Figure 2. Fourier transforms of the rubidium K-edge transmission EX-AFS for Rb⁺(18C6)·SCN⁻(—), Rb⁺(18C6)·Rb⁻ (···), Rb⁺(18C6)·e⁻ (---).

of such states,[14,15] shows remarkable differences. the X-ray absorption spectrum of the rubidide Cs⁺(18C6)₂·Rb⁻ (curve b) is very similar to that of Kr gas[15] (curve a). The white line is virtually absent because of the low density of vacant bound excited states. Also, there is no discernible EXAFS, a result of the very large size of Rb⁻ (estimated radius 3.4 Å;[16] nearest-neighbor distance ~5.5 Å). By contrast, Rb⁺18C6·Br⁻·2H₂O (curve c) shows a large white line and distinctive[17,18] EXAFS, characteristic of Rb⁺.

The area A of the white line, normalized to unit edge jump, for all compounds studied, is given in Table I. On the one hand, the complexed *rubidiums* such as Rb⁺(18C6)·Br⁻·2H₂O, Rb⁺-(18C6)·SCN⁻, Rb⁺(18C6)·Na⁻, and Rb⁺(15C5)₂·Na⁻ have the largest white lines with areas ranging from 20 to 30, very close to the range of 26 to 34 observed for the oxidized complexes. On the other hand, the *rubidides* Cs⁺(18C6)₂·Rb⁻ and K⁺C222·Rb⁻ have the smallest areas ($A = 1$ and 3, respectively). When both are present, e.g., Rb⁺(18C6)·Rb⁻ and Rb⁺(15C5)₂·Rb⁻, $A = 12$ and 18, respectively, roughly half the A values observed for the complexed rubidium systems, consistent with the fact that half of the rubidiums exist as Rb⁺. Finally, there are systems that are apparently mixtures. For example, RbK(18C6), with an A value of 10 may be a mixture of Rb⁺(18C6)·K⁻ and K⁺(18C6)·Rb⁻ and RbK(15C5)₂ with $A = 16$ is probably a mixture of Rb⁺-(15C5)₂·K⁻ and K⁺(15C5)₂·Rb⁻.

The spread of A values from 20 to 30 for complexed Rb⁺ may be due to donation of electron density from the anion. Thus, the "protected" Rb⁺ in Rb⁺(15C5)₂·Na⁻ has $A = 29$ while for Rb⁺-18C6·Na⁻ $A = 19$. Also, within the 18C6 series, A decreases with decreasing ionization potential of the anions, SCN⁻ ≳ Br⁻ > Na⁻ > e⁻.

Fourier transformed (FT) EXAFS[17] for alkalides with the Rb⁺(18C6) moiety are similar to those of the model compounds as illustrated in Figure 2 for Rb⁺(18C6)·SCN⁻ (a), Rb⁺-(18C6)·Rb⁻ (b), and Rb⁺(18C6)·e⁻ (c). In the former, Rb⁺ is coordinated to six crown ether oxygens (Rb–O, 2.93–3.15 Å)[9] and to two thiocyanate anions [Rb–N(S), 3.23 and 3.31 Å]. The FT shows a broad peak (phase-shift corrected) at 2.95 Å (Rb⁺–O) that extends to 3.4 Å, thus masking the Rb⁺–thiocyanate peaks. A second peak at 3.95 Å corresponds to the Rb⁺ ··· C distances. The FT for the rubidide, Rb⁺(18C6)·Rb⁻ is very similar, with main

peaks at 2.95 Å (Rb⁺–O) and 3.80 Å (Rb⁺ ··· C). The attenuation in the FT peaks from Rb⁺(18C6)·SCN⁻ (a) to Rb⁺(18C6)·Rb⁻ (b) results from dilution of the Rb⁺ concentration (from 100% to 50%) and the absence of Rb⁻ EXAFS. The EXAFS of the other systems containing mixtures are also consistent with the presence of Rb⁺ and Rb⁻. The FT of the electride,[19] Rb⁺(18C6)·e⁻, in addition to the Rb–O (2.7 Å) and Rb ··· C (3.8 Å) distances, has a peak at 3.4 Å which is tentatively assigned to Rb ··· O(C) distances. The presence of this new peak, and the shifts of the Rb–O and Rb ··· C peaks to lower distances, indicates a significant change in the local structure around Rb⁺.

