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# Cooperative Reactivity of Unsupported Early−Late Heterobimetallics: Ring Opening and Subsequent Decarbonylation of Biaryllactones

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*Summary: Reaction of the heterodinuclear complex [HC{$SiMe_2N(2\text{-}FC_6H_3)$}$_3$Zr−FeCp(CO)$_2$] (**1**) with 1,3-dimethyl-6H-benzo[b]naphtho[1,2-d]pyranone (**2**) and 1,3-dimethoxy-6H-benzo[b]-naphtho-[1,2-d]pyranone (**3**) led to immediate ring opening of the lactones to yield products which combine the biaryl fragment with aryloxyzirconium and acyl−FeCp(CO)$_2$ units. The latter slowly decarbonylate to yield the corresponding heterobimetallic complexes in which the {MCp(CO)$_2$} fragment is directly bonded to the naphthalene ring.*

Heterobimetallic complexes containing one or more metal−metal bonds between metals of the Ti−triad and late transition metals have been studied with the aim of utilizing the cooperative reactivity of the electrophilic and nucleophilic metal centers in reactions with polar organic substrates.[1] The combination of complementary metal complex fragments may, in principle, lead to highly selective conversions, although direct experimental evidence is still rare.[2] Stabilizing the early transition metal center by coordination of a tridentate amido ligand provided unsupported heterobimetallics which are kinetically sufficiently stable to allow the systematic investigation of their reactivity.[3,4] A characteristic feature of all the conversions involving zirconium−iron and −ruthenium complexes studied to date is the high reactivity of the heterodinuclear compounds and, consequently, the extremely mild reaction conditions which may be chosen, as well as the selectivity of the chemical transformations. In this paper, we report the reactivity of Zr−Fe heterobimetallics toward two configuratively unstable biaryl lactones, 1,3-dimethyl-6*H*-benzo[*b*]naphtho[1,2-d]pyranone (**2**) and 1,3-dimethoxy-6*H*-benzo[*b*]-naphtho-[1,2-*d*]-pyranone (**3**),[5a] which constitute substrates for asymmetric lactone cleavage reactions[5b] as, e.g., employed in the synthesis of axially chiral biaryl alkaloids.[6,7]

Reaction of **2** and **3** with the heterodinuclear complex [HC{$SiMe_2N(2\text{-}FC_6H_3)$}$_3$Zr−FeCp(CO)$_2$] (**1**)[8] cleanly led to the ring opening of the lactones with concomitant cleavage of the metal−metal bond, yielding compounds **4** and **5** (Scheme 1).[9] A characteristic feature of the $^1$H and $^{13}$C NMR spectra of both compounds is the diastereotopic splitting of the methyl resonances of the $SiMe_2$ units in the tripod ligand and the chemical shift of the signal assigned to the acyl carbon nuclei which is observed at $\delta$ 296.0 and 297.6 for **4** and **5**, respectively. These chemical shifts at extremely low field are indicative of the coordination of the acyl oxygen atoms to the Lewis acidic zirconium centers, thus forming an eight-membered metallacycle in which the biaryl unit is

