Table I. ^{57}Fe Hyperfine Interaction Tensors (MHz) for MoFe Protein[a]

α	A_3	A_2	A_1
1	8.3	11.5	9.9
2	9.0	12.6	9.9
3	10.7	11.5	11.8
4	11.5	15.3	18.9
5	14.3	18.2[b]	19.9
6	20.5	17.0	20.6

[a] Calculated from observed hyperfine interactions by assuming coaxial A and g tensors and $g_3 = 4.32, g_2 = 3.65, g_1 = g_e$. Uncertainties: A_3, A_1, ±0.1 MHz; A_2, ±0.25 MHz (estimated). Assignment of $A_1(\alpha)$ to a particular site (α) made as described in text. [b] The assumption of coaxial tensors is likely to be inadequate for Fe(5),[11] and therefore this entry is likely to be underestimated.

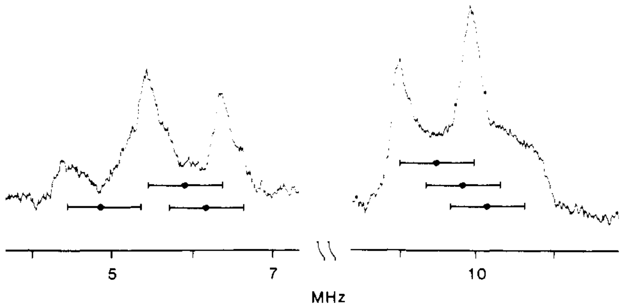

Figure 2. ^{57}Fe ENDOR of *Azotobacter vinelandii* MoFe protein at $g = g_1$. Conditions: H_0 = 3350 G (position A of Figure 1, inset). Other conditions are as in Figure 1.

quite been obtained. The ENDOR responses of irons 1–4 are extremely narrow, and each shows only one of the expected pair of lines, most probably the higher frequency partner. With the provisional assumption the hyperfine and g tensor axes are colinear, the frequencies of these resonances may be used in eq 1 to calculate the A_3' principal axis value for six chemically distinct iron sites (Table I).

When the magnetic field is set to the extreme high-field edge of the EPR spectrum, a single-crystal-like ENDOR spectrum is again obtained; this time it arises from those molecules oriented such that the magnetic field lies along the g_1 axis of the g tensor (Figure 2). In this case, each of the six iron sites contributes a resolvable doublet (eq 1). The six doublets are grouped into trios having very similar hyperfine parameters, one centered at $A_1'/2 \simeq$ 5–6 MHz and the other at $A_1'/2 \simeq 10$ MHz. A series of spectra have also been taken at fields intermediate between the g_2 and g_3 values. The truly exceptional resolution of the ^{57}Fe endor spectra has allowed us to perform an analysis which gives preliminary values of the A_2' hyperfine constants.[11] Table I presents the ^{57}Fe hyperfine tensor components $A_i(\alpha)$ for the six individual iron atoms (α = 1–6, i = 1–3). The association of an $A_3(\alpha)$ and $A_2(\alpha)$ pair is experimentally determined, but as yet it has not been possible to correlate a particular value of A_1 with its corresponding A_3, A_2 pair. Thus, the table has been completed through aid of the reasonable, but unsupported, device of assigning a measured A_1 to a particular site, α, so that the order of the individual sites in a series having decreasing $A_1(\alpha)$ is the same as that for decreasing $A_2(\alpha)$. This is one of several possible assignments that minimizes the assigned anisotropy of the hyperfine tensors.