In summary, the XANES and EXAFS results are fully consistent and can be used to differentiate between Rb⁺ and Rb⁻, thus providing new insights into the nature of alkalides and electrides.

(19) This salt could be the rubidide Rb⁺(18C6)₂·Rb⁻.

Reductive Homologation of CO to a Ketenecarboxylate by a Low-Valent Organolanthanide Complex: Synthesis and X-ray Crystal Structure of [(C₅Me₅)₄Sm₂(O₂CCCO)(THF)]₂[1]

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As part of our general investigation of low-valent lanthanide chemistry[3] we reported that the divalent complex (C₅Me₅)₂Sm-(THF)₂ (I) reacts with CO at atmospheric pressure.[4] The reaction was complex and separation of the many products formed has proven difficult. Multiple products are also formed when I reacts with CO at 90 psi, but under the proper conditions one product separates in crystalline form. We report here the structure of this remarkable product and discuss its implications in the areas of CO reduction[5] and low-valent lanthanide chemistry.

Reaction of CO at 90 psi with (C₅Me₅)₂Sm(THF)₂ (162 mg, 0.29 mmol) in 5 mL of THF in a 3-oz Fischer-Porter aerosol

(15) Stern, E. A.; Heald, S. M. In "Handbook on Synchrotron Radiation"; Koch, E. E., Ed.; North-Holland Publishing Co.: Amsterdam 1983; Vol. 1, pp 955–1014.

(16) Dye, J. L. *Angew. Chem.* **1979**, *18*, 587–598.

(17) For details of the data analysis see: (a) Teo, B. K.; Shulman, R. G.; Brown, G. R.; Meixner, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 5624–5631. (b) Teo, B. K. *Acc. Chem. Res.* **1980**, *13*, 412–419. (c) Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *53*, 769–806.

(18) The high Debye–Waller factors (ca. 0.14–0.17) and hence weak EX-AFS signals are consistent with large static disorder and weak ionic bonds.

(1) Presented in part at the Third China–Japan–U.S. Symposium on Organometallic Chemistry and Catalysis, August 5–9, 1984, Santa Cruz, CA.

(2) (a) Alfred P. Sloan Research Fellow. (b) University of California, Irvine. (c) University of Alabama.

(3) (a) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217–226 and references therein. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. (c) Evans, W. J.; Bloom, I.; Engerer, S. C. *J. Catal.* **1983**, *84*, 468–476. (d) Evans, W. J. In "The Rare Earths in Modern Science and Technology"; McCarthy, G,. J., Rhyne, J. J. Silber, H. E., Eds.; Plenum Press: New York, 1982, Vol. 3, pp 61–70.

(4) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

(5) (a) Storch, H. H.; Golumbic, N.; Anderson, R. B. "The Fischer–Tropsch Reaction and Related Syntheses;" Wiley: New York, 1951. (b) Ponec, V. *Catal. Rev.–Sci. Eng.* **1978**, *18*, 1515–171. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (d) Kung, H. H. *Catal. Rev.–Sci. Eng.* **1980**, *22*, 235–259. (e) Klier,. K. *Adv. Catal.* **1982**, *31*, 243–313. (f) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325–416. (g) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (h) Bercaw, J. E.; Wolczanski, P. T. *Acc. Chem. Res.* **1980**, *13*, 121–127. Barger, P. T.; Santasiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178–5186 and references therein. (i) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109.
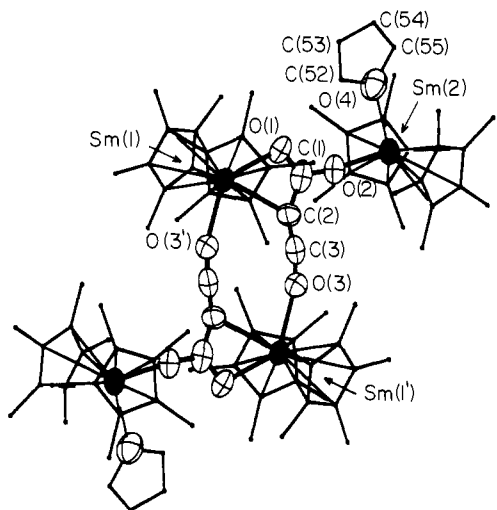
Figure 1. ORTEP plot of the molecular structure of $[(C_5Me_5)_4Sm_2\text{-}(O_2CCCO)(THF)]_2$. Sm atoms are shown as darkened ellipsoids. C_5Me_5 and C_4H_8O carbon atoms are shown as dots for clarity.
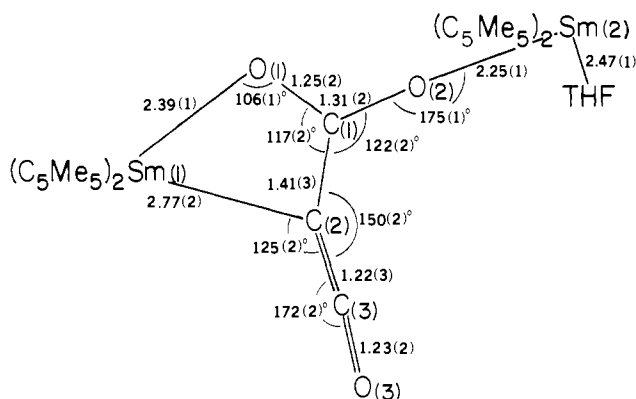