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(9) Data for **4** are as follows. Anal. Calcd for $C_{51}H_{50}F_3FeN_3O_4Si_3Zr$: C, 57.99; H, 4.74; N, 3.98. Found: C, 57.69; H, 4.78; N, 3.52. $^1$H NMR ($C_6D_6$, 295 K): $\delta$ −0.18 (s, HC(Si...)$_3$), 0.42, 0.55 (s, (Si(CH$_3$)$_2$), 1.74 (6′-CH$_3$), 2.09 (4′-CH$_3$), 3.85 (s, $C_5H_5$), 5.62−7.57 (m, 2-FC$_6$H$_4$ and lactone **2**). $^{13}$C NMR ($C_6D_6$, 295 K): $\delta$ 3.9, 4.8 (Si(CH$_3$)$_2$), 7.7 (HC(Si...)$_3$), 20.9 (ArCH$_3$), 21.1 (ArCH$_3$), 87.2 ($C_5H_5$), 115.2 (d, $^2J_{FC} = 22.1$ Hz, C$^3$ of 2-FC$_6$H$_4$), 120.3 (C$^4$ of 2-FC$_6$H$_4$), 124.2 (C$^5$ of 2-FC$_6$H$_4$), 126.7 (C$^6$ of 2-FC$_6$H$_4$), 141.8 (d, $^2J_{FC} = 13.1$ Hz, C$^1$ of 2-FC$_6$H$_4$), 157.9 (d, $^1J_{FC} =$ 235.4 Hz, C$^2$ of 2-FC$_6$H$_4$), 211.2, 212.2 (CO), 296.2 (ZrO(...)*C*OFe), 115.9, 117.0, 119.4, 121.8, 122.7, 126.1, 126.7, 127.5, 128.5, 132.7, 132.9, 155.2, 161.8 (lactone **2**). $^{19}$F NMR ($C_6D_6$, 295 K): $\delta$ −122.0. $^{29}$Si NMR ($C_6D_6$, 295 K): $\delta$ 2.0. IR (benzene): $\nu$(CO) 2028, 1985 cm$^{-1}$. Data for **5** are as follows. Anal. Calcd for $C_{51}H_{50}F_3FeN_3O_6Si_3Zr$: C, 56.28; H, 4.60; N, 3.86. Found: C, 56.36; H, 4.77; N, 3.58. $^1$H NMR ($C_6D_6$, 295 K): $\delta$ −0.17 (s, HC(Si...)$_3$), 0.43, 0.54 (s, (Si(CH$_3$)$_2$), 2.96 (6′-CH$_3$), 3.41 (4′-OCH$_3$), 3.93 (s, $C_5H_5$), 5.60−7.50 (m, 2-FC$_6$H$_4$ and lactone **3**). $^{13}$C NMR ($C_6D_6$, 295 K): $\delta$ 4.0, 4.3 (Si(CH$_3$)$_2$), 7.8 (HC(Si...)$_3$), 54.6 (OCH$_3$), 55.4 (OCH$_3$), 87.1 ($C_5H_5$), 115.2 (d, $^2J_{FC} = 22.1$ Hz, C$^3$ of 2-FC$_6$H$_4$), 120.3 (C$^4$ of 2-FC$_6$H$_4$), 124.2 (C$^5$ of 2-FC$_6$H$_4$), 126.7 (C$^6$ of 2-FC$_6$H$_4$), 141.7 (d, $^2J_{FC} = 13.1$ Hz, C$^1$ of 2-FC$_6$H$_4$), 157.9 (d, $^1J_{FC} = 235.4$ Hz, C$^2$ of 2-FC$_6$H$_4$), 210.6, 211.5 (CO), 297.6 (ZrO(...)*C*OFe), 115.9, 117.8, 121.8, 123.1, 126.0, 129.5, 132.9, 133.5, 155.7, 158.7, 161.9, 163.7 (lactone **3**). $^{19}$F NMR ($C_6D_6$, 295 K): $\delta$ −121.9. $^{29}$Si NMR ($C_6D_6$, 295 K): $\delta$ 2.1. IR (benzene): $\nu$(CO) 2030, 1991 cm$^{-1}$.