Table I shows that the FeMo-co cluster must have an extraordinarily complex structure, for no two iron sites have the same characteristics. Since the site inequivalence must have a structural origin, this result will provide a stringent test of any postulated model for the cluster. Nevertheless, it is possible to see that Fe(1), Fe(2), and Fe(3) are broadly similar and, as concluded from the Mössbauer studies,[6] have roughly isotropic hyperfine tensors, as expected for high-spin ferric ions. The hyperfine constants are much reduced from that of a mononuclear Fe^{3+}, as in rubredoxin,[12] and from that in the two and four iron ferredoxins, as well.[13] This presumably results from the spin coupling that produces the net $S = {}^3/_2$ cluster spin. The other three iron atoms have larger and more anisotropic hyperfine interactions. The anisotropy of Fe(4), Fe(5),[11b] and, to a lesser extent, Fe(6) is suggestive of what might be expected for high-spin ferrous ions engaged in spin coupling.[13] These observations are consistent with the requirement that an Fe$_6$Mo cluster having an even-spin molybdenum[4] must include an odd number of formally ferric (and ferrous) iron atoms in order to achieve the net cluster spin of $S = {}^3/_2$. To the extent that these analogies to iron atoms in well-defined oxidation states correctly reflect the resting state of what must in fact be a complex and highly covalent system, then the ENDOR results give a starting point for discussions of the cluster charge. They also suggest that no more than 3 equiv can be associated with the formally ferric/ferrous iron couple during reduction (or superoxidation) of the molybdenum–iron cofactor of MoFe.

Acknowledgment. This work has been supported by NSF Grant PCM 7681304 and the donors of the Petroleum Research Fund, administered by the American Chemical Society (B.M.H.), and NSF Grant PCM 800087330 (W.H.O.-J.). We thank Drs. Michael Henzl and Joseph Smith for helping prepare isotopically enriched nitrogenase and Dr. Eckard Munck for stimulating discussions.

Registry No. FeMo-*co*, 72994-52-6.

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[11] (a) To be submitted for publication. (b) Spectra taken at intermediate fields give indications that the provisional treatment in terms of coaxial g and hyperfine tensors is inadequate to describe Fe(5). Calculations of the Mössbauer spectrum of this center, based on the values in Table I, give the same indications (E. Munck, private communication).

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C–C Bond Formation by Reductive Coupling of Two Carbonyl Ligands of Binuclear Transition-Metal Complexes

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Received April 15, 1982

Among the most important reactions in organo-transition metal chemistry are those that generate new carbon–carbon bonds. Several different types of processes effect C–C coupling: (i) reductive elimination;[3] (ii) nucleophilic attack of carbanions at carbonyl[4] or olefin[5] ligands; (iii) alkyl migration to carbonyl or carbene ligands;[6] (iv) coupling of alkynes,[7] nitriles,[8] isonitriles,[9]

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[1] NSF Predoctoral Fellow, 1979–1982.

[2] Camille and Henry Dreyfus Teacher-Scholar, 1977–1982.

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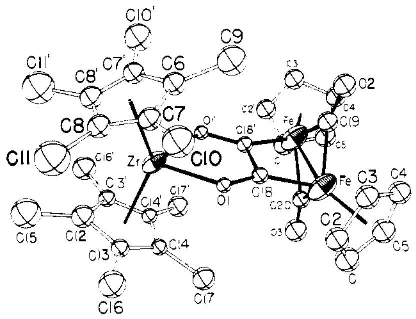
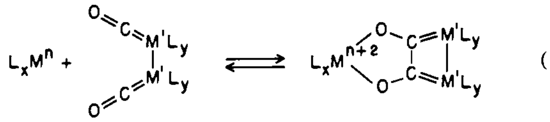


Figure 1.

olefins,[10] and/or aldehydes,[11] normally affording metallacyclic products; (v) addition of alkynes,[12] olefins,[13] aldehydes, ketones, or esters[13a,14] to metal carbenes, yielding four-membered metallacycles; (vi) bimolecular carbene–carbene coupling to olefins;[15] and the less extensively documented processes (vii) olefin insertion into metal–alkyl bonds;[16] (viii) carbene–carbonyl coupling to afford coordinated ketenes.[17] We report the first examples of a new type of carbon–carbon bond-forming reaction: the direct coupling of two carbonyl ligands of a binuclear transition-metal complex (eq 1).



