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Novel Intramolecular Chemistry Involving Thiolate, Vinyl, and Carbonyl Ligands in Reactions of Acetylenes with Li[(μ-RS)(μ-CO)$Fe_2(CO)_6$]

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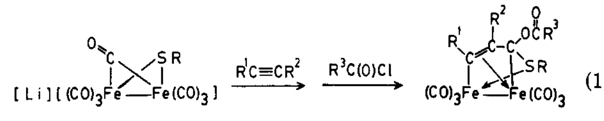
Summary: The products obtained in a reaction sequence involving the addition of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ anions to acetylenes and subsequent reaction of the anionic product with an electrophile depend on the counterion (Et_3NH^+ vs. Li^+), on the substituents on the acetylene, on the organic group of the RS ligand, on the reaction temperature, and on the added electrophile.

The reactions of acetylenes, $R^1C{\equiv}CR^2$, with the triethylammonium salt of the $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ anions, **1**,[1] proceed straightforwardly with loss of CO to give as final products complexes of type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}CHR^2)(\mu\text{-RS})Fe_2(CO)_6$, generally in good yield.[2] In these conversions, the vinylic proton is supplied by the Et_3NH^+ counterion. In order to expand the scope of this chemistry through other reactions of the presumed intermediate anion $[(\mu\text{-}\sigma,\pi\text{-}R^1C{=}\bar{C}R^2)(\mu\text{-RS})Fe_2(CO)_6]$ (**2**) with electrophiles other than the proton, we prepared the Li^+ salts of anions of type **1** by the action of RSLi on $Fe_3(CO)_{12}$.[1] In our initial studies, acid chlorides were the electrophiles added to react with the presumed **2**. We report here our initial results at the present time because some novel chemistry involving thiolato, vinyl, and carbonyl ligands has been encountered.

Reaction of Li[(μ-RS)(μ-CO)$Fe_2(CO)_6$] with the activated acetylenes $CH_3O_2CC{\equiv}CCO_2CH_3$, $HC{\equiv}CCO_2CH_3$, and $HC{\equiv}CC(O)CH_3$ followed by addition of an acid chloride, $R_3C(O)Cl$ (R^3 = CH_3, $(CH_3)_3C$, C_6H_5), gave, in generally good yields, products of type **3** (eq 1).[3] These products were unexpected and unusual in that (1) a carbonyl ligand has been incorporated into the organic framework through bridging between the vinyl and thiolato ligands while a bond to its parent metal center is retained, (2) the originally symmetrical thiolato bridge has been cleaved in the process and only a dative S–Fe bond is retained, and (3) a new anion, **4** (cf. Scheme I), in which the negative charge is on the oxygen atom of the "inserted" CO, has been generated.



(1)

a	$R^1 = R^2 = CO_2Me$	$R^3 = Me$	$R = {}^tBu$	87 %
b	$R^1 = R^2 = CO_2Me$	$R^3 = Me$	$R = Et$	77 %
c	$R^1 = R^2 = CO_2Me$	$R^3 = Me$	$R = Ph$	60 %
d	$R^1 = R^2 = CO_2Me$	$R^3 = Ph$	$R = {}^tBu$	90 %
e	$R^1 = R^2 = CO_2Me$	$R^3 = {}^tBu$	$R = {}^tBu$	52 %
f	$R^1 = H$ $R^2 = CO_2Me$	$R^3 = Me$	$R = {}^tBu$	65 %
g	$R^1 = H$ $R^2 = C(O)Me$	$R^3 = Me$	$R = {}^tBu$	68 %