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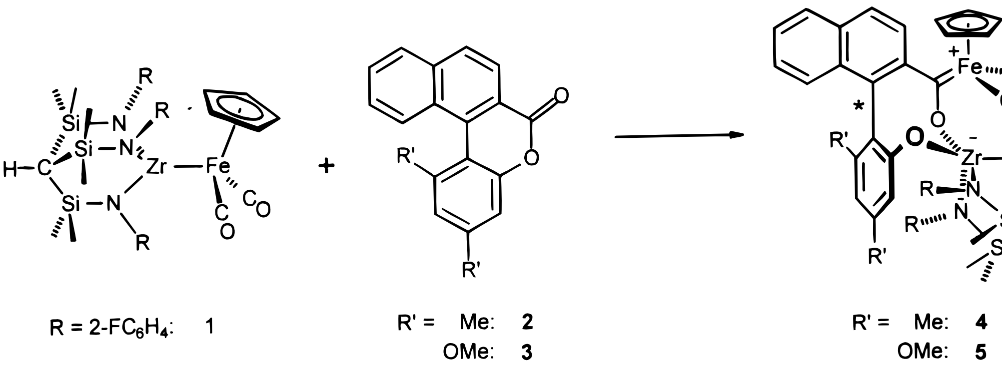
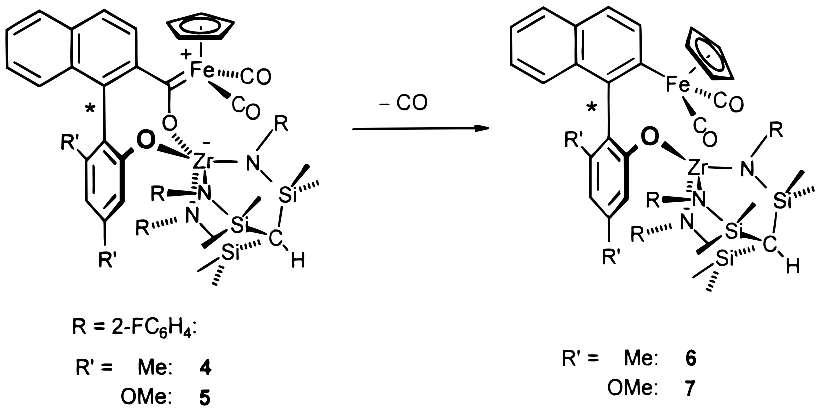
**Scheme 1**



**Scheme 2**



conformationally stable on the NMR time scale, as reflected in the diastereotopicity of the $SiMe_2$ signals mentioned above. On the basis of the low-field $^{13}C$ NMR resonances, which should be compared with those observed at ca. $\delta$ 254 in $[Cp(CO)_2Fe(COR)]$ (R = Me, Ph),[10] the acyl–metal groups in **4** and **5** are thought to be more adequately formulated as carbene metal units, implying a formally zwitterionic nature of the dinuclear complexes as depicted in Scheme 1.[11]

Upon stirring **4** and **5** in pentane solution, slow decarbonylation occurs, yielding the dinuclear complexes **6** and **7** in which the $\{Cp(CO)_2Fe\}$ fragment is directly bonded to the naphthalene ring (Scheme 2).[12] The most characteristic spectroscopic changes accompanying this conversion is the shift of the (CO) infrared bands by ca. 30 $cm^{-1}$ to lower wavenumbers (**4** 2030, 1991 $cm^{-1}$; **5** 2028, 1985 $cm^{-1}$ to **6** 2000, 1956 $cm^{-1}$; **7** 1997, 1954 $cm^{-1}$), the disappearance of the acyl/carbene resonance just below 300 $cm^{-1}$, and the $^1H$ NMR shift of the Cp signal to higher field (**4** $\delta$ 3.93; **5** $\delta$ 3.85 to **6** $\delta$ 4.23; **7** $\delta$ 4.15, recorded in $C_6D_6$). We note that the thermally and photochemically induced decarbonylation of acyliron complexes has been reported previously.[13]

To fully establish the structures of the decarbonylation products **6** and **7**, a single-crystal X-ray structure analysis of **7** was carried out (Figure 1).[14] Although the crystal diffracted weakly, a consequence of the presence of a disordered toluene solvent, resulting in relatively large esd's on all parameters, the structure of the compound is well established. The structural center

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[10] (a) Kuhlmann, E. J.; Alexander, J. J. *Inorg. Chem. Acta* **1979**, *34*, L193. (b) Felkin, H.; Meunier, B.; Pascard, C.; Prange, T. *J. Organomet. Chem.* **1977**, *135*, 361.

