transition-metal ion is smaller than that of HNC (see above) and neutral HCN is more stable than HNC (by at least 10 kcal/mol[23]), intermediate **9** should prefer to decompose via path d rather than path b; in contrast, for **12** a branching ratio b:d > 1 should be observed. This is precisely borne out by the experimental results (Scheme I).[24]

The detailed mechanism by which the transformations **8** → **9** and **11** → **12** proceed deserves further comment. Superficially, it could be concluded that the reaction commences analogous to the mechanism which was proposed earlier for the eliminations of hydrogen halides and water from alkyl halides and alcohols by alkali-metal ions[25] and which is commonly referred to as "dissociative attachment". Early work with these two classes of substrates revealed that for transition-metal ions a different mechanism seemed to be operative, although in most cases the reaction products were the same.[26] For alkali-metal ions it was proposed that the reaction proceeds via hydroxide or halide abstraction followed by intramolecular protonation of the resulting neutral by the alkyl cation.[26] The site of protonation was assumed to be the non-metal fragment. For transition-metal ions initial insertion into the polar C–X bond (X = OH, halogen) was postulated, followed by β-hydrogen shift.[1a,b,27] While it remains to be established if the different behavior of the alkali-metal ions is not only deceptive, it is obvious, however, that in all cases studied so far, irrespective of the actual mechanism (i.e. Scheme II versus Scheme III), *no* distinction was possible between the site of complexation *before* and *after* insertion because it is the same atom that is involved in both cases (i.e., the halide or the oxygen). So, no further insight was possible about the exact nature of the initial step of the now commonly accepted insertion/β-hydrogen shift mechanism. The results presented here provide for the first time evidence that a *precoordination of the metal ion is maintained in the course of the reaction.* However, some questions remain open to speculation, like, for example, the actual way in which the cleavage of the polar C–X bond proceeds. This could be a multicenter mechanism with rotation of the $-XM^+$ entity or a simple rupture followed by rearrangements in the resulting ion/dipole complex.

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The Iridium Complex Catalyzed Reduction of Carbon Dioxide to Methoxide by Alkylsilanes

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Summary: The reduction of CO_2 by alkylsilanes catalyzed by Ir(CN)(CO)dppe in C_6D_6 occurs at ambient temperatures and pressures. Reactions with Me_2SiH_2, Et_2SiH_2, and Me_3SiH ultimately yield reduction of CO_2 to the methoxide level. Concurrent formation of siloxanes serves to drive these reductions through the formation of silicon–oxygen bonds. Various reduced carbon intermediates including formates, acetals, and methoxides are identified during the course of the reactions with the source of carbon confirmed through the use of $^{13}CO_2$.

Previous reports of transition-metal-catalyzed chemical reduction of CO_2 have focused on the use of hydrogen as the reducing agent.[1,2] For most simple reductions, however, these reactions are thermodynamically unfavorable and require higher pressures and/or temperatures. In order to overcome unfavorable thermodynamics, alkylsilanes, $R_{3-x}SiH_{1+x}$, can be used to reduce CO_2 with the reactions then becoming favorable via the formation of stable Si–O bonds. To date, however, only a few examples of silane reduction of CO_2 have been reported, and these have shown silyl formates and coordinated CO to be the predominant reduced carbon products.[3-6] In this paper, we report the Ir(I)-catalyzed reduction of CO_2 using alkylsilanes to the methoxide level at near ambient temperature and pressure. The overall reduction stoichiometry corresponds to eq 1 for Me_3SiH with intermediate reduction products observed and identified by using $^{13}CO_2$.

$$3Me_3SiH + CO_2 \rightarrow CH_3O\text{–}SiMe_3 + Me_3Si\text{–}O\text{–}SiMe_3 \tag{1}$$