(1)

Treatment of 1 equiv of $\{Cp_2{}^*ZrN_2\}_2N_2$ (**1**) ($Cp^* \equiv \eta^5\text{-}C_5Me_5$)[18] with 2 equiv of $\{(\eta^5\text{-}C_5H_4R)Fe(CO)_2\}_2$ (**2a**, R = H; **b**, R = Me) in toluene above −20 °C results in evolution of 3 equiv of N_2 and >95% (^{1}H NMR) yields of dark red-brown compounds with the stoichiometries $Cp_2{}^*Zr(CO)_4Fe_2(\eta^5\text{-}C_5H_4R)_2$ (**3a**, R = H; **b**, R = Me) (eq 2).[19] The ^{1}H NMR spectrum (benzene-d_6, 34 °C)

$$\underset{\mathbf{1}}{\{Cp_2{}^*ZrN_2\}_2N_2} + 2\underset{\substack{\mathbf{2a},\ R = H\\ \mathbf{b},\ R = Me}}{\{(\eta^5\text{-}C_5H_4R)Fe(CO)_2\}_2} \longrightarrow 3N_2 + 2\underset{\substack{\mathbf{3a},\ R = H\\ \mathbf{b},\ R = Me}}{Cp_2{}^*Zr(CO)_4Fe_2(\eta^5\text{-}C_5H_4R)_2} \quad (2)$$

for **3a** reveals only two resonances, at δ 1.69 and 4.81, attributable to $\eta^5\text{-}C_5Me_5$ and $\eta^5\text{-}C_5H_5$ ligands, respectively. Significantly, the infrared spectrum for **3a** exhibits four bands due to $\nu(CO)$: 1768 (w), 1729 (s), 1295 (ms), 1282 (ms) cm^{-1} ($\nu(^{13}CO)$: 1730, 1686, 1260 cm^{-1} (br, unresolved)).[20] These infrared data, in particular the two extremely low values for ν(CO) and the absence of any bands attributable to terminal carbonyl ligands, would seem to eliminate structures for **3a** and **3b** derived from those of $Cp_2{}^*ZrCo(CO)_2Cp$ ($Cp \equiv \eta^5\text{-}C_5H_5$),[21] $Cp_2{}^*ZrMo_2(CO)_6Cp_2$,[22] $Cp_2{}^*Ti(CH_3)Mo(CO)_3Cp$,[23] or $Cp_2{}^*YbCo(CO)_4(THF)$.[24] A structure determination for **3a** was therefore undertaken.

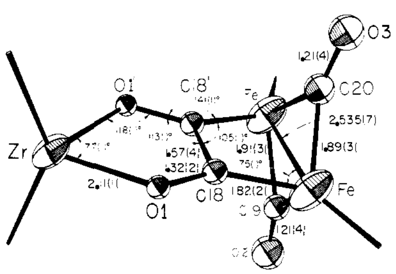
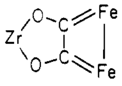


Figure 2.

Small, single crystals were obtained by slow cooling of a warm toluene solution of **3a**, and its structure was determined from X-ray diffraction data.[25] The molecular geometry is shown in Figure 1 and a skeletal view in Figure 2. The ZrO_2C_2 unit bridging the two iron atoms (A) is clearly the most interesting structural feature. These seven atoms all lie approximately in the same plane with a perpendicular cyrstallographic mirror plane containing the zirconium atom bisecting the C–C and Fe–Fe bonds. The bond distances (C–C = 1.57 (4), C–O = 1.32 (2), Zr–O = 2.11 (1), Fe–C = 1.82 (2), Fe–Fe = 2.535 (7) Å) are in accord with the dioxozirconacyclopenta-3,4-diylidene diiron formulation indicated in A. Thus, **3** may be viewed as a derivative of *cis*-$[CpFe(CO)_2]_2$



A

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(19) Anal. Calcd for $C_{34}H_{40}Fe_2O_4Zr$ (**3a**): C, 57.07; H, 5.64; Zr, 12.75. Found: C, 56.94; H, 5.71; Zr, 12.54.

