mg, 71%. ^1H NMR ($CDCl_3$): δ = 7.24–6.80 (m, 3 H, $Me_2C_6H_3$), 4.45, 4.02 (s, 10 H, Cp), 2.68 (s, 3 H, $C_\gamma Me$), 2.40 (s, 3 H, NMe), 2.28, 1.52 (s, 6 H, $Me_2C_6H_3$), 0.45 (s, 3 H, $C_\beta Me$), 0.39 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 291.0 (μ-CO), 179.5 (C_α), 155.1 (C_δ), 143.0 (*ipso*-$Me_2C_6H_3$), 135.4, 134.8, 128.5, 127.8, 127.3 ($Me_2C_6H_3$), 120.2, 104.3 ($C\equiv C$), 97.3 (C_γ), 85.4, 83.7 (Cp), 52.3 (C_β), 39.4 (NMe), 22.1 ($C_\beta Me$), 20.7 ($C_\gamma Me$), 18.2, 17.3 ($Me_2C_6H_3$), 1.21 ($SiMe_3$) ppm. IR (CH_2Cl_2): ṽ = 2101 w ($C\equiv C$), 1758 vs. (μ-CO), 1515 w ($C_\alpha O$) cm^{-1}.

7: $C_{31}H_{33}Fe_2NO_2$ (563.29): calcd. C 66.10, H 5.91, N 2.49; found C 65.99, H 5.94, N 2.50. Yield: 55 mg, 65%. ^1H NMR ($CDCl_3$): δ = 7.23–6.80 (m, 3 H, $Me_2C_6H_3$), 5.47, 5.31 (m, 2 H, CH_2), 4.50, 4.05 (s, 10 H, Cp), 2.68 (s, 3 H, $C_\gamma Me$), 2.41 (s, 3 H, NMe), 2.28, 1.53 (s, 6 H, $Me_2C_6H_3$), 2.23 (s, 3 H, $C\equiv CCMe$), 0.45 (s, 3 H, $C_\beta Me$) ppm. ^{13}C{^1H} NMR ($CDCl_3$): δ = 327.8 (μ-C), 253.9 (μ-CO), 208.1 (t-CO), 133.5–129.5 ($Me_2C_6H_3$), 91.4, 89.9 (Cp), 56.3 (NMe), 19.3, 18.2 ($Me_2C_6H_3$) ppm. IR (CH_2Cl_2): ṽ = 2160 w ($C\equiv C$), 1757 vs. (μ-CO), 1514 w ($C_\alpha O$) cm^{-1}.

Synthesis of ^{13}CO-Labelled 2: The aminocarbyne complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$ (450 mg, 0.938 mmol), prepared by published method,[14] was dissolved in CH_2Cl_2 (10 mL). ^{13}CO was bubbled through the solution, then $AgSO_3CF_3$ (289 mg, 1.12 mmol) was added. The mixture was stirred for 20 minutes, then it was filtered through an alumina column. Elution with methanol gave $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(^{13}CO)_2(Cp)_2][SO_3CF_3]$. ^{13}CO enrichment occurred exclusively at the terminally coordinated CO.

Conversion of ^{13}CO labelled $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(^{13}CO)_2(Cp)_2][SO_3CF_3]$ into ^{13}C-labelled **2** was performed in further five steps, according to known procedures,[1,14] including the reaction described in this paper. The sequence included: $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}^{13}CO)(^{13}CO)(NCMe)(Cp)_2][SO_3CF_3]$, $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}^{13}CO)(^{13}CO)(Cl)(Cp)_2]$, ^{13}CO-enriched **1** and ^{13}C-labelled **2**. At each step the products were isolated and characterized to reveal the enhanced signals.

^{13}C-Labelled 2: ^1H NMR ($CDCl_3$): δ = 7.61–6.81 (m, 7 H, $Me_2C_6H_3$ and C_6H_4Me), 4.56, 4.08 (s, 10 H, Cp), 2.76 (d, $^3J_{CH}$ = 3.66 Hz, 3 H, $C_\gamma Me$), 2.42 (s, 3 H, NMe), 2.40 (s, 3 H, C_6H_4Me), 2.30, 1.56 (s, 6 H, $Me_2C_6H_3$), 0.48 (s, 3 H, $C_\beta Me$) ppm. ^{13}C{^1H} NMR ($CDCl_3$): δ = 291.6 (μ-CO), 179.7 (C_α), 155.8 (C_δ), 143.1 (*ipso*-$Me_2C_6H_3$), 136.8–123.5 ($Me_2C_6H_3$ and C_6H_4Me), 104.5, 101.6 ($C\equiv C$), 96.1 (d, $^1J_{CC}$ = 50.7 Hz, C_γ), 85.4, 82.9 (Cp), 52.4 (d, $^2J_{CC}$ = 11.9 Hz, C_β), 39.7 (NMe), 22.2 ($C_\beta Me$), 21.4 (C_6H_4Me), 20.9 (d, $^2J_{CC}$ = 4.5 Hz, $C_\gamma Me$), 18.5, 17.3 ($Me_2C_6H_3$) ppm. IR (CH_2Cl_2): ṽ = 2169 w ($C\equiv C$), 1750 vs. (μ-CO), 1717 s (μ-^{13}CO), 1511 w ($C_\alpha O$) cm^{-1}.