Figure 2. Bond distances (Å) and angles for one of the monomeric units of $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$.

reaction vessel ($\sim$85 cm^3) changes the red-purple color of I to dark brown over a 3-day period. Orange-brown crystals suitable for X-ray diffraction[6] are formed under these conditions and have been identified as $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$ (II) (30 mg, 20%). An ORTEP plot of complex II is shown in Figure 1, and a schematic diagram with important bond distances and angles is presented in Figure 2.[7]

The structure contains an O_2CCCO moiety with bond lengths and angles consistent with a dimetal-substituted ketenecarboxylic acid. The C(3)–O(3) and C(2)–C(3) distances are comparable to those in other metal-substituted ketene complexes,[8,9] and the C(2)–C(3)–O(3) angle is 172(2)°. Sm(2) interacts with the

(6) The space group is P1 with a = 13.047 (4) Å, b = 13.564 (6) Å, c = 16.028 (5) Å, α = 78.51 (5)°, β = 70.60 (4)°, γ = 68.63 (6)°, U = 2481.6 Å^3, and D_c = 1.33 for Z = 1 (tetrameric unit). Least-squares refinement on the basis of 3297 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.068. Hydrogen atoms were not included, and the ring carbon atoms were refined with isotropic temperature factors. The thermal motion of all other atoms was dealt with anisotropically.

(7) Full crystallographic data are given as supplementary material.

(8) $(C_5H_5)(CO)(PMe_3)_2W$—$C(C_6H_4Me$=C=O has C=C = 1.24 (3) Å, C=O = 1.21 (3) Å: Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, L. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632–633.

(9) Bent η^2-ketene complexes generally have longer C=C and C=O distances: Redhouse, A. D.; Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615–616. Hermann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133–3135. Fachinetti, G.; Biran, C.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995–3002. Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173–1178. Bristow, G. W.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462–464. Moore, E. J.; Straus, D. A.; Armantrout, J.; Santasiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.

O_2CCCO ligand via a 2.25 (1) Å Sm(2)–O(2) connection. This distance is short compared to oxygen samarium donor bond distances[10–13] and is consistent with a single-bond interaction.[14–16] However, the C(1)–O(2) bond distance of 1.31 (2) Å is shorter than normal C–O single bonds.[17] Sm(1) is connected to the O_2CCCO moiety through O(1) and C(2) with Sm(1)–O(1) and Sm(1)–C(2) distances of 2.39 (1) and 2.77 (2) Å, respectively. The Sm(1)–O(1) length is closer to the O → Sm(III) donor bond range,[10] e.g., Sm(2)–O(4) = 2.47 (1) Å, than to a single-bond distance,[14] while the Sm–C length is longer than the few previously observed C–Sm(III) distances.[18,19] The dimer is held together by O(3)–Sm(1)′ connections of 2.38 (1) Å consistent with an oxygen-to-metal donor bond.[10]

Complex II exhibits a strong IR absorption at 2100 cm^{-1} in the ketene region[20] and is too insoluble in inert solvents to give an NMR spectrum.