[11] $^{13}C$ NMR data of related alkoxycarbeneiron complexes: (a) Casey, C. P.; Miles, W. H.; Tukuda, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (b) Akita, M.; Kawahara, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1356. (c) Brookhart, M.; Studabaker, G. R.; Husk, G. R. *Organometallics* **1987**, *6*, 1141.

[12] Data for **6** are as follows. Anal. Calcd for $C_{50}H_{50}F_3FeN_3O_3Si_3Zr$: C, 58.35; H, 4.90; N, 4.08. Found: C, 57.98; H, 4.73; N, 3.94. $^1H$ NMR ($C_6D_6$, 295 K): $\delta$ −0.35 (s, HC(Si...)$_3$), 0.22, 0.31 (s, $(Si(CH_3)_2)$), 1.70 (6′-$CH_3$), 2.10 (4′-$CH_3$), 4.23 (s, $C_5H_5$), 6.33−7.64 (m, 2-$FC_6H_4$ and lactone **2**). $^{13}C$ NMR ($C_6D_6$, 295 K): $\delta$ 3.1, 4.9 $(Si(CH_3)_2)$, 8.8 (HC(Si...)$_3$), 20.9 ($ArCH_3$), 21.5 ($ArCH_3$), 86.4 ($C_5H_5$), 115.0 (d, $^2J_{FC}$ = 23.1 Hz, $C^3$ of 2-$FC_6H_4$), 120.1 ($C^4$ of 2-$FC_6H_4$), 122.2 ($C^5$ of 2-$FC_6H_4$), 125.3 ($C^6$ of 2-$FC_6H_4$), 139.9 (d, $^2J_{FC}$ = 12.1 Hz, $C^1$ of 2-$FC_6H_4$), 158.1 (d, $^1J_{FC}$ = 227.4 Hz, $C^2$ of 2-$FC_6H_4$), 214.2, 217.2 (CO), 117.1, 119.0, 124.1, 124.6, 124.9, 125.6, 129.3, 132.1, 132.7, 144.8, 146.9, 148.4, 160.5 (lactone **2**). $^{19}F$ NMR ($C_6D_6$, 295 K): $\delta$ −123.0. $^{29}Si$ NMR ($C_6D_6$, 295 K): $\delta$ 3.3. IR (benzene): $\nu$(CO) 2000, 1956 $cm^{-1}$. Data for **7** are as follows. Anal. Calcd for $C_{50}H_{50}F_3FeN_3O_5Si_3Zr$: C, 56.59; H, 4.75; N, 3.96. Found: C, 56.39; H, 4.49; N, 3.90. $^1H$ NMR ($C_6D_6$, 295 K): $\delta$ −0.37 (s, HC(Si...)$_3$), 0.24, 0.30 (s, $(Si(CH_3)_2)$), 3.01 (6′-$OCH_3$), 3.48 (4′-$OCH_3$), 4.15 (s, $C_5H_5$), 6.30−7.68 (m, 2-$FC_6H_4$ and lactone 3). $^{13}C$ NMR ($C_6D_6$, 295 K): $\delta$ 3.0, 5.1 $(Si(CH_3)_2)$, 8.7 (HC(Si...)$_3$), 54.2 ($ArOCH_3$), 55.1 ($ArOCH_3$), 86.8 ($C_5H_5$), 114.4 (d, $^2J_{FC}$ = 22.8 Hz, $C^3$ of 2-$FC_6H_4$), 120.0 ($C^4$ of 2-$FC_6H_4$), 122.6 ($C^5$ of 2-$FC_6H_4$), 125.4 ($C^6$ of 2-$FC_6H_4$), 140.3 (d, $^2J_{FC}$ = 12.0 Hz, $C^1$ of 2-$FC_6H_4$), 158.5 (d, $^1J_{FC}$ = 228.6 Hz, $C^2$ of 2-$FC_6H_4$), 214.1, 217.8 (CO), 117.2, 119.3, 124.1, 124.7, 124.7, 125.5, 129.9, 133.0, 132.8, 145.2, 146.7, 148.9, 161.3 (lactone **3**). $^{19}F$ NMR ($C_6D_6$, 295 K): $\delta$ −124.1. $^{29}Si$ NMR ($C_6D_6$, 295 K): $\delta$ 3.4. IR (benzene): 1997, 1954 $cm^{-1}$.