The oxidative addition of trialkylsilanes to Ir(CN)(CO)dppe (**1**; dppe = 1,2-bis(diphenylphosphino)ethane) has previously been shown to proceed stereospecifically, leading to cis silyl hydride iridium(III) products.[7] When the alkylsilanes Me_3SiH, Me_2SiH_2, and Et_2SiH_2 are allowed to react with Ir(CN)(CO)dppe under an atmosphere of CO_2, analogous oxidative addition chemistry occurs with the formation of isomers of $IrH(SiR_3)(CN)(CO)$dppe, followed by chemistry leading to stepwise CO_2 reduction. In a typical experiment, 0.07 mmol (500 Torr in 2.5 mL) of the alkylsilane and 0.11 mmol (800 Torr in 2.5 mL) of CO_2 were added to a 5-mm NMR tube containing 0.005 mmol (3.0 mg) of Ir(CN)(CO)dppe in 0.5 mL of C_6D_6. The

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tube was then flame-sealed and the progress of the reaction monitored by ^{1}H NMR spectroscopy; additional product analyses were performed by MS and ^{13}C NMR spectroscopies.[8]

Of the silanes investigated, Me_3SiH gives the simplest reaction products, although it proved to give the slowest overall reduction of CO_2. With Me_3SiH, the initial CO_2 reduction product is $Me_3SiO(O)CH$ (eq 2) which is readily

$$Me_3SiH + CO_2 \rightleftharpoons Me_3SiO(O)CH \qquad (2)$$

observed by the formate proton resonance (δ 7.69 ppm (s)) after 1 day of reaction at 40 °C.[9] The source of the formate carbon as carbon dioxide was confirmed by the use of $^{13}CO_2$, resulting in the formate proton resonance appearing as a doublet ($^1J_{C\text{-}H}$ = 223 Hz). By ^{13}C NMR spectroscopy, the formate carbon appears as a singlet at δ 160.2 ppm in the proton-decoupled spectrum and as a doublet ($^1J_{C\text{-}H}$ = 223 Hz) when protons are not decoupled.

In the presence of complex 1, this formal insertion of CO_2 into a Si–H bond is reversible. This is shown by exchange of the ^{13}C label as represented in eq 3, with equilibrium being reached after 1 week at 60 °C. The same reaction at room temperature yields $IrH(CO)_2dppe$[10] and $IrH_2(CN)(CO)dppe$[7] as the major iridium hydride complexes after 1 week, with ^{13}CO incorporation into the dicarbonyl complex seen by ^{13}C coupling in the hydride resonance ($^2J_{C\text{-}H}$ = 6 Hz).[11] The formate proton of $Me_3SiO(O)CH$ may also be exchanged for deuterium as represented in eq 4 using D_2. This is observed in the ^{1}H NMR spectrum by a decrease in the formate proton resonance and the appearance of HD and H_2.[12]

$$Me_3SiO(O)CH + {}^{13}CO_2 \rightleftharpoons Me_3SiO(O){}^{13}CH + CO_2 \qquad (3)$$

$$Me_3SiO(O)CH + D_2 \rightleftharpoons Me_3SiO(O)CD + HD \qquad (4)$$

Subsequent reduction of the formate carbon generated in eq 2 by Me_3SiH at 40 °C yields the intermediate $Me_3SiOCH_2OSiMe_3$. This reduction shown in eq 5 requires the presence of the catalyst. Small quantities of $Me_3SiOCH_2OSiMe_3$ are observed by the acetal ^{1}H resonance which appears as a singlet at δ 5.02 and is split by 164 Hz when $^{13}CO_2$ is used.[13] This compound has previously been identified by Rathke, using GC–MS, as an intermediate in the thermal decomposition of Me_3SiOCH_3.[14] A compound of this type has also been proposed by Koinuma and co-workers in the reduction of $Et_2MeSiO(O)CH$, but it was not observed directly.[3]

$$Me_3SiO(O)CH + Me_3SiH \rightarrow Me_3SiOCH_2OSiMe_3 \qquad (5)$$

$$Me_3SiOCH_2OSiMe_3 + Me_3SiH \rightarrow CH_3OSiMe_3 + Me_3SiOSiMe_3 \qquad (6)$$