(20) Spectroscopic data for **3b**: ^{1}H NMR (benzene-d_6) δ 4.79 (m, 8 H, $CH_3C_5H_4$), 2.12 (s, 6 H, $C_5H_4CH_3$), 1.67 (s, 30 H, $C_5(CH_3)_5$); ^{13}C NMR (benzene-d_6) δ 304 (μ-C_2O_4), 269 (μ-CO), 124 ($C_5(CH_3)_5$), 101, 99, 90 (1:2:2, $CH_3C_5H_4$), 13 ($CH_3C_5H_4$), 11 ($C_5(CH_3)_5$); IR (Nujol) ν(CO) 1755 (w), 1713 (s), 1287 (s,b) cm^{-1}.

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(22) Treatment of $[CpMo(CO)_3]_2$ with $(Cp_2{}^*ZrN_2)_2N_2$ gives a quantitative yield of red-brown solid with the stoichiometry $Cp_2{}^*Zr(CO)_6Mo_2Cp_2$. A single-crystal X-ray diffraction study revealed a symmetrical structure containing two μ_2-η^1,η^1-CO linkages between $Cp_2{}^*Zr$ and two $CpMo(CO)_2$ moieties. This is analogous to the bonding observed in ref 23 and 24. Berry, D. H.; Bercaw, J. E., to be submitted for publication.

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(25) A single crystal (0.1 × 0.1 × 0.1 mm) was mounted in a glass capillary under N_2 and found to be orthorhombic with cell dimensions a = 10.241 (9) Å, b = 16.476 (20) Å, c = 19.183 (17) Å, V = 3837 Å^3. Systematic absences $0kl$, $k + l \neq 2n$ and $hk0$, $h \neq 2n$ indicated *Pnma* or the nonstandard setting $pn2_1a$ as possible space groups. Data were collected on a fully automated Syntex $P2_1$ diffractometer equipped with a pulse-height analyzer and scintillation counter. Graphite-monochromated Mo K$\bar{\alpha}$ radiation. Data (4409 reflections) were collected ($2\theta_{max}$ = 60°) and the resulting 1104 independent reflections with $I > 3\sigma(I)$ were treated as described previously.[26] Neither absorption nor decay corrections were applied, the former due to the crystal size and the small linear absorption coefficient of 12.53 cm^{-1}, and the latter because the observed random average variation in intensity of standard reflections of 2.6% was considered negligible. The heavy-atom positions were determined from a Patterson map. At this point one of the atoms, later determined to be Zr, was found to lie at $^1/_4$ in Y. This observation, along with density measurements indicating Z = 4, led to the choice of *Pnma* as space group with the Zr located on the mirror plane $Y = {}^1/_4$. Refinement was accomplished with full-matrix, least-squares techniques minimizing the function $\sum w(|F_o| - |F_c|)^2$. The data were weighted according to $1/\sigma = 4LpI/(\sigma I)^2$. Successful refinement confirmed the space group assignment. Convergence was achieved at R_1 = 0.104 and R_2 = 0.092, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The goodness-of-fit, $(\sum w\Delta^2/(n_{ref} - n_{par}))^{1/2}$, is 2.84. Due to the small size of the crystal, there are sufficient data to refine only the metal atoms anisotropically (106 final variables). Attempts are being made to grow larger crystals.

