= 1.1-1.2) for spectroscopic investigations (Figure 1).[18]

A variety of catalyst precursors were studied to probe the influence of catalyst structure on the stereochemistry of phenylsilane oligomerization. The microstructure of the fractionated polyphenylsilanes was studied by ^{29}Si NMR spectroscopy (Figure 1). As previously reported,[4] we find that oligomerization of phenylsilane (1.73 M) with Cp_2ZrMe_2 in toluene at room temperature affords oligomers which show a broad series of resonances between -50 and -65 ppm in the ^{29}Si NMR spectrum (Figure 1a).[19] Since the ^{29}Si NMR chemical shift of each stereogenic silicon atom is sensitive to the relative stereochemistry of adjacent silicon atoms, these broad series of resonances are indicative of an atactic microstructure. In contrast, the ^{29}Si NMR spectrum of oligomers obtained from the chiral racemic (ethylenebis(indenyl))zirconocene dibutyl precursors (eq 1) displays a much narrower set of resonances between -60 and -63 ppm, indicative of a stereoregular microstructure (Figure 1b). (DEPT experiments establish that the sharp resonance at -58 ppm is due to SiH_2 end groups.) Remarkably, we find a very similar microstructure when phenylsilane is polymerized at a higher concentration (5.6 M) with achiral catalyst precursors such as Cp_2ZrMe_2 and Cp_2ZrHCl.[20] The effect of concentration on the stereochemistry of phenylsilane polymerization with Cp_2ZrMe_2[21] was unexpected and is not completely understood. Nevertheless, the fact that similar microstructures are obtained in the presence of chiral and achiral metallocenes implies that chiral catalysts, although effective, are not necessary for stereoregulation in the catalytic oligomerization of phenylsilane.

Because there are few stereochemically defined model compounds for spectroscopic comparison, only a tentative assignment of the microstructure is possible. For the atactic material, several broad resonances are discernible in the ^{29}Si NMR spectrum. The narrow set of resonances for the stereoregular oligomers are coincident with the high-field resonance of the atactic material and are centered at δ = -61 ppm. This chemical shift corresponds closely to the ^{29}Si NMR chemical shift (-61.6 ppm) of the known crystalline hexaphenylcyclohexasilane,[22,23] which has been assigned as the trans (or syndiotactic[24]) isomer. On the basis of this, we assign a predominantly syndiotactic microstructure to the linear stereoregular oligosilanes.[25]

In summary, we report the synthesis and characterization of predominantly syndiotactic polyphenylsilane. The stereochemistry of phenylsilane polymerization with chiral and achiral zirconocene derivatives suggests that the stereochemistry of the growing chain end is involved in stereodifferentiation and may be more important than the chirality of the catalyst.

Acknowledgment. This work was initiated with support from the Center of Materials Research at Stanford under the NSF-MRL Program. We gratefully acknowledge the Exxon Educational Foundation for a Research and Training Grant. R.M.W. is the recipient of a Du Pont Young Faculty Award, for which he is grateful. We thank Dr. I. Farnan and Prof. J. Stebbins for assistance in obtaining the solid-state ^{29}Si NMR spectra, Frauke Josuweit for technical assistance, and Dr. Luigi Resconi for helpful discussions.

Supplementary Material Available: Text giving experimental details, a table of experimental data, and ^{29}Si NMR spectra (4 pages). Ordering information is given on any current masthead page.

(18) The absorption properties polysilanes are dependent on molecular weight,[1] and thus for comparisons of samples of different microstructures it is important to have reasonably narrow polydispersities.

(19) A similar microstructure is observed using Cp_2ZrCl_2/*n*-BuLi as a catalyst precursor.

(20) ^{29}Si NMR spectra of oligomers obtained from these precursors are very similar to that shown in Figure 1b (see supplementary material).

(21) There appears to be no concentration dependence on the stereochemistry for polymers produced with (EBI)$ZrCl_2$ or $Cp_2Zr(H)Cl$ catalyst precursors.

(22) (a) Hengge, E.; Lunzer, F. *Monatsh. Chem.* **1976**, *107*, 371. (b) Hennge, E. *J. Organomet. Chem. Libr.* **1979**, *9*, 261.

(23) This compound can be isolated from polymerization mixtures obtained with (EBI)$ZrCl_2$ precursors at low phenylsilane concentration. A singlet at -60.2 ppm in the solid-state ^{29}Si NMR spectrum is consistent with the trans isomer.