The final carbon product in this reduction sequence is Me_3SiOCH_3[15] which forms according to eq 6, with ~2.4 equiv of methoxide observed after 2 weeks at 40 °C.[16] In this product, only the methoxy group becomes ^{13}C-labeled when $^{13}CO_2$ is used as indicated by a splitting of the methoxy ^{1}H resonance into a doublet ($^1J_{C\text{-}H}$ = 141 Hz). At the end of the reduction sequence, the predominant iridium complexes present are the isomers of $IrH(SiMe_3)(CN)(CO)dppe$ formed initially, although small quantities of other complexes including $IrH_2(CN)(CO)dppe$ are also seen. This latter complex was previously reported to form slowly and as a secondary product in silane oxidative addition to Ir(CN)(CO)dppe.[7] Concurrent formation of $Me_3SiOSiMe_3$, identified by ^{1}H NMR spectroscopy,[17] also takes place in eq 5, verifying the siloxane as the oxygen sink in this reduction of CO_2.

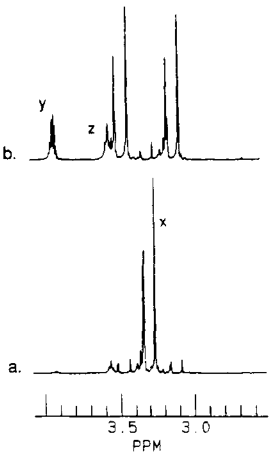

Figure 1. ^{1}H NMR spectra of the methoxy region for the reaction of Ir(CN)(CO)dppe + 500 Torr of Me_2SiH_2 after approximately 2 weeks of reaction at 40 °C: (a) with 800 Torr of CO_2 added; (b) with 800 Torr of $^{13}CO_2$ added (x = $Me_2HSiOCH_3$; y = Me_2SiH_2; z = solvent impurity).

When dialylsilanes are allowed to react with Ir(CN)(CO)dppe in the presence of CO_2, reduction proceeds more rapidly, but since each silane has two Si–H bonds, the resultant products are more varied and complex. With Me_2SiH_2, the initial silyl formate is $Me_2HSiO(O)CH$, as identified by the formate ^{1}H resonance at δ 7.58 ppm. This peak becomes a doublet with $^1J_{C\text{-}H}$ = 226 Hz when $^{13}CO_2$ is used and an enriched peak at 159.4 ppm is observed in the $^{13}C\{^1H\}$ NMR spectrum.[18] Other silyl formates are also produced in this system via functionalization of both Si–H bonds of the secondary silane. While these species can be detected by both ^{1}H and ^{13}C NMR spectroscopy, positive identification of each has not been made to date.[19]

Continued reaction of the sealed reaction system at 40 °C gives further reduction of the silyl formates to acetal products of the formula $RMe_2SiOCH_2OSiMe_2R'$ where R and R′ are either H, a formate from a second CO_2 insertion, or a siloxy group. Small amounts of these products are obtained in the reaction mixture after heating at 40 °C for 1 day. In the ^{1}H NMR spectrum, three acetal type proton resonances are seen at δ 5.02, 5.08, and 5.12 which become split by approximately 164 Hz when $^{13}CO_2$ is utilized in the reactions. The $^{13}C\{^1H\}$ NMR spectrum shows these $-OCH_2O-$ groups at 85.4, 84.5, and 83.8 ppm while the

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(8) Samples were prepared on a high vacuum line. All solvents and alkylsilanes were degassed by using three freeze–pump–thaw cycles. All NMR spectra were recorded in C_6D_6 solutions with ^{1}H spectra recorded at 400 MHz on a Bruker WH-400 spectrometer and ^{13}C spectra recorded at 75 MHz on a GE QE-300 spectrometer.

(9) $Me_3SiO(O)CH$: ^{1}H NMR δ 7.6 (s, 1 H), 0.14 (s, 9 H). $Me_3SiO(O)^{13}CH$: ^{1}H NMR δ 7.69 (d, $J_{C\text{-}H}$ = 222.9 Hz); $^{13}C\{^1H\}$ NMR, formate carbon at 160.2 ppm.

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(11) $IrH(^{13}CO)_2dppe$: Ir–H triplet of triplets at −10.35 ppm ($J_{H\text{-}C}$ = 6 Hz, $J_{H\text{-}P}$ = 41 Hz).

(12) ^{1}H NMR: H_2 δ 4.46 (s), HD appears as a 1:1:1 triplet at 4.42 ppm ($^1J_{H\text{-}D}$ = 43 Hz).