X-ray Crystallographic Study: Crystal data and collection details for **2** are reported in Table 2. The diffraction experiments were carried out with a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo-K_α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[15] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[16] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Table 2. Crystal data and experimental details for **2**.

Complex	2
Formula	$C_{35}H_{35}Fe_2NO_2$
Mol. mass	613.34
T [K]	293(2)
λ [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.5614(6)
b [Å]	10.2070(6)
c [Å]	16.7137(11)
α [°	104.786(2)
β [°	98.907(2)
γ [°	101.339(2)
Cell volume [Å]^3	1509.76(16)
Z	2
D_c [g·cm^{-3}]	1.349
μ [mm^{-1}]	0.992
F(000)	640
Crystal size, mm	0.26×0.23×0.13
θ limits [°]	1.29–26.37
Reflections collected	15228
Independent reflections	6171 (R_{int} = 0.0665)
Data / restraints / parameters	6171 / 0 / 367
Goodness on fit on F^2	0.900
R_1 [$I > 2\sigma(I)$]	0.0578
wR_2 (all data)	0.1531
Largest diff. peak and hole, e·Å^{-3}	0.733 / –0.618

CCDC-276446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* **2003**, *22*, 1326–1331; b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* **2004**, *689*, 528–538.

[2] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* **2004**, *23*, 3348–3353; b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* **2005**, *690*, 837–846.

[3] R. E. Colborn, A. F. Dyke, B. P. Gracey, S. A. R. Knox, K. A. Macpherson, K. A. Mead, A. G. Orpen, *J. Chem. Soc., Dalton Trans.* **1990**, 761–771.

[4] S. Doherty, M. R. J. Elsegood, W. Clegg, M. Waugh, *Organometallics* **1996**, *15*, 2688–2691.

[5] G. Hogarth, M. H. Lavender, *J. Chem. Soc., Dalton Trans.* **1994**, 3389–3396.

[6] V. G. Albano, L. Busetto, C. Camiletti, C. Castellari, M. Monari, V. Zanotti, *J. Chem. Soc., Dalton Trans.* **1997**, 4671–4676.

[7] S. Bordoni, L. Busetto, C. Camiletti, V. Zanotti, V. G. Albano, M. Monari, F. Prestopino, *Organometallics* **1997**, *16*, 1224–1232.

[8] a) P. M. Maitlis, *J. Organomet. Chem.* **2004**, *689*, 4366–4374; b) M. L. Turner, N. Marsih, B. E. Mann, R. Quyoum, H. C. Long, P. M. Maitlis, *J. Am. Chem. Soc.* **2002**, *124*, 10456–10472; c) M. J. Overett, R. O. Hill, J. R. Moss, *Coord. Chem. Rev.* **2000**, *206–207*, 581–605; d) M. W. Roberts, *Chem. Soc. Rev.* **1977**, *6*, 373–391.

[9] a) D. F. Shriver, M. J. Sailor, *Acc. Chem. Res.* **1988**, *21*, 374–379; b) C. P. Horwitz, D. F. Shriver, *J. Am. Chem. Soc.* **1985**, *107*, 8147–8153; c) C. P. Horwitz, D. F. Shriver, *Adv. Organomet. Chem.* **1984**, *23*, 219–305; d) E. L. Muetterties, J. Stein, *Chem. Rev.* **1979**, *79*, 479–490; e) B. E. Kahn, R. D. Rieke, *Chem. Rev.* **1988**, *88*, 733–745.

[10] a) D. R. Neithamer, R. E. LaPointe, T. A. Wheeler, D. S. Richeson, G. D. Van Duyne, P. T. Wolczanski, *J. Am. Chem. Soc.* **1989**, *111*, 9056–9072; b) F. Calderazzo, U. Englert, A. Guarini, F. Marchetti, G. Pampaloni, A. Segre, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1188–1189; c) R. L. Miller, R. Toreki, R. E. LaPointe, P. T. Wolczanski, G. D. Van Duyne, C. Roe, *J. Am. Chem. Soc.* **1993**, *115*, 5570–5588.

[11] a) R. L. Miller, P. T. Wolczanski, *J. Am. Chem. Soc.* **1993**, *115*, 10422–10423; b) M. H. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib, J. C. Huffman, *J. Am. Chem. Soc.* **1992**, *114*, 7056–7065.

[12] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* **1993**, *31*, 287–292.

[13] K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199–4200.

[14] V. G. Albano, L. Busetto, M. Monari, V. Zanotti, *J. Organomet. Chem.* **2000**, *606*, 163.

[15] G. M. Sheldrick, *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.

[16] G. M. Sheldrick, *SHELX97*, Program for crystal structure determination, University of Göttingen, Germany, **1997**.

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