The ketenecarboxylate skeleton in II can be formally derived from three CO molecules by two one-electron reductions (2Sm(II) → 2Sm(III) + 2e) plus the appropriate coupling. One-electron reduction of CO has been reported in the past primarily with alkali metal reducing agents.[21] Less precedent exists in the literature for the CO coupling observed in II, since a C=C—C linkage derived from CO requires cleavage of a carbon–oxygen bond in CO. Although cleavage of the CO triple bond followed by homologation is thought to occur in the heterogeneous Fischer–Tropsch systems,[5] cleavage of CO by homogeneous systems rarely gives homologated products.[22]

The results described above suggest that one-electron reduction chemistry of CO is a viable alternative to the heavily studied metal hydride approach to CO reduction and homologation.[5] The strongly reducing soluble divalent organosamarium complexes such as I[23,24] provide some unique features in this regard. Alkali and alkaline earth metals are strong enough reducing agents to effect CO reduction,[21] but since they carry no solubilizing coligands, neither these reagents nor their CO reduction products are generally soluble. The latter fact limits the possibility of multiple

(10) Complex, O → Sm donor bond distance(s) (Å): $(C_5Me_5)_2SmCl$-(THF),[11] 2.48 (2), 2.44 (2); $(C_5Me_5)_2SmI(THF)$,[11] 2.45 (1); $(C_5Me_5)_2Sm$-$(C_6H_5)(THF)$,[12] 2.511 (4); $[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-OCH}=CHO)$,[13] cis isomer 2.39 (1), trans isomer 2.36 (1), 2.39 (1).

(11) Evans, W. J.; Grate, J. W.; Levan, K. R.; Doedens, R. J.; Hunter, W. E.; Zhang, H.; Atwood, J. L., in preparation.

(12) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112–118.

(13) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

(14) Complex, Sm–O distance (Å): $[(C_5Me_5)_2Sm]_2(\mu\text{-O})$,[15] 2.094 (1); $(C_5Me_5)_2SmOC_6Me_4H$,[16] 2.13 (1); $[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-OCH}=CHO)$,[13] cis isomer 2.147 (10), 2.179 (10), trans isomer 2.122 (8), 2.107) (7). Large Sm–O–C angles as found in II are also observed in the above examples.[15,16]

(15) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

(16) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta*, in press.

(17) C–O single bond distances vary from 1.36 (1) Å for Ar–OH and acid and ester RCO–OR′ to 1.43 (10) Å for aliphatic alcohols and ethers: *Spec. Publ. Chem. Soc.* **1965**, *18*, M665. Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197–6200 and references therein.

(18) Complex, Sm–C distance (Å): $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[12] 2.511 (8); $[(CH_3C_5H_4)_2Sm(\mu\text{-C}$≡$CCMe_3)]_2$,[19] 2.55 (1).

(19) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709–714.

(20) IR of crystalline sample whose identity as II was confirmed by determining the unit cell parameters of two crystals in the sample (KBr, cm^{-1}): 2900 (vs, br), 2100 (vs), 1530 (w), 1480 (vs), 1450 (vs), 1370 (m), 1250 (vs), 1170 (m), 1070 (m), 1010 (s), 865 (s), 760 (m).

(21) (a) Liebig, J. *Ann.* **1834**, *11*, 182. (b) Joannis, A. *C. R. Hebd. Seanses Acad. Sci* **1893**, *116*, 1518; **1914**, *158*, 874–876. (c) Orchin, M.; Wender, I. *Catalysis* **1957**, *5*, Chapter 1 and references therein. (d) Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 2111–2120. (e) Weiss, E.; Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 1121–1127. (f) Büchner, W. *Chem. Ber.* **1966**, *99*, 1485–1492 and references therein. (g) Besson, J.; Renaud, M. *Rev. Chim. Miner.* **1969**, *6*, 157–168.

(22) Cf.: Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774–7775 and references therein.

(23) The related divalent organosamarium complexes $(C_5Me_5)_2Sm$[3b] and $[(C_5Me_5)Sm(\mu\text{-I})(THF)_2]_2$[24] are also available and do in fact react with CO.

(24) Evans, W. J.; Grate, J. W.; Bloom, I.; Choi, H. W.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

CO homologation. Soluble, strongly reducing, low-valent, transition-metal complexes are available, but with CO they form carbonyl complexes.[25] Hence, the low affinity of lanthanide ions to form stable CO complexes, the high oxophilicity of the lanthanides, and the strongly reducing Sm(II) → Sm(III) couple in soluble complexes allow distinctive CO chemistry to occur with organosamarium reagents. Further studies on these and related systems are in progress.

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(25) Titanocene chemistry provides one example: Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238. Bottrill, M.; Gavens, P. D.; McMeeking, J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds., Pergamon Press: Oxford, 1982; Chapter 22.2.