(24) For assignments of relative stereochemistry for polymers with stereogenic centers at each backbone atom, see: Farina, M. *Top. Stereochem.* **1987**, *17*, 1.

(25) West has used a similar analysis to assign the microstructure of polyphenylmethylsilane.[3]

Reduction of the Heterobimetallic μ-$\eta^1(C)$:$\eta^2(O,O')$-CO_2 Complex $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ to Its μ-$\eta^1(C)$:$\eta^1(O)$-Formaldehyde Derivative $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$: Hydride Transfer Occurs at Ligated Carbon Monoxide

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Summary: Treatment of the previously characterized RuZr μ-$\eta^1(C)$:$\eta^2(O,O')$-CO_2 complex $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ (**5**) with $Cp_2Zr(H)Cl$ (2 equiv) cleanly affords the stable μ-formaldehyde compound $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$ (**7**), which has been isolated and fully characterized. The ^{13}C-labeled CO_2 complex $Cp(CO)_2Ru(^{13}CO_2)Zr(Cl)Cp_2$ (**5a**) is available from $^{13}CO_2$ (99% labeled); combining **5a** and $Cp_2Zr(H)Cl$ at -78 °C selectively produces $Cp(^{13}CO)(CO)Ru(CH_2O)Zr(Cl)Cp_2$ (**7a**). Complex **5a** transforms to a 1:1.3 mixture of **5a** and its isotopomer $Cp(^{13}CO)(CO)Ru(CO_2)Zr(Cl)Cp_2$ (**5b**) at room temperature (benzene or toluene solutions for 8-12 h). $Cp_2Zr(H)Cl$ then reduces **5a/5b** to a 3:1 mixture of **7a** and its isotopomer $Cp(CO)_2Ru(^{13}CH_2O)Zr(Cl)Cp_2$ (**7b**). IR and NMR (^{1}H, ^{13}C) spectral data are presented for **5/5a/5b** and **7/7a/7b**, and credible mechanistic pathways for ^{13}C-labeled exchange between carboxylate and terminal carbonyl sites for **5a** ⇔ **5b** and for regioselective hydride transfer ($Cp_2Zr(H)Cl$) to a terminal carbonyl (not the carboxylate center) of **5** are discussed.

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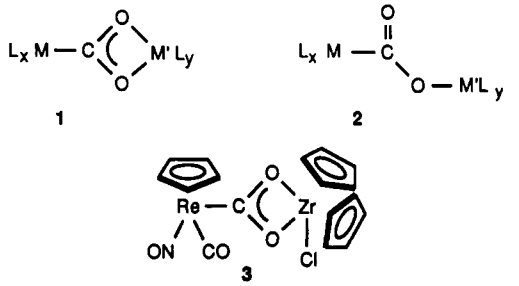
Organotransition-metal heterobimetallic μ-$\eta^1(C)$:$\eta^2(O,O')$- and μ-$\eta^1(C)$:$\eta^1(O)$-carbon dioxide complexes (1 and 2, respectively) could promote the reduction of ligated carbon dioxide,[1] especially if pairing electron-rich (ML_x) and oxophilic ($M'L_y$) metal centers on 1/2 synergistically activates the μ-carboxylate ligand as a hydride acceptor.[2,3] ReZr

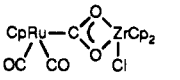
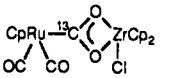
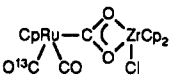
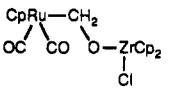
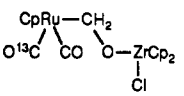
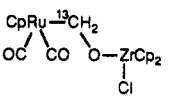