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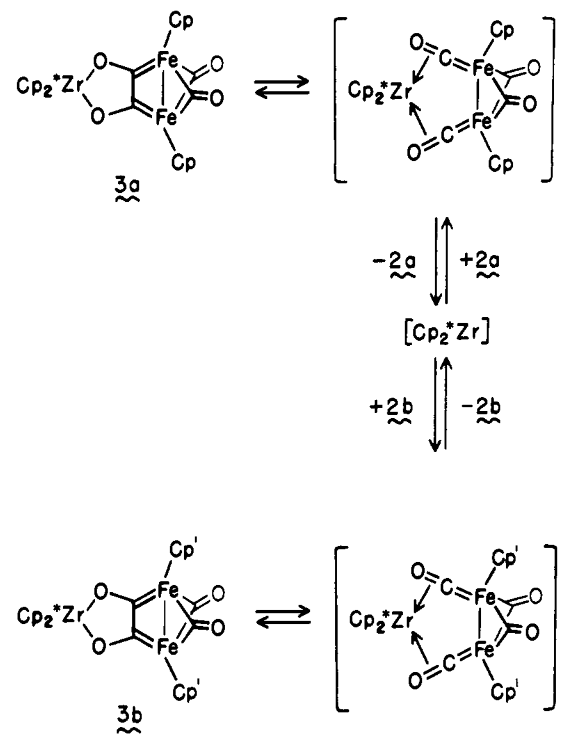
Scheme I

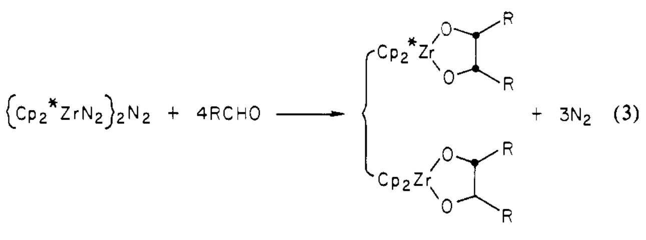


^{a} Cp* = η^5-C_5Me_5; Cp = η^5-C_5H_5; Cp' = η^5-C_5H_4Me.

with the two terminal carbonyls replaced by carbene ligands. Indeed, none of the bond distances for the CpFe(μ-CO)$_2$FeCp moiety of **3** are statistically different from those for *cis*-**2a**.[27] That the Fe–C(carbene) distance for **3** is 0.09 Å longer that the Fe–C(terminal carbonyl) for *cis*-**2a** is also expected, in view of the order of bond lengths typically found for "Fischer-type" carbenes (M–C(carbene) > M–C(carbonyl)).[4] The coordination about zirconium is normal, with the exception of the small O–Zr–O angle of 77 (1)°, imposed by the five-membered ring.

The spectral features for **3a** are readily interpretable in light of its structure. Thus the IR bands at 1768 and 1729 cm^{-1} are attributed to the bridging carbonyls of the CpFe(μ-CO)$_2$FeCp unit (cf. 1800 and 1765 cm^{-1} for *cis*-**2a**),[27] and the two low-energy bands at 1295 and 1282 cm^{-1} (principally) to the ν(CO) modes of the dioxozirconacyclopenta-3,4-diylidene moiety. ^{13}C NMR spectra (benzene-d_6, 34 °C) for **3a** show two downfield resonances, at δ 305 and 268 (1:1). ^{13}C NMR spectra of *cis*-**2a** at low temperatures exhibit resonances at δ 212 and 276 due to terminal and bridging carbonyls, respectively.[28] Hence, the most straightforward assignment for **3a** is that the δ 268 and 305 resonances are due to the bridging carbonyl and carbene carbons.

The formation of **3** may be viewed as a reductive coupling of the two terminal carbonyl ligands of **2** with oxidation of zirconium from the divalent to tetravalent state. Hence, reaction 2 may be likened to the reductive coupling of aldehydes and terminal olefins by permethylzirconocene[11,29] (eq 3 and 4). While radical pathways cannot be excluded, it appears likely that all of these processes involve intramolecular coupling of two π-bound ligands. Indeed, there is precedent for "side-on" π bonding between zirconium and a bridging carbonyl group, e.g., in Cp$_2$*Zr(μ-CO)(μ_2-η^1,η^2-CO)CoCp.[21] Significantly, treatment of **3a** with CO (2 atm, 25 °C) results in the release of **2a** over a period of several days with concurrent formation of Cp$_2$*Zr(CO)$_2$. When ^{13}CO is used, Cp$_2$*Zr(^{13}CO)$_2$ is the exclusive product during the early stages of the reaction (eq 5).[30] These observations suggest that the formation of **3** from **2** and Cp$_2$*Zr(II) is reversible.[31] In agreement, we find that an equilibrium between **2a**, **3a**, **2b**, and **3b** is slowly established in benzene solution (25 °C, days;[32] (Scheme I)).