[13] Representative examples: (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. (b) Labinger, J. A.; Bonfiglio, J. N.; Grimmet, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733.

[14] Crystal data for **7**·$^1/_2C_7H_8$: $C_{53.5}H_{54}F_3FeN_3O_5Si_3Zr$, $M$ = 1107.34, monoclinic, space group $C2/c$, $a$ = 40.373(7) Å, $b$ = 13.056(4) Å, $c$ = 20.130(4) Å, $\beta$ = 96.067(10)°, $V$ = 10551(4) Å$^3$, $Z$ = 8, $F(000)$ = 4568, $D_c$ = 1.394 g $cm^{-3}$, $\mu$(Mo K$\alpha$) 0.600 $mm^{-1}$, $\lambda$(Mo K$\alpha$) = 0.710 73 Å. All samples examined diffracted weakly. Of 6662 data collected from a yellow block (0.34 × 0.36 × 0.44 mm) using a Siemens P4 four-circle diffractometer, 5668 unique reflections corrected for absorption by $\Psi$-scans ($R_{int}$ = 0.0867, $T_{max}$ 0.603, $T_{min}$ 0.547) in the limited $\theta$-range 1.01−21.00° were used in subsequent analysis. The structure was solved by direct methods and refined on $F^2$ to convergence at $R_1$ [$I > 2\sigma(I)$] = 0.0852 and w$R_2$ = 0.1623 (w$R_2$ (all data) = 0.2310) for 581 parameters (GooF on $F^2$ = 0.998). SHELXTL-PC (version 5.03; Siemens Analytical X-ray: Madison, WI, 1996) running on an AT486-66 PC was used for all computations.