1 2

3

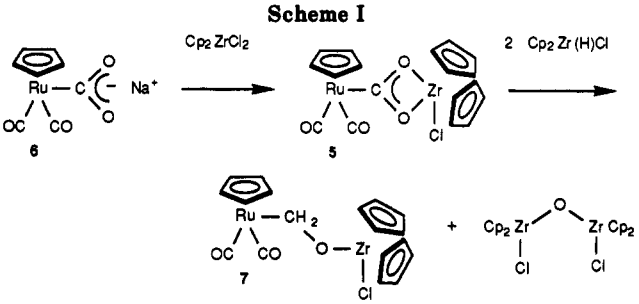
μ-η^1(C):$\eta^2(O,O')$-CO_2 complex 3 reacts with $Cp_2Zr(H)Cl$ (2 equiv) and converts to its μ-$\eta^1(C)$:$\eta^1(O)$-formaldehyde derivative $Cp(NO)(CO)Re(CH_2O)Zr(Cl)Cp_2$ (4).[4] The carboxylate carbon on 3 is a plausible hydride acceptor, since $Cp_2Zr(H)Cl$ reduces zirconocene $\eta^2(O,O')$-carboxylates $Cp_2(Cl)Zr(OCRO)$ (R = H, CH_3, Ph, ^{t}Bu) and releases aldehydes RCHO.[5,6] Results of a ^{13}C-labeling study are now reported for analogous $Cp_2Zr(H)Cl$ reduction of the fully characterized RuZr μ-$\eta^1(C)$:$\eta^2(O,O')$ dimetallo carboxylate $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ (5).[7]

Table I. Selected Spectral Data for RuZr μ-CO_2 and μ-CH_2O Isomers

RuZr complex	IR, cm^{-1} ν(CO)	IR, cm^{-1} ν(OCO)	^1H NMR (C_6D_6), δ
 5	2040[a] 1982	1349 1292	
 5a	2040[a] 1982	1312 1264	
 5b	2024[a] 1955	1348 1290	
 7	2008[b] 1944		5.69 (s, $RuCH_2$)[c]
 7a	1991[b] 1913		5.68 (d, $^2J_{CH}$ = 1.2 Hz, $RuCH_2$)
 7b	2008[b] 1945		5.68 (d, $^1J_{CH}$ = 154 Hz, $RuCH_2$)

[a] THF. [b] C_6H_6. [c] 7: ^1H NMR (C_6D_6) δ 5.99 (s, Cp_2Zr), 5.69 (s, $RuCH_2$), 4.90 (s, CpRu); ^{13}C NMR (C_6D_6) δ 202.7 (RuCO), 113.2 (Cp_2Zr), 89.4 (CpRu), 58.6 ($RuCH_2$, $^1J_{CH}$ = 150 Hz). Anal. Calcd for $C_{18}H_{17}O_3ClRuZr$: C, 42.47; H, 3.37; Cl, 6.96. Found: C, 42.36; H, 3.08; Cl, 6.86.

Scheme I



Treatment of the stable RuZr μ-CO_2 compound 5 with 2.0 equiv of $Cp_2Zr(H)Cl$ produces a 1:1 mixture of the RuZr μ-$\eta^1(C)$:$\eta^1(O)$-methyleneoxo complex $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$ (7) (>90% spectroscopic yield) and the μ-oxo byproduct $(Cp_2(Cl)Zr)_2O$ (Scheme I). Complex 7 was isolated in 70% yield (85–90% pure, contaminated with $(Cp_2(Cl)Zr)_2O$) by extracting with ether and hexane, and additional recrystallization from hexane provided analytically pure 7. NMR spectral data for 7 (and for its ^{13}C-labeled isotopomers, vide infra) are in accord with the proposed structure; its Ru–CH_2 ^{13}C NMR absorption (δ 57.8, $^1J_{CH}$ = 154 Hz) resembles those of 4[4] (δ 53.1, $^1J_{CH}$ = 147 Hz) and of $Cp(CO)_2Ru(CH_2OCH_3)$[8] (δ 59.8, all data in C_6D_6).

Other relevant examples of μ-formaldehyde compounds include Bercaw's[9,10] FeZr and RuZr systems $Cp(PMe_3)_2M(CH_2O)Zr(H)(\eta^5\text{-}C_5Me_5)_2$ and the series of zirconocene metallaoxirane μ-$\eta^2(C,O)$:η^1(O) species[11] $Cp_2(X)Zr$-

(1) (a) Reviews on CO_2 complexes: Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, Federal Republic of Germany, 1988. Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. Ayers, W. M. *ACS Symp. Ser.* **1988**, *No. 363*. Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (b) Heterobimetallic activation of coordinated ligands: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(2) Hydride transfer to or net hydrogenation of CO_2 complexes has not been established,[1a] although hydridometal complexes commonly "insert" exogenous CO_2 and produce formato compounds.[2a] In addition, metal complexes that bind CO_2 often reduce it to carbon monoxide, either by reductive disproportionation[2b] or by oxygen atom abstraction.[2c] (a) Selected recent examples: Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.* **1990**, *112*, 9252. Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 297. Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223. Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876. Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500. (b) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033. Recent examples: Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004. Reinking, M. K.; Ni, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 6459. (c) Fu, P.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 382. Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826. Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. Alt, H. G.; Schwind, K. H.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *321*, C9. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