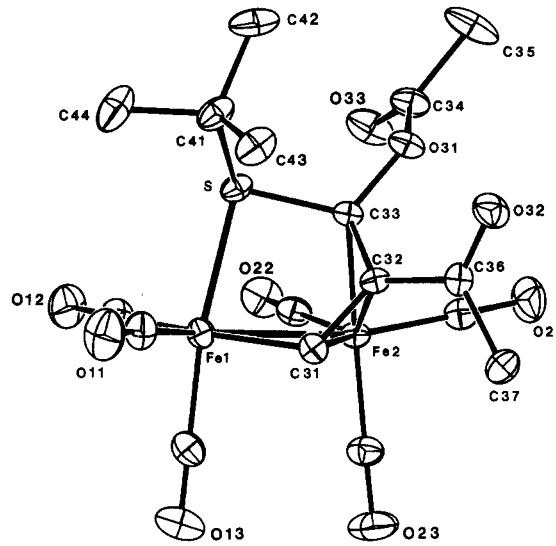


Figure 1. ORTEP diagram of **3g** showing the 30% probability thermal ellipsoids and the atom labeling scheme. Hydrogen atoms have been omitted. Bond lengths (in Å) are as follows: Fe(1)–Fe(2) = 2.267 (1), Fe(1)–S = 2.291 (1), Fe(1)–C(31) = 1.945 (4), Fe(2)–C(31) = 2.065 (4), Fe(2)–C(32) = 2.055 (4), Fe(2)–C(33) = 2.060 (4), C(31)–C(32) = 1.408 (6), C(32)–C(33) = 1.449 (6), C(33)–S = 1.767 (5), C(41)–S = 1.874 (5), C(33)–O(31) = 1.408 (5), O(31)–C(34) = 1.380 (5), C(34)–O(33) = 1.188 (6), C(34)–C(35) = 1.502 (7), C(32)–C(36) = 1.489 (6), C(36)–O(32) = 1.212 (6), C(36)–C(37) = 1.522 (7), C(41)–CH_3(mean) = 1.545, Fe–CO(mean) = 1.795, FeC–O(mean) = 1.138.

Structure proof of complexes **3** by IR and NMR spectroscopy was not straightforward,[4] so a single-crystal X-ray diffraction study of the product **3g** was undertaken.[5] The structure is shown in Figure 1. It consists of two inequivalent $Fe(CO)_3$ units linked via an Fe–Fe single bond and the complex vinyl, thioketal bridge. More detailed discussion of the structure will be given in the full paper, but it may be noted that bond distances in the C(31), C(32), C(33), Fe(2) unit are such that at the limit an η^3-allyl-Fe system is suggested. A possible mechanism describing the complex intramolecular step that may lead to formation of **3** is outlined in Scheme I. The initial step, Michael addition of anion **1** to the activated acetylene, leads to formation of a σ-bonded vinyl anion that subse-

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[1] Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

[2] Seyferth, D.; Womack, G. B., Hoke, J. B., report in preparation.

[3] In a typical experiment, Li[(μ-*t*-BuS)(μ-CO)$Fe_2(CO)_6$] was prepared in situ by sequential addition of 3.0 mmol each of *t*-BuSH and *n*-BuLi (in hexane) to 3.0 mmol of $Fe_3(CO)_{12}$ in 30 mL of THF at -78 °C (under nitrogen). The mixture was stirred for 10 min; subsequent warming to room temperature resulted in a color change from green to brown-red. Three millimoles of $HC{\equiv}CC(O)CH_3$ was added at room temperature. The mixture was stirred for 20 min, and then 3.5 mmol of $CH_3C(O)Cl$ was added. This mixture was stirred for 35 h and then was evaporated in vacuo. The red residue was subjected to filtration chromatography (silicic acid; pentane and then 6:4 and 2:8 pentane/CH_2Cl_2); **3g** (2.04 mmol, 68%) was obtained as a brown-orange solid. When an acid chloride was the electrophile added, long reaction times (35 h as above to several days when $MeO_2CC{\equiv}CCO_2Me$ was the acetylene used) were required. Protonation, on the other hand, is immediate.