Carboxylate Bridge Exchange Reactions in the {Fe₂O(O₂CR)₂}²⁺ Core. Synthesis, Structure, and Properties of Phosphodiester-Bridged Complexes

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The recently reported binuclear iron(III) complexes containing the {Fe₂O(O₂CR)₂}²⁺ core[1,2] are currently the best available structural and spectroscopic models for the spin-coupled diiron(III) centers in hemerythrin[3] and ribonucleotide reductase.[4] Reactivity studies of this core structure have been initiated.[1b,5,6] In the hydrotris(1-pyrazolyl)borate derivative, [(HB(pz)₃)FeO-(O₂CCH₃)₂Fe(HB(pz)₃)] (**1**), facile ¹⁸O-exchange[1b] and protonation[5] reactions of the bridging oxygen atom have been observed. The fact that protonation of the oxo bridge is accompanied by expansion of the core suggested to us that concomitant exchange reactions of the bridging carboxylate groups might be feasible. Here we describe the results of initial investigations of carboxylate bridge exchange reactions with carboxylic and diesterified phosphoric acids. Interaction of the μ-oxodiiron(III) center with phosphate esters is of interest since iron(III) phosphate interactions occur in ferritin,[7] phosvitin,[8] and Fe^III–ATP model complexes[9] and are possibly involved in the phosphate-containing form of uteroferrin[10] and the binding of nucleoside diphosphate substrates

to ribonucleotide reductase. Moreover, we are concerned with the iron-promoted hydrolysis of phosphate esters[11] which may be of relevance to the phosphatase activity displayed by the purple acid phosphatases and uteroferrin.[10]

In both **1**[1] and its protonated derivative, [(HB(pz)₃)Fe-(OH)(O₂CCH₃)₂Fe(HB(pz)₃)](ClO₄) (**2**),[5] the bridging acetate groups exchange readily with perdeuterioacetic acid in solution as revealed by proton NMR spectroscopy (Figure 1). These reactions (eq 1 and 2) were carried out at room temperature with addition of 10 and 12.5 equiv of CD₃COOD for **1** and **2**, respectively. ¹H NMR spectra of the reactions, recorded ~0.5

$$[Fe_2O(O_2CCH_3)_2(HB(pz)_3)_2] + \text{excess } CD_3COOD \xrightarrow{CD_2Cl_2}$$
$$[Fe_2O(O_2CCD_3)_2(HB(pz)_3)_2] \quad (1)$$

$$[Fe_2(OH)(O_2CCH_3)_2(HB(pz)_3)_2]^+ +$$
$$\text{excess } CD_3COOD \xrightarrow{CD_3CN} [Fe_2(OD)(O_2CCD_3)_2(HB(pz)_3)_2]^+ \quad (2)$$

h after mixing, reveal that the bridged diiron(III) structures remain intact and that resonances associated with C*H₃* of the coordinated acetate groups vanish as the perdeuterioacetate analogues are formed.

By making use of a related reaction (eq 3) we have prepared the diphenylphosphate-bridged complex, [Fe₂O{O₂P(OC₆H₅)₂}₂-(HB(pz)₃)₂] (**3**). To a solution of 1.002 g (1.491 mmol) of **1** in

$$[Fe_2O(O_2CCH_3)_2(HB(pz)_3)_2] + 2(C_6H_5O)_2PO_2H \xrightarrow{CH_2Cl_2}$$
$$[Fe_2O\{O_2P(OC_6H_5)_2\}_2(HB(pz)_3)_2] + 2CH_3COOH \quad (3)$$

500 mL of CH₂Cl₂ was added a solution of 0.742 g (2.98 mmol) of (C₆H₅O)₂PO₂H in 50 mL of CH₂Cl₂ dropwise over approximately 5 min. The brown-green color of **1** in solution quickly changed to emerald-green. The reaction mixture was stirred for 1 h and then the solvent was stripped off with a rotary evaporator to yield a dark green oil. This oil was dissolved in 30 mL of CCl₄, and the resulting solution was allowed to stand for 3 days at ambient temperature during which time a microcrystalline green precipitate formed. The solid was filtered, washed with 10 mL of CCl₄ and then 2 × 10 mL portions of hexanes, powdered, and dried under vacuum to afford 1.394 g (75.6%) of the CCl₄ solvate of **3**. A similar procedure was used to prepare [Fe₂O{O₂P-(OC₂H₅)₂}₂(HB(pz)₃)₂]. Further purification of **3** was achieved by recrystallization from CHCl₃ with hexanes layered on top. Crystals of **3**·CHCl₃ suitable for X-ray diffraction studies[12] and elemental analysis[13] were obtained by this method.