(13) $Me_3SiOCH_2OSiMe_3$: ^{1}H NMR, acetal protons, δ 5.03. $Me_3SiO^{13}CH_2OSiMe_3$: $J_{C\text{-}H}$ = 164 Hz.

(14) Klingler, R. J.; Rathke, J. W. *Organometallics* **1986**, *5*, 2568–70.

(15) Me_3SiOCH_3: ^{1}H NMR δ 3.24 (s, 3 H), 0.04 (s, 9 H). $Me_3SiO^{13}CH_3$: $J_{C\text{-}H}$ = 140.6 Hz; $^{13}C\{^1H\}$ NMR, methoxy carbon 49.4 ppm.

(16) The quantities of the final methoxide species for both the Me_3SiH and the Me_2SiH_2 reactions were determined based on integration of their ^{1}H NMR resonances compared to the total of the phenyl protons on the iridium complexes.

(17) $Me_3SiOSiMe_3$: ^{1}H NMR δ 0.12.

(18) $Me_2HSiO(O)CH$: ^{1}H NMR δ 7.58 (s, 1 H), 4.84 (m, 1 H), 0.08 (s, 6 H). $Me_2HSiO(O)^{13}CH$: $J_{C\text{-}H}$ = 226 Hz; $^{13}C\{^1H\}$ NMR, formate carbon at 159.4 ppm.

(19) In the ^{1}H NMR, these other formate proton resonances appear at δ 7.64 and 7.61 ($J_{C\text{-}H}$ = 224 Hz). The $^{13}C\{^1H\}$ NMR shows two other formate carbon resonances at 158.5 and 158.7 ppm.

^1H-coupled ^{13}C spectrum reveals them as triplets with $^1J_{C-H}$ = 164 Hz.

As seen with the Me_3SiH reactions, longer reaction times yield methoxysilanes, $Me_2RSiOCH_3$ (~3 equiv of methoxide species after 9 days at 40 °C), as the final reduced carbon products.[16] The predominant methoxysilane obtained in this system is $Me_2HSiOCH_3$.[20] For this compound, the methoxy proton resonance appears at δ 3.26 ppm and is split by 142 Hz when $^{13}CO_2$ is used in the reaction. Two additional methoxysilane compounds are also formed and are observed directly by the methoxy proton and carbon resonances.[21] This is shown in Figure 1 with the ^1H NMR spectra of both the $^{12}CO_2$ and $^{13}CO_2$ reactions after 2 weeks, indicating the CO_2-derived methoxy groups present. The methyl groups directly bound to silicon and the various dimethylsiloxanes that are formed as the oxygen acceptors are not directly identified by ^1H NMR, as this region of the spectrum becomes a complicated collection of singlets and multiplets.

Reactions with other silanes are still being investigated. Et_2SiH_2 shows CO_2 reduction chemistry similar to that of Me_2SiH_2 with the exception of slightly slower reaction times. Future studies will involve the reactions of primary silanes in order to investigate the possibilities of branched oligomers and faster rates of reduction.

From this study we have demonstrated that CO_2 can be reduced under very mild conditions to the methoxide level by alkylsilanes. This is closely related to the reduction of CO_2 to methanol by H_2 in that hydrolysis of the final reaction mixtures yield siloxanes and methanol. In these reactions, the silanes serve as both reducing agent and oxygen atom acceptor, driving the reaction through the formation of Si–O bonds.

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(20) $Me_2HSiOCH_3$: ^1H NMR δ 4.79 (m, 1 H), 3.26 (s, 3 H), 0.08 (d, 6 H). $Me_2HSiO^{13}CH_3$: J_{C-H} = 142 Hz; $^{13}C\{^1H\}$ NMR, methoxy carbon at 50.2 ppm.

(21) These methoxy groups appear at δ 3.35 and 3.34 in the ^1H NMR and become split by 142 Hz when $^{13}CO_2$ is used. $^{31}C\{^1H\}$ NMR: additional resonances at 49.7 and 48.5 ppm.