[4] For **3g**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.08 (s, 9 H, $SC(CH_3)_3$), 2.11 (s, 3 H, $OC(O)CH_3$), 2.46 (s, 3 H, $C(O)CH_3$), 8.76 (s, 1 H, FeHC=); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 21.14 (q, *J* = 131.0 Hz, $OC(O)CH_3$), 27.06 (q, *J* = 127.8 Hz, $SC(CH_3)_3$), 27.98 (q, *J* = 128.2 Hz, $C(O)CH_3$), 53.66 (s, $SC(CH_3)_3$), 88.28 (d, *J* = 13.8 Hz, $COC(O)CH_3$), 101.96 (s, FeHC=*C*), 153.56 (d, *J* = 160.8 Hz, FeH*C*=), 167.64 (s, $OC(O)CH_3$), 197.48 (s, $C(O)CH_3$), 209.04 and 210.08 (both br s, Fe–CO); IR (CCl_4) 1770 vs (C=O), 1690 vs (C=O) cm^{-1}; terminal carbonyl region (pentane): 2070 s, 2025 vs, 2010 vs, 1992 s, 1980 s cm^{-1}. Anal. Calcd for $C_{17}H_{16}Fe_2O_9S$: C, 40.19; H, 3.17. Found: C 40.26; H, 3.22.

[5] (a) Crystal data for **3g**: a = 9.810 (1) Å, b = 15.629 (1) Å, c = 7.438 (1) Å, α = 96.66 (1)°, β = 111.18 (1)°, γ = 86.65 (1)°, V = 1056.0 Å^3, z = 2, space group $P\bar{1}$. Data in the range $3° \leq 2\theta \leq 55°$ ($\pm h,\pm k,+l$) were collected by using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[4b] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final R_1 = 0.049 and R_2 = 0.064 for 3634 observed reflections [$I_o > 2\sigma(I_o)$] and 262 variables. (b) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

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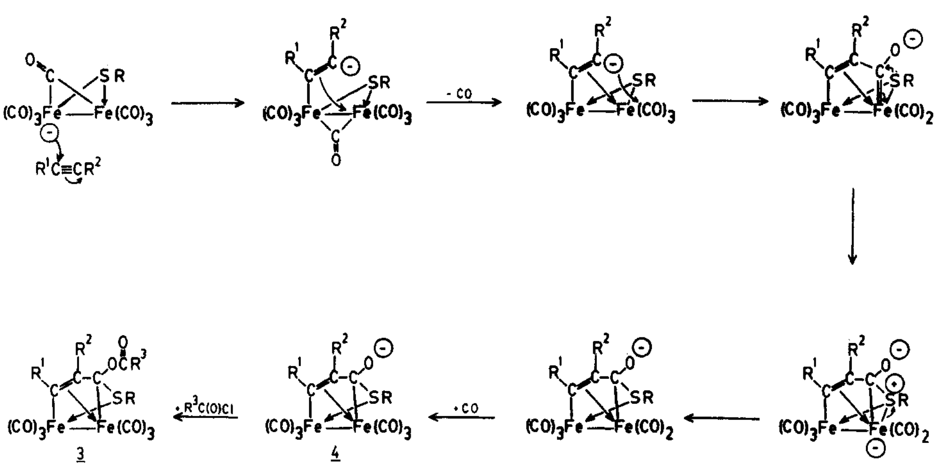
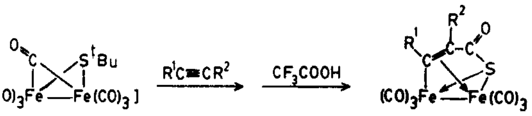
Scheme I



quently forms a bridging π bond to the other iron atom with expulsion of CO. In analogy with known RLi reactions,[6] this intermediate vinyl anion (Li^+ counterion) attacks at the C atom of a terminal CO ligand in a novel dinuclear, intramolecular example of the well-known Fischer acylmetalate formation.[6] The electrophilic carbene carbon atom thus formed undergoes nucleophilic attack by the neighboring bridging sulfur atom, generating an unstable, dipolar, cyclic metallasulfonium species. (This step would be especially likely with the sulfur lone pair occupying an axial position on the thiolato bridge.) Ring opening as indicated and readdition of CO then give anion 4 whose reaction with $R^3C(O)Cl$ produces 3. (Note that drastically reduced product yields result when CO is purged from the reaction mixture by a stream of nitrogen.)