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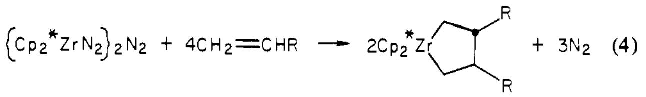

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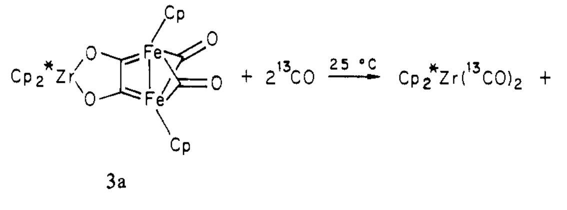

3a

2a

This reductive coupling of carbonyl ligands (eq 1) bears some resemblance to the alkali metal reduction of carbon monoxide to M$^+$$^-$OC≡CO$^-M^+$ and its oligomers[33] and to the recently reported reductive coupling of coordinated alkyl isocyanides in seven-coordinate Mo(II) and W(II) complexes.[9,34] On the other hand, the reductant in the present case, Cp$_2$*Zr(II), reacts with free CO to form the stable dicarbonyl compound Cp$_2$*Zr(CO)$_2$, and with a mononuclear dicarbonyl compound, CpCo(CO)$_2$, to yield a quite different type of mixed-metal species, Cp$_2$*Zr(μ_2-CO)(μ_2-η^1,η^2-CO)CoCp.[21] The C–C coupling process observed may well be encouraged by the favorable disposition of the two terminal carbonyls of *cis*-**2** and the rigid Fe(μ-CO)$_2$Fe unit. In this regard, we have noted that products analogous to **3** are ob-

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(29) For example, treatment of **1** with 2 equiv of CH$_3$CHO in toluene at −80 °C affords, after slow warming to 25 °C, a ~1:1 mixture of *cis*- and *trans*-Cp$_2$*ZrOCHMeCHMeO (>95%, ^{1}H NMR): ^{1}H NMR (500 MHz, benzene-d_6) δ 1.97, 1.94 (s, s, C$_5$(C*H*$_3$)$_5$), 5.22, 4.57 (m, m; ZrOC*H*MeC*H*MeO), 1.24, 1.19 (m, m, ZrOCH(C*H*$_3$)CH(C*H*$_3$)O); ^{13}C{^{1}H} NMR (22.5 MHz, benzene-d_6) δ 120.4, 120.2 (s, br s, *C*$_5$(CH$_3$)$_5$), 91.3, 88.6 (s, s, ZrO*C*HMe*C*HMeO), 23.4, 21.2 (s, s, ZrOCH*C*H$_3$CH*C*H$_3$O), 11.6, 11.2, 11.1 (s, s, s, C$_5$(*C*H$_3$)$_5$).

(30) At longer reaction times ^{13}CO is incorporated into **2a** by a secondary exchange process.

(31) We have previously observed the stepwise, facile conversion of ethylene and 3,4-diethylzirconacyclopentane, Cp$_2$*ZrCH$_2$CHEtCHEtCH$_2$, to Cp$_2$*ZrCH$_2$CHEtCH$_2$CH$_2$ and subsequently to Cp$_2$*ZrCH$_2$(CH$_2$)$_2$CH$_2$ with release of 1-butene (Erwin, D. K. Ph.D. Thesis, California Insitute of Technology, Pasadena, CA, 1979), indicating a rapid interconversion of metallacyclopentane and bis(olefin) complexes analogous to those reported for related nickel and titanium systems. Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300.