(3) Little precedent exists for alkylating, silylating, metalating, or otherwise derivatizing CO_2 complexes. (a) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363 and references therein. (b) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. Senn, D. R.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Inorg. Chem.* **1987**, *26*, 2737. Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870. Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967. Lundquist, E. G.; Huffman, J. C.; Folting, K.; Mann, B. E. Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 128. (c) pH-dependent reactions involving $\eta^1(C)$ metallo carboxylate or $\eta^2(C,O)$-CO_2 metallo carboxylic acid–carbonyl ligands are thoroughly documented.[3a] Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139. Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 6591 and references cited therein. Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 450. Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1991**, *10*, 29.

(4) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

(5) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877.

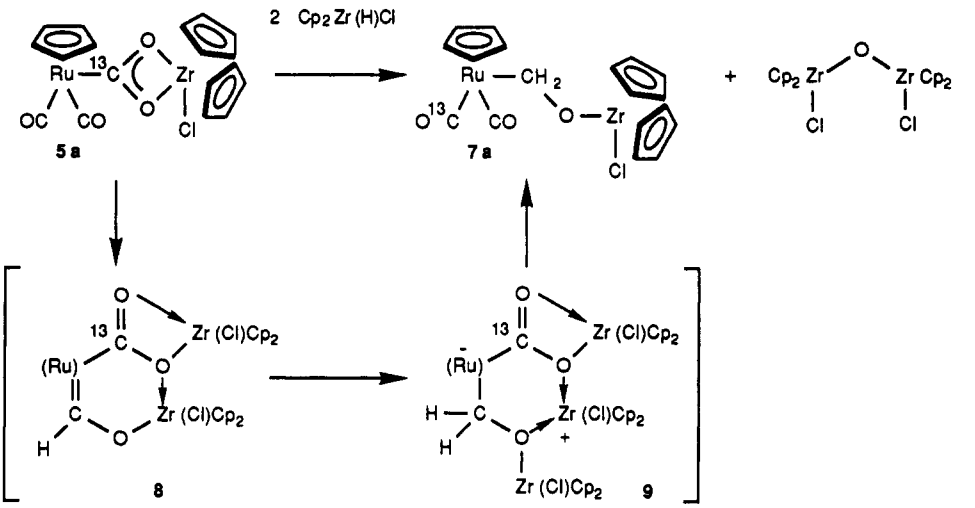
(6) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

(7) Vites, J. C.; Steffey, B. D.; Giuseppetti-Dery, M. E.; Cutler, A. R. *Organometallics* **1991**, *10*, 2827.

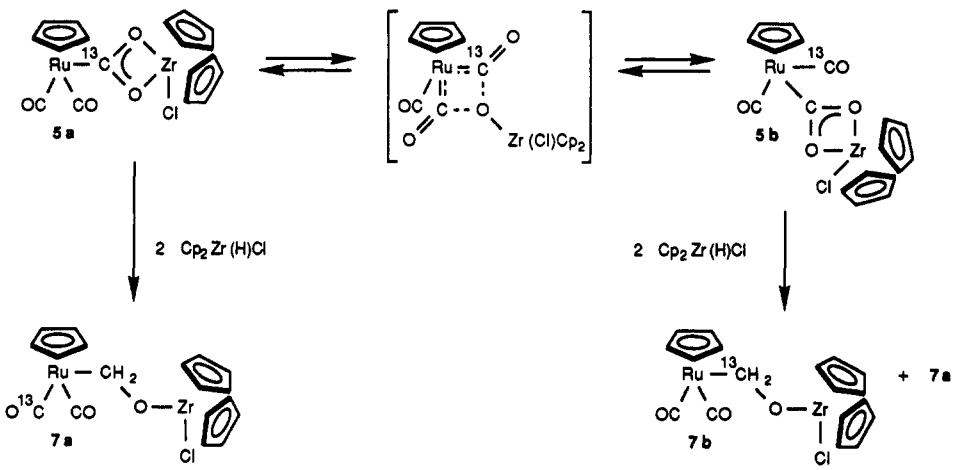
(8) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221.