Attempted interception of anion 4 by protonation rather than acylation led to unexpected results. Addition of an equimolar amount of CF_3CO_2H at room temperature to the Li[1]/acetylene reaction mixture, when 1 contained the $(CH_3)_3CS$ bridging ligand, gave a product, 5, in which the *tert*-butyl group no longer was present (eq 2).[7] A



(2)

$\underline{a}$ $R^1 = H$ $R^2 = CO_2Me$ 69 %
$\underline{b}$ $R^1 = H$ $R^2 = C(O)Me$ 51 %
$\underline{c}$ $R^1 = R^2 = CO_2Me$ 66 %

structure determination of **5b** by single-crystal X-ray diffraction gave the result shown in Figure 2.[8] Here also, a CO ligand has been incorporated into the organic framework, bridging the vinyl and the sulfur moieties, although, in this instance, with loss of the original Fe–C interaction. The sulfur atom has lost its *tert*-butyl substituent that has been replaced by the substituted acryloyl ligand. The bonding of the vinylic portion of the bridging ligand in **5b** is very similar to that in **3g** and, therefore,

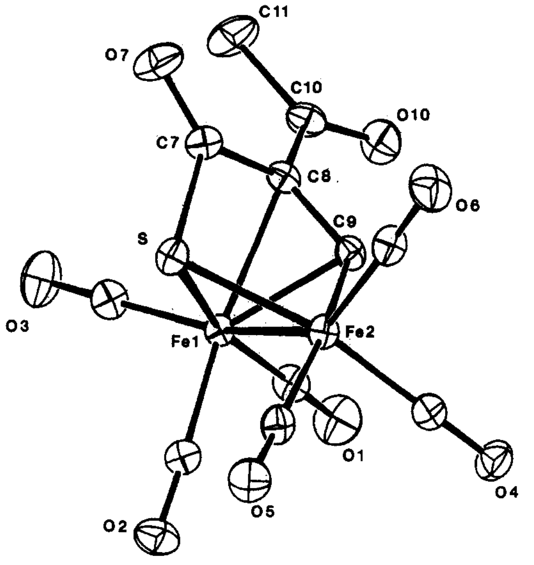
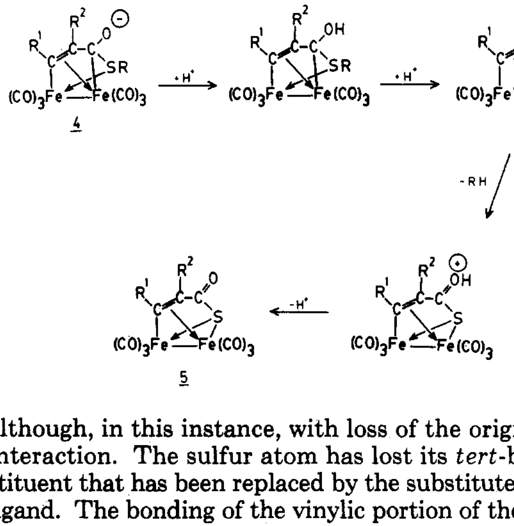


Figure 2. ORTEP diagram of **5b** showing the 30% probability thermal ellipsoids and the atom labeling scheme. Hydrogen atoms have been omitted. Bond lengths (in Å) are as follows: Fe(1)–Fe(2) = 2.539 (1), Fe(2)–C(9) = 1.925 (5), Fe(1)–C(9) = 2.075 (5), Fe(1)–C(8) = 2.137 (5), C(8)–C(9) = 1.411 (7), C(8)–C(10) = 1.518 (7), C(10)–O(10) = 1.208 (7), C(10)–C(11) = 1.528 (8), C(7)–C(8) = 1.476 (7), C(7)–O(7) = 1.207 (6), C(7)–S = 1.824 (5), Fe(1)–S = 2.294 (1), Fe(2)–S = 2.240 (1), Fe–CO(mean) = 1.807, FeC–O(mean) = 1.126.