The structure of **3** (Figure 2) reveals that the oxo-bridged diiron(III) core is retained upon exchange of carboxylate for diphenylphosphate ligands. Two bidentate diphenylphosphate bridges now span the μ-oxodiiron(III) core, and the resulting {Fe₂O[O₂P(OPh)₂]₂}²⁺ unit is capped by hydrotris(1-pyrazolyl)-borate ligands. The Fe–O_oxo distances are slightly longer in **3** than in **1**, 1.808 (4) vs. 1.784 (4) Å, respectively. The larger Fe–O–Fe angles, 134.7 (3)° vs. 123.6 (1)°, and resulting greater Fe···Fe separation, 3.337 (1) vs. 3.146 (1) Å, in **3** are presumably due to the increased O···O separation in phosphate compared to carboxylate ligands. The Fe–N and Fe–O_phosphate bond distances are typical for high-spin iron(III), and lengthening of Fe–N distances trans to the bridging oxo atoms for **3** is a feature also

(1) (a) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837–4838. (b) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *Ibid.* **1984**, *106*, 3653–3667. (c) Spool, A.; Williams, I. D.; Lippard, S. J. *Inorg. Chem.*, in press.

(2) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727.

(3) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618–622. (b) Klotz, I. M.; Kurtz, D. M., Jr. *Acc. Chem. Res.* **1984**, *17*, 16–22. (c) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51–85. (d) Sanders-Loehr, J.; Loehr, T. M. *Ibid.* **1979**, *1*, 235–252.

(4) (a) Reichard, P.; Ehrenberg, A. *Science (Washington, D.C.)* **1983**, *221*, 514–519. (b) Sjöberg, B.-M.; Graslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87–110. (c) Lammers, M.; Follman, H. *Struct. Bonding (Berlin)* **1983**, *54*, 27–91.

(5) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4632–4633.

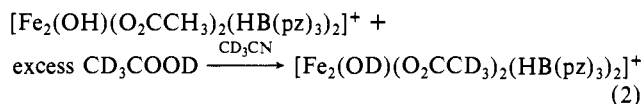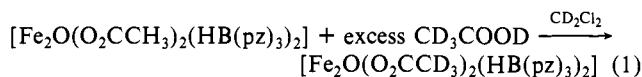(6) Wieghardt, K.; Pohl, K.; Ventur, D. *Angew. Chem.*, in press.

(7) Theil, E. C. *Adv. Inorg. Biochem.* **1983**, *5*, 1–38.

(8) Taborsky, G. *Adv. Inorg. Biochem.* **1983**, *5*, 235–279.

(9) Mansour, A. N.; Thompson, C.; Theil, E. C.; Chasteen, N. D.; Sayers, D. E. *J. Biol. Chem.*, in press.
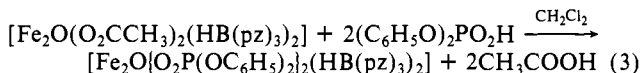
(10) Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111–136.

(11) For related work see: Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 7807–7819 and references cited therein.

(12) X-ray analysis: The compound [Fe₂O{O₂P(OC₆H₅)₂}₂(HB(pz)₃)₂]·CHCl₃ crystallizes in the monoclinic system, space group P2₁/n, with a = 11.940 (2) Å, b = 20.105 (4) Å, c = 22.155 (3) Å, β = 96.56 (1)°, V = 5283.6 Å³, ρ_obsd = 1.48 (1) g cm⁻³, ρ_calcd = 1.473 g cm⁻³, Z = 4. With the use of 4693 unique reflections (F₀ > 6σ(F₀)) collected at ca. 296 K with Mo Kα (λ = 0.7107 Å) radiation out to 2θ = 46° on a single crystal X-ray diffractometer, the structure was solved by standard direct and difference Fourier methods and refined by using 540 variables to a current value of the discrepancy index R₁ of 0.059. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

(13) Elemental analysis: Calcd for Fe₂C₄₃H₄₁B₂Cl₃N₁₂O₉P₂(3·CHCl₃): Fe, 9.53; C, 44.09; H, 3.53; Cl, 9.08; N, 14.35; P, 5.29. Found: Fe, 9.28; C, 43.72; H, 3.50; Cl, 9.09; N, 14.44; P, 5.06.