(9) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

Scheme II



Scheme III



$(CH_2O)Zr(X)Cp_2$. These μ-CH_2O groups originate from reduction of ligated carbon monoxide.

Repeating the sequence outlined in Scheme I using $^{13}CO_2$ (99% labeled) and keeping the in situ generated $Cp(CO)_2Ru(^{13}CO_2)Zr(Cl)Cp_2$ (**5a**) at −78 °C affords ^{13}C-labeled **7a** (Scheme II). IR spectral monitoring during the reduction of **5a** indicates that a single Ru-containing species **7a** having ν(CO) bands consistent with the monosubstituted $CpRu(^{13}CO)(CO)$ moiety[12] forms (Table I). The ^1H NMR spectrum for **7a** retains a small $^3J_{CH}$ coupling (1.2 Hz) for the $RuCH_2$ doublet, and the ^{13}C NMR spectrum has an intense RuCO peak (δ 202.7) vs the weak $RuCH_2$ absorption (δ 58.6, d, $^2J_{CC}$ = 4.0 Hz). Thus, $Cp_2Zr(H)Cl$ reduction of $Cp(CO)_2Ru(^{13}CO_2)Zr(Cl)Cp_2$ (**5a**) transfers its carboxylate ^{13}C label to a terminal carbonyl on **7a**.

Regioselective reduction of ^{13}C-carboxylate-labeled **5a** to the CO-labeled μ-formaldehyde product **7a** is consistent with the transience of the intermediates depicted in Scheme II. Initial hydride transfer to the carbonyl ligand of **5a** affords a zirconoxycarbene intermediate, perhaps existing as the chelate **8**. Similar reduction of terminal carbonyl groups by zirconocene hydrides as noted above[9,11b] has been established. The second equivalent of $Cp_2Zr(H)Cl$ then adds to the zirconoxycarbene ligand on **8** and gives **9**, which fragments to the observed products. This postulated mechanism of course requires that the ^{13}C label in **5a** remains at the initial carboxylate site under the conditions of the reaction.

The labeled CO_2 complex **5a** does shuttle the label between the carboxylate and carbonyl centers (Scheme III),[13] but only above −20 °C. A C_6D_6 solution of **5a** approaches a 1:1.3 mixture of **5a** and $Cp(^{13}CO)(CO)Ru(CO_2)Zr(Cl)Cp_2$ (**5b**) after 7–8 h (22 °C, N_2 atmosphere). IR spectral data

(10) Recent examples of FeZr or RuZr heterobimetallic complexes with bridging ligands: (a) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549. Sartain, W. J.; Selegue, J. P. *Organometallics* **1989**, *8*, 2153. Bullock, R. M.; Lemke, F. R.; Szalda, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 3244, and references cited. (b) Weinstock, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 8298. Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1990**, *9*, 1990.

(11) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (d) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Erker, G.; Dorf, V.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. Erker, G.; Schlund, R.; Kruger, C. *Organometallics* **1989**, *8*, 2349. Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. Erker, G.; Hoffmann, U.; Zwettler, R.; Betz, P.; Krueger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630.

(12) (a) Alexander, J. J.; Wojcicki, A. J. *Inorg. Chem.* **1973**, *12*, 74. Alexander, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1729. (b) Fettes, D. J.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2311. Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. (c) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. (d) Bodnar, T. C.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

(13) Analogous label shuttling between carboxylate and terminal carbonyl sites on $Cp(CO)_2Fe(^{13}CO_2)Li^+$ or $Cp(CO)_2Fe(C^{18}O_2)Li^+$ [13a] and on $[Cp(CO)_2Fe(=C(^{17}O)O)WCp_2]^+$ [13b] has been documented. Metallo anhydride species (cf. Scheme III) also serve as proposed intermediates. (a) Lee, G. R.; Cooper, N. *J. Organometallics* **1985**, *4*, 794, 1467. (b) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333.

for both the terminal carbonyl ν(CO) and the moderately intense carboxylate ν(OCO) regions (Table I) establish the relative concentrations of $Cp(CO)_2Ru/Cp(^{13}CO)(CO)Ru$ and $Ru(CO_2)Zr/Ru(^{13}CO_2)Zr$ groups, ^1H NMR spectra indicate the absence of other products (particularly $Cp(CO)_2RuH$), and ^{13}C NMR spectra additionally demonstrate the presence of the ^{13}C label at both the carboxylate and terminal carbonyl sites (ca. 1:1). This 1:1.3 mixture of **5a**/**5b** was used to generate the remaining μ-methyleneoxo isotopomer $Cp(CO)_2Ru(^{13}CH_2O)Zr(Cl)Cp_2$ (**7b**).