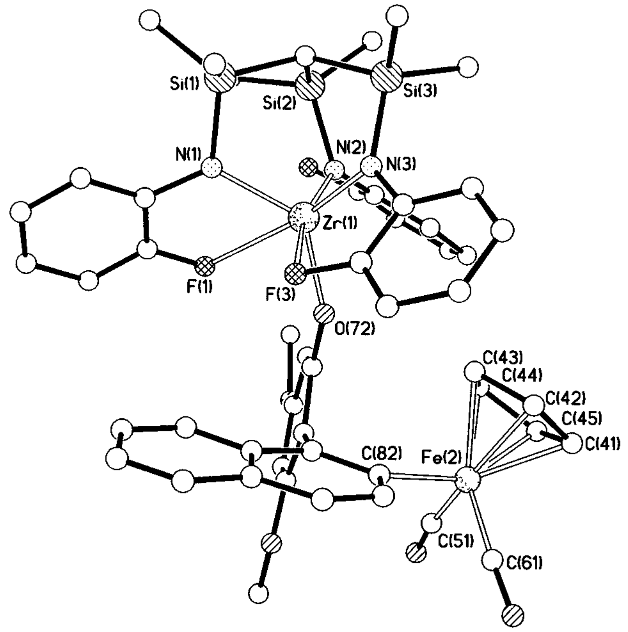

**Figure 1.** Molecular structure of **7**. Principal bond lengths (Å) and interbond angles (deg): Zr(1)–O(72) 1.965(9), Zr(1)–N(1) 2.061(11), Zr(1)–N(2) 2.075(11), Zr(1)–N(3) 2.099(10), Zr(1)–F(3) 2.548(8), Zr(1)–F(1) 2.591(9), Fe(2)–C(41) 2.12(2), Fe(2)–C(42) 2.15(2), Fe(2)–C(43) 2.11(2), Fe(2)–C(44) 2.12(2), Fe(2)–C(45) 2.115(14), Fe(2)–C(51) 1.72(2), Fe(2)–C(61) 1.75(2), Fe(2)–C(82) 1.993(14), O(72)–Zr(1)–N(1) 131.3(4), O(72)–Zr(1)–N(2) 106.6(4), N(1)–Zr(1)–N(2) 100.8(4), O(72)–Zr(1)–N(3) 114.5(4), N(1)–Zr(1)–N(3) 100.3(4), N(2)–Zr(1)–N(3) 98.0(4), O(72)–Zr(1)–F(3) 74.7(3), N(1)–Zr(1)–F(3) 88.8(3), N(2)–Zr(1)–F(3) 164.8(3), N(3)–Zr(1)–F(3) 68.4(3), O(72)–Zr(1)–F(1) 73.8(3), N(1)–Zr(1)–F(1) 67.1(4), N(2)–Zr(1)–F(1) 89.2(4), N(3)–Zr(1)–F(1) 166.6(4), F(3)–Zr(1)–F(1) 105.6(3), C(51)–Fe(2)–C(61) 89.9(8), C(51)–Fe(2)–C(82) 95.6(6), C(61)–Fe(2)–C(82) 90.8(7).

piece is the ring-opened and decarbonylated biaryl lactone with the {Fe(CO)$_2$Cp} unit bonded to the 2-position of the naphthyl group (Fe–C(82) 1.993(14)). The aromatic units of the biaryl lactone lie in a virtually orthogonal disposition (dihedral angle 87.5°), which appears to be fixed by the steric interplay of the {Fe(CO)$_2$Cp} unit with the periphery of the tripodal trisilylmethane ligand. The orientation of the two methoxy groups, which is coplanar with the phenyl ring, is an indication of $\pi$-interaction between the aromatic ring and the substituents. Coordination of two of the fluorine atoms of the tripodal ligand to the zirconium center in the complex generates a hexacoordinate metal center with a highly distorted ligand polyhedon that may be best viewed as a bicapped tetrahedron with the two fluorine donors capping the faces. We previously observed the participation of potentially binding peripheral donor atoms in the coordination to an early transition metal center in [HC{SiMe$_2$N(2-FC$_6$H$_3$)}$_3$-ZrCl$_2$Li(OEt$_2$)$_2$] and [HC{SiMe$_2$N(2-FC$_6$H$_3$)}$_3$Y(OEt$_2$)] in which, respectively, one and three F atoms coordinate to the metal center.[8] In this system, we envisage that the coordinated fluorines play a role in shielding open portions of the high-valent metal center.

This first study of the reactivity of unsupported Zr–Fe heterobimetallics toward biaryl lactones has shown that they not only achieve the ring opening to generate the axially chiral substrates but, in addition, remove the "auxiliary" carbonyl function of the lactone. This is of importance for the synthesis of natural products containing a biaryl axis but lacking such a C$_1$ unit next to the axis.[6] In present and future studies, we investigate the potential of chiral early–late heterobimetallics, containing a previously reported $C_3$-chiral tripodal amido ligand,[15] in order to achieve stereoselectivity in the ring-opening reactions of the lactones.

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**Supporting Information Available:** Detailed preparative procedures as well as tables of atomic coordinates, thermal parameters, and full bond lengths and angles (17 pages). Ordering information is given on any current masthead page.

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(15) (a) Memmler, H.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1994**, *33*, 3064. (b) Memmler, H.; Kauper, U.; Gade, L. H.; Stalke, D.; Lauher, J. W. *Organometallics* **1996**, *15*, 3637.