Scheme II



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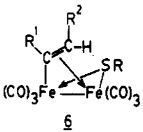
(6) Review: Fischer, H. In *Transition Metal Carbene Complexes*; Dötz, K.-H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983; pp 1–68.

(7) For **5b**: ^1H NMR (250 MHz, $CDCl_3$) δ 2.54 (s, 3 H, CH_3), 9.49 (s, 1 H, FeHC=); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 28.60 (q, J = 128.8 Hz, CH_3), 95.91 (s, FeHC=*C*), 170.07 (d, J = 162.0 Hz, FeHC=), 185.22 (d, J = 11.8 Hz, SC(O)), 196.16 (s, *C*(O)CH_3), 202.97, 205.33, 206.38 (all s, Fe–CO); IR ($CHCl_3$) 1715 vs (C=O), 1690 s (C=O) cm^{-1}; terminal carbonyl region (pentane) 2090 m, 2059 vs, 2030 s, 2020 vs, 2010 s cm^{-1}; mass spectrum (EI, 70 eV): M^+ and $M^+ - n$CO (n = 1–6). Anal. Calcd for $C_{11}H_4Fe_2O_8S$: C, 32.39; H, 0.99. Found: C, 32.44; H, 1.13.

(8) Crystal data for **5b**: a = 8.939 (4) Å, b = 12.275 (2) Å, c = 6.934 (3) Å, α = 93.89 (2)°, β = 100.44 (3)°, γ = 108.72 (3)°, V = 702.15 Å^3, z = 2, space group $P\bar{1}$. Data in the range $3° \le 2\theta \le 55°$ ($\pm h,\pm k,+l$) were collected at −7 °C by using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[4b] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final R_1 = 0.049 and R_2 = 0.060 for 2406 observed reflections [$F_o > 6\sigma(F_o)$] and 199 variables.

is comparable to other diiron μ-σ,π-vinyl systems. The parent compound of this class, **5**, $R^1 = R^2 = H$, had been prepared by Hoffmann and Weiss[9] some years ago by the reaction of thiomaleic anhydride with $Fe(CO)_5$, and its structure was determined by means of X-ray crystallography.

A plausible mechansim for the formation of **5** is shown in Scheme II starting with the anionic intermediate **4**, postulated in Scheme I. Reaction with CF_3CO_2H presumably yields the neutral O-protonated product that may then spontaneously undergo acid-catalyzed, metal-assisted intramolecular oxidation to give the observed product. In analogy with the known acid-catalyzed oxidation of organic hemimercaptals,[9] further protonation at sulfur would take place, yielding an unstable metallasulfonium species. Unable to eliminate RSH (as occurs in the acid-catalyzed oxidation of hemimercaptals), this intermediate undergoes a metal-assisted oxidation to a protonated oxonium species with concomitant formation of an Fe–S bond and elimination of RH. Subsequent loss of a proton then gives the neutral product **5**. This complex is only a minor (6–9%) product in such reactions of $[(\mu\text{-}C_2H_5S)(\mu\text{-}CO)Fe_2(CO)_6]^-$ and $[(\mu\text{-}C_6H_5CH_2S)(\mu\text{-}CO)Fe_2(CO)_6]^-$ and is not formed at all in the analogous reaction of $[(\mu\text{-}C_6H_5S)(\mu\text{-}CO)Fe_2(CO)_6]^-$. In these cases, the major products (obtained in ca. 40% yield) are complexes of type **6**. The provenance of these products is, at this time, obscure. In any case, it appears that this complicated chemistry of Schemes I and II is much slower at low temperatures since even when R in RS is *t*-Bu, at −78 °C products of type **6** are formed, presumably via direct protonation of the intermediate vinyl anion. Thus, when the $Li[(\mu\text{-}(CH_3)_3CS)(\mu\text{-}CO)Fe_2(CO)_6]/CH_3O_2CC{\equiv}CCO_2CH_3$ reaction mixture (reaction for 1 h at −78 °C) was protonated, also at −78 °C, **6** (R = *t*-Bu) was formed in 71% yield and **5** in only 10% yield. In the case of the reaction of methyl propiolate with $Li[(\mu\text{-}(CH_3)_3CS)(\mu\text{-}CO)Fe_2(CO)_6]$ at −78 °C, followed by addition of CF_3CO_2H and warming to room temperature, a major (30%) product was **5a**, but *two* μ-vinyl products, **7a** and **7b**, also were formed, each in 23% yield. Formation of **7b** was unexpected since **7a**, the expected Michael addition product, was the only product of the reaction of $HC{\equiv}CCO_2CH_3$ with $[Et_3NH][(\mu\text{-}(CH_3)_3CS)(\mu\text{-}CO)Fe_2(CO)_6]$ at room temperature or at −78 °C.[2] It may be that at low temperature in the absence of a proton source, the initially formed anion **8a** has a chance to undergo isomerization to **8b**, possibly via **9** (eq 3). Similar results were obtained for the corresponding reactions of 3-butyn-2-one.