(32) The initial equilibrium mixture observed is consistent with simple exchange involving only **2a** and **2b** (scheme). After longer reaction times (>2 weeks) two new species are observed by ^{1}H NMR. Comparison with authentic samples confirms that these compounds are [(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)Fe$_2$(CO)$_4$]$_2$ (**2c**) and Cp$_2$*Zr(CO)$_4$Fe$_2$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (**3c**). A benzene solution of a mixture of **2a** and **2b** scrambles to a statistical mixture of **2a**, **2b**, and **2c** within 30 days. This same scrambling process is greatly accelerated by addition of Na[(η^5-C$_5$H$_5$)Fe(CO)$_2$]·THF.

(33) (a) Weiss, E.; Buechner, W. *Helv. Chim. Acta* **1963**, *46*, 1121. (b) Buechner, W.; Weiss, E. *Ibid.* **1964**, *47*, 1415.

(34) The planar arrangement of the C$_2$Fe$_2$ unit for **3** is quite different from the pseudotetrahedral arrangement found for compounds containing acetylene bridging two metals, however.

tained from **1** and $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ and from $\{Cp_2^*HfN_2\}_2N_2$[35] and **2a**. We are presently further investigating the generality of this process and the chemistry of the diylidene moiety.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE8024869). We acknowledge use of the Southern California Regional NMR Facility and the support of NSF Grant No. 7916324. We also thank Dennis P. Lawlor for assistance in the X-ray structure determination while an NSF–URP participant at the University of Kansas.

Registry No. 1, 54387-50-7; **2a**, 12154-95-9; **2b**, 32028-30-1; **3a**, 82482-56-2; **3b**, 82482-57-3; *cis*-Cp_2^*ZrOCHMeCHMeO, 82482-58-4; *trans*-Cp_2^*ZrOCHMeCHMeO, 82534-93-8; Fe, 7439-89-6.

Supplementary Material Available: Listings of fractional coordinates and thermal parameters, bond distances and angles, and structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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[35] Prepared by reduction of $Cp_2^*HfI_2$ with Na-K alloy in DME at −40 °C under 1 atm of nitrogen: Seidler, P.; Hillhouse, G., to be submitted for publication.

Structure of the NO Dimer

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Received June 1, 1982

The structure of the NO dimer in the gas phase was determined from measurements of rotational transition frequencies for $^{14}NO\text{–}^{14}NO$, $^{15}NO\text{–}^{15}NO$, and $^{14}NO\text{–}^{15}NO$. Microwave transition frequencies were measured by using the Flygare–Balle spectrometer.[1,2] The measurement of rotational transition frequencies for different isotopic combinations allowed an unambiguous determination of the NNO angle (θ) of 99.6(4)°. The NN bond length is 2.237 (2) Å, and the NO bond length is 1.161 (6) Å. This is the structure for the $v = 0$ vibrational state.

The NO dimer is weakly bound in the gas phase with a binding energy of about 4 kcal. The structure of the dimer in a crystal lattice was studied some time ago.[3,4] The solid-phase data were interpreted[4] as due to a planar cis structure with an NNO angle of 101° and an NN bond of 2.18 Å. The existence of a cis structure as well as other conformations for $(NO)_2$ were indicated by matrix isolation studies.[5] The NO dimer was observed in the gas phase by molecular beam spectroscopy,[6,7] and rotational constants for one isotopic species were obtained. The cis planar structure was confirmed, but since only two independent moments of inertia were obtained, the structure could not be unambiguously determined. Their data were consistent with an NNO angle of 85 (5) or 95 (5)°.