$Cp_2Zr(H)Cl$ (2 equiv) reduces **5a**/**5b** to the anticipated 1:3 mixture of **7b**/**7a** (Scheme III). Salient spectral data for **7b** appear in Table I; the same value for the methylene $^1J_{CH}$ (154 Hz) was determined by ^1H NMR spectroscopy (100 and 200 MHz). With the availability of spectral data for the three (μ-CO_2)RuZr isomers **5**, **5a**, and **5b** and for the three (μ-formaldehyde)RuZr isomers **7**, **7a**, and **7b**, we conclude that our apparent "CO_2 reduction" of $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ (**5**) by $Cp_2Zr(H)Cl$ (Scheme I) engenders reduction of ligated carbon monoxide and not hydride delivery to the carboxylate (CO_2) ligand. Studies in progress focus on optimizing the choice organometallic systems L_xM and L_yM' in **1** and **2** for coupling CO_2 reduction with CO_2 insertion into metal–metal bonds.

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Easy Route for the Synthesis of Iminoacyl Niobocene Complexes. The First X-ray Structure of an (η^2-Iminoacyl)niobium Complex, $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}EtPhHCCNPh\}^+BF_4^-$

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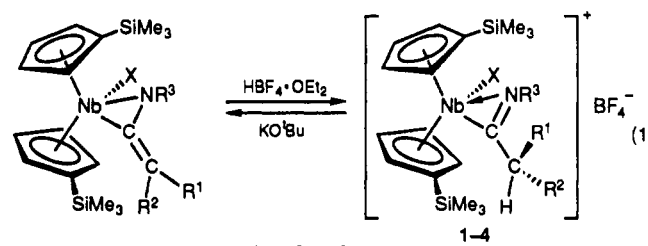
Summary: $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2CCNR^3$ (X = Cl, Br) species react with 1 equiv of $HBF_4{\cdot}OEt_2$ to yield in one step the ionic iminoacyl complexes $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2HCCNR^3\}^+BF_4^-$. The electrochemical and the chemical reductions (Na/Hg) of these cationic complexes give the starting ketenimine complexes with the elimination of H_2. The molecular structure of $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}EtPhHCCNPh\}^+BF_4^-$ shows an η^2(C,N)-bonded iminoacyl ligand.

Although several extensive studies have been reported on the spectroscopic and structural properties of the group 4 metal η^2-iminoacyl derivatives,[1] the study of analogous 5 metal species has been much less thorough; indeed, it is practically restricted to tantalum complexes containing ancillary aryloxide ligands[2] and to a few niobocene complexes prepared by some of us.[3]

Our studies on substituted niobocene complexes have made available to us a series of niobocene compounds containing the ketenimine group.[4] Thus, we decided to try a route for the synthesis of η^2-iminoacyl niobocene complexes based on the electrophilic attack at the free terminus of the complexed ketenimine ligands.

We report herein our initial observations, which include (i) the discovery of facile protonation of coordinated ketenimine in niobocene complexes to give iminoacyl complexes and (ii) the first X-ray structure of an (η^2-iminoacyl)niobium complex.

Red THF solutions of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2CCNR^3)$ react at room temperature with 1 equiv of $HBF_4{\cdot}OEt_2$ to give, through a protonation process, white solids corresponding to the η^2-iminoacyl complexes $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2HCCNR^3\}^+BF_4^-$ in essentially quantitative yield (eq 1).



(1)

1–4

1: X = Cl, $R^1 = R^2 = R^3 = C_6H_5$
2: X = Br, $R^1 = R^2 = R^3 = C_6H_5$
3: X = Cl, $R^1 = C_6H_5$, $R^2 = C_2H_5$, $R^3 = C_6H_5$
4: X = Br, $R^1 = C_6H_5$, $R^2 = C_2H_5$, $R^3 = C_6H_5$

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