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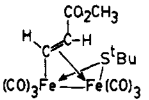
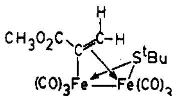
($R^1, R^2 = CO_2CH_3$ when $CH_3O_2C{\equiv}CCO_2CH_3$ is the acetylene used)

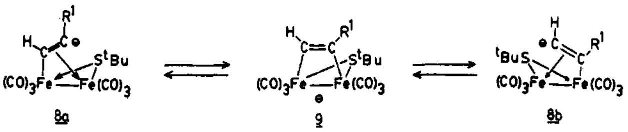


7a



7b

The action of the $[(\mu\text{-}RS)(\mu\text{-}CO)Fe_2(CO)_6]^-$ anions on acetylenes, a reaction which we originally thought was simple and straightforward, thus turns out to be quite complicated. Its course, according to our studies thus far, is dependent on the counterion (Et_3NH^+ vs. Li^+), on the substituents on the acetylenic carbon atoms, on the organic group of the RS ligand, on the reaction temperature, and on the electrophile added to react with the anionic intermediate. We are continuing our studies using other types of acetylenes.



(3)

All new compounds have been characterized by analysis and NMR and IR spectroscopy. Characterizing data are provided as supplementary material.

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Supplementary Material Available: Tables of final positional and thermal parameters for **3g** and **5b** and characterization data for compounds **3a–g** and **5a–c** (12 pages); tables of observed and calculated structure factors for **3g** and **5b** (26 pages). Ordering information is given on any current masthead page.

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[9] Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 225.

[10] Reid, E. E. *Organic Chemistry of Bivalent Sulfur*; Plenum: New York, 1977; p 320.

Synthesis of a Diamagnetic Fulvalene Zirconium(III) Derivative. The Crystal Structure of $(\eta^5:\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$

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Summary: The comproportionation reaction between $Cp_2Zr^{IV}Cl_2$ and $Cp_2Zr^{II}[P(CH_3)_3]_2$ leads to $(\eta^5:\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$ (**1**) in good yields. Its structure has been determined by X-ray diffraction methods. It crystallizes in a monoclinic space group of $P2_1/n$ symmetry with a = 8.234 (4) Å, b = 15.199 (5) Å, c = 14.096 (5) Å, β = 93.65 (3)°, and Z = 4. Its diamagnetism and the Zr–Zr distance of 3.233 (1) Å are consistent with the presence of a metal–metal bond.

The reduction of zirconocene dichloride is a fascinating topic that for a long time has attracted the attention of chemists. This interest has been stimulated by several features displayed by the low-valent zirconium(II, III) organometallic compounds, like dinitrogen fixation,[1] for-

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[†] University of Groningen.

[‡] Columbia University.

[1] (a) Gynana, M. J. S.; Jeffery, J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 34. (b) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351 and references therein.

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