In the present work the $2_{12} \rightarrow 3_{03}$ transitions were measured for $^{14}NO\text{–}^{14}NO$ and $^{15}NO\text{–}^{15}NO$, and the $1_{01} \rightarrow 1_{10}$ transitions were measured for $^{14}NO\text{–}^{15}NO$ and $^{15}NO\text{–}^{15}NO$. The measured frequencies are listed in Table I. The four available transition frequencies for the most common isotopic form, used to determine the rotational constants for $^{14}NO\text{–}^{14}NO$, are $A = 25829.71$, $B = 5614.542$, $C = 4605.671$, and the distortion constant $D_J = 0.029$ MHz. Of the three possible symmetric top basis distortion constants, the data set is most sensitive to D_J. Rather few rotational transitions for this complex are available in the normal microwave range since $(NO)_2$ has a *b*-axis dipole moment and the rotational constants are fairly large.

Table I. Transition Frequencies for the NO Dimer (MHz)

	$^{14}NO\text{–}^{14}NO$	$^{15}NO\text{–}^{15}NO$	$^{14}NO\text{–}^{15}NO$
$1_{01} \rightarrow 1_{10}$	21 224.041^a	20 444.831 (10)	20 827.68 (3)
$1_{11} \rightarrow 2_{02}$	187.501^a		
$2_{02} \rightarrow 2_{11}$	22 269.738^a		
$2_{12} \rightarrow 3_{03}$	11 267.403 (10)	11 159.303 (3)	

^{a} Calculated from data in ref 7.

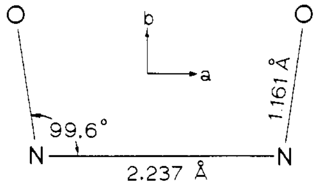

Figure 1. Structure of the NO dimer.

The inertial defect is $\Delta = 0.151$ amu Å^2, and this indicates a planar structure. Although the inertial defect is small, it complicates the structure determination somewhat so structures were determined by using each of the three possible pairs of rotational constants. In order to obtain rotation constants for $^{15}NO\text{–}^{15}NO$, it was assumed that D_J and Δ would be the same as observed for $^{14}NO\text{–}^{14}NO$. Using the observed transition frequencies, we obtained the rotational constants for $^{15}NO\text{–}^{15}NO$ of $A = 24919.63$, $B = 5463.130$, and $C = 4474.797$ MHz.

The dimers were formed by expanding a 5% mixture of NO in argon at 1 atm pressure through an 0.8-mm nozzle into the Fabry–Perot microwave cavity. The beam and microwave signal were pulsed and superheterodyne detection was used.

The N–N bond length was obtained directly from the difference in *B* rotational constants for $^{14}NO\text{–}^{14}NO$ and $^{15}NO\text{–}^{15}NO$ as with the Kraitchman method.[8] The value of the N–N bond length is 2.237 (2) Å and includes error estimates for rotational distortion and vibration effects. The *b*-axis component of the N–O separation was obtained from the *A* rotational constants. The *a*-axis component of the NO bond length was found by fixing the N–N bond length and adjusting the structure to fit the rotational constants. These components were used to obtain the N–O bond length and NNO angle. Using *A* and *B*, we find 1.1609 Å and 99.59°. Using *A* and *C* gives 1.1612 Å and 99.68°, and for *B* and *C* we have 1.1652 Å and 99.55°. The most consistent results were obtained by using the *A* and *B* or *A* and *C* rotational constants. Favoring the *A*,*B* and *A*,*C* results, we have an N–O bond length of 1.161 (6) Å and NNO angle $\theta = 99.6(4)°$. The structure is shown in Figure 1. Hyperfine structure was observed on all transitions, but this will be discussed in a later publication. So that the structure could be confirmed, rotational constants were calculated for the $^{15}NO\text{–}^{14}NO$ $1_{01} \rightarrow 1_{10}$ transition. The calculated frequency was 20824.5 MHz, in good agreement with the observed frequency of 20827.68 MHz.

The observed N–N bond length of 2.236 Å is much longer than calculated values[9,10] of 1.77 and 1.62 Å. The N–O bond length of 1.161 Å is only slightly longer than the NO free-molecule bond length of 1.154 Å. The measured NNO angle $\theta = 99.6°$ is reasonably close to calculated values[9,10] of 106 and 112°. A

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