Highly Reactive Dihydrogen Complexes of Ruthenium and Rhenium: Facile Heterolysis of Coordinated Dihydrogen

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Summary: The moderately stable cationic dihydrogen complexes $[(\eta\text{-}C_5Me_5)Ru(CO)_2(\eta^2\text{-}H_2)]BF_4$ and $[(\eta\text{-}C_5Me_5)Re(CO)(NO)(\eta^2\text{-}H_2)]\ BF_4$ have been prepared by protonation of the corresponding neutral hydrides. These are the first examples of dihydrogen complexes not containing phosphine coligands to be characterized by NMR methods. The coordinated dihydrogen ligand in these complexes is highly activated toward heterolytic cleavage, as demonstrated by deprotonation with very weak bases such as Et_2O. The estimated pK_a value for coordinated H_2 in the rhenium complex is −2 (CH_2Cl_2).

Since the initial discovery by Kubas,[1] transition-metal dihydrogen complexes have been intensively studied.[2] Although some understanding of the factors favoring H_2 coordination rather than the more commonly observed oxidative addition of H_2 is beginning to emerge, the ligand systems employed successfully to date in stabilizing H_2 complexes are extremely limited in scope. Virtually all isolable H_2 complexes reported to date contain tertiary phosphine ligands. Calculations seem to indicate that mixtures of σ-donor and strong π-acceptor coligands are optimal for H_2 binding, particularly when an acceptor ligand (such as CO) is trans to H_2[3]. In addition to the isolable complexes, there are several examples of dihydrogen complexes which have been characterized only by infrared spectroscopy at very low temperatures. Complexes containing only acceptor ligands, such as $Cr(CO)_5(\eta^2\text{-}H_2)$, are observable in significant concentrations only in liquid Xe at ca. 220 K.[4] Also characterized in liquid Xe are $Fe(CO)(NO)_2(\eta^2\text{-}H_2)$ and $Co(CO)_2(NO)(\eta^2\text{-}H_2)$, the only reported examples of dihydrogen complexes containing NO ligands.[5]

We have previously reported the synthesis and properties of complexes such as $[(\eta\text{-}C_5H_5)Ru(PR_3)(CO)(\eta^2\text{-}H_2)]BF_4$ (PR_3 = PMe_3, PPh_3, PMe_2Ph, and PCy_3). In the case of the PCy_3-containing complex, an equilibrium between the dihydrogen complex and a small amount of the dihydride complex was observed,[6] demonstrating that the more basic metal center favors the oxidative addition reaction. We now report the preparation of moderately stable phosphine-free dihydrogen complexes of ruthenium and rhenium and some preliminary studies of their reactivity.

Protonation ($HBF_4 \cdot Et_2O$, 1.2 equiv) of the neutral hydride $(\eta\text{-}C_5Me_5)Ru(CO)_2H$[7] in dichloromethane at 220 K affords $[(\eta\text{-}C_5Me_5)Ru(CO)_2(\eta^2\text{-}H_2)]BF_4$ (**1**).[11] Formulation of **1** as a dihydrogen complex is based on the observation of $^1J_{H-D}$ = 32 Hz in the H–D derivative.[12] Complex **1** was

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(7) We have prepared $(\eta\text{-}C_5Me_5)Ru(CO)_2H$ by $NaBH_4$ reduction of $(\eta\text{-}C_5Me_5)Ru(CO)_2Br$.[8] The deuteride was prepared by reduction with $NaBD_4$. This hydride has been previously reported as one of the products of reduction of the cation $[(\eta\text{-}C_5Me_5)Ru(CO)_3]BF_4$[9] and from protonation of $K[(\eta\text{-}C_5Me_5)Ru(CO)_2]$.[10]

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(9) Nelson, G. O. *Organometallics* **1983**, *2*, 1474–1475.

(10) Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C18–C22.

(11) ^1H NMR of **1** (CD_2Cl_2, δ, 195 K): 2.07 (s, 15 H), −5.69 (s, 2 H).

(12) The H–D derivative was prepared by protonation of $(\eta\text{-}C_5Me_5)Ru(CO)_2D$. Due to facile intermolecular proton exchange, a statistical mixture of **1**-d_0 and **1**-d_1 was observed immediately, even when protonation was carried out at 190 K.

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