ORGANOMETALLICS

Article

Solvent-Controlled CO₂ Reduction by a Triphos–Iron Hydride Complex

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S Supporting Information

ABSTRACT: The selective reduction of CO_2 is of high interest toward future applications as a C1-building block. Therefore, metal complexes that allow for the formation of specific CO_2 reduction products under distinct reaction conditions are necessary. A detailed understanding of the CO_2 reduction pathways on a molecular level is, however, required to help in designing catalytic platforms for efficient CO_2 conversion with specific product formation. Reported herein is a unique example of a solvent-controlled reduction of CO_2 using a Triphos-based iron hydride complex. In THF, CO_2 reduction selectively leads to CO formation, whereas experiments in acetonitrile exclusively afford formate, HCOO⁻. In order to explain the experimental findings, theoretical



calculations of the reaction pathways were performed and further demonstrate the importance of the applied solvent for a selective reduction of CO_2 .

INTRODUCTION

Carbon dioxide is one of the major greenhouse gases, and its activation is an important area owing to its scientific and social relevance. However, only a handful of catalytic systems have been reported that allow for an efficient conversion of this greenhouse gas. The majority of these systems are based on precious metals such as Ru and Ir, rendering them unsuitable for large-scale sustainable applications due to their high price and low natural abundance. Consequently, more abundant alternatives based on Fe, Co, and Ni have recently attracted more attention with Fe based systems being most prominent. While heterogeneous systems based on Fe often result in a broad variety of products, e.g., CO, formic acid, and methanol, homogeneous catalysts usually lead to a more narrow product distribution and can thus serve to provide an in-depth understanding of the underlying mechanistic details.^{1,2} One of the most potent classes of Fe-based complexes are Fehydrides, which allow for an efficient hydrogenation of CO_2 to formate (Scheme 1). A prominent example is $Fe(dmpe)_2(H)_2$ (1, dmpe = 1,2-bis(dimethylphosphino)ethane) that was shown to effectively reduce CO₂ to formate.^{3,4} Likewise, lowcoordinated diiron $[(\beta - diketiminate)Fe(\mu - H)]_2$ (2) and its derivatives react stoichiometrically with CO₂ in pentane at low temperatures to afford η^2 -formato bridging diiron complexes.⁵ On the other hand, the reaction of CO₂ with $[(\beta -$

diketiminate)Fe(μ -N)]₂ leads to formation of CO₃⁻ and CO.⁶ A selective catalytic hydrogenation of CO₂ to formic acid was achieved utilizing trans- $[({}^{t}Bu-PNP)Fe(H)_{2}(CO)]$ (3) at 6.66 bar of H_2 and 3.33 bar of CO_2 pressure in H_2O/THF mixtures with turnover numbers of up to 788.7 When modifying the PNP ligand using a 2,6-diaminopyridine scaffold instead of 2,6-dimethylpyridine (4, Figure 1), a significant increase of the turnover numbers of up to 10275 was reported, although at much higher temperatures and pressures, 80 °C and 80 bar of H2/CO2 (1:1).8 An efficient catalytic hydrogenation of CO2 was also reported utilizing [Si(o- $C_6H_4PR_2)_3$ Fe(H₂)(H)] (5, R = ^{*i*}Pr, Ph) or [(PhBP^{*i*Pr}₃)Fe-(H)₃(PMe₃)] (6) at elevated temperatures and pressures of CO₂ and H₂. For both complexes, formation of (Et₃NH)-(OCHO) and MeOCHO was observed in methanol at 100 °C and a total pressure of 58 bar of H_2/CO_2 (1:1) in the presence of trimethylamine.⁹ While Triphos^C/Fe(BF₄)₂ mixtures (Triphos^C = CH₃C(CH₂PPh₂)₃) were recently reported to be unreactive toward the reduction of CO₂,¹¹ [(Triphos^C)Ru-(acetate)] (7) is an active catalyst for its conversion and affords methanol with turnover numbers of up to 442 at a CO_2/H_2 pressure of 80 bar and 140 °C.⁸ Notably, the solvent

Received: October 1, 2018

Scheme 1. Selected Literature Reported Metal-Hydride Complexes for the Conversion of CO_2^{3-10}



intermediate $[(Triphos^{C})Ru(\eta_2 - O_2CH)(solvent)]$ was suggested as a key intermediate in this transformation. Furthermore, $[(Triphos^{C}Cu)_{2}(H)]$ (8) was reported to allow for reduction of CO₂ to afford formic acid.¹⁰

We recently showed that (Triphos)Fe complexes exhibit an unusual solvent-dependent κ^2 - vs κ^3 -binding flexibility of the Triphos ligand leading to an altered reactivity of the structurally equivalent complexes [(Triphos^C)FeCl₂] and [(Triphos^{\$i})FeCl₂].¹² The previously observed strong solvent-dependent reactivity of such iron complexes prompted us to investigate the reaction of CO_2 and $(Triphos^{C/Si})$ -derived Fe-hydride complexes in different solvents. Furthermore, $[(Triphos^{C})Fe(H)(BH_{4})]$ was previously shown to possess a temperature-dependent flexible H^-/H_2 bonding of the BH₄ moiety to iron.^{13,14} Inspired by these observations, we focused on the reaction of $[(Triphos^{C})Fe(H)(BH_{4})]$ as a well-defined Triphos-Fe hydride with CO2. We herein report on its solvent-controlled reaction with CO₂, leading exclusively to the formation of either CO or formate. A detailed spectroscopic investigation together with extensive computational studies rationalizes the experimental observations on a molecular level.

EXPERIMENTAL SECTION

General. All reactions were performed under a dry N_2 or Ar atmosphere, either using standard Schlenk techniques or by working in a glovebox. All solvents applied were dried according to standard methods. The tripodal phosphine ligands Triphos^C and Triphos^{Si 15} as well as their iron complexes [(Triphos^C)FeCl₂] (9) and [(Triphos^{Si})-FeCl₂] (10)¹² were synthesized according to literature procedures. All other compounds were obtained by commercial vendors and used without further purification. UV–vis measurements were performed with a Varian Cary 100 or a Jasco V-670 utilizing an inert cuvette with a septum seal. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX-250 NMR spectrometer at room temperature under inert conditions. ESI mass spectra were obtained with a Bruker Daltronics Esquire6000 instrument. GC-MS measurements were performed with a Shimadzu QP-2010. IR spectra were measured with a Bruker Tensor



Figure 1. (a) UV/vis spectra of complex 11 in THF and acetonitrile as well as after reaction with CO_2 under various reaction conditions. (b) ATR-IR spectra of complexes 13 (black), 14 (red), and 15 (blue).

27 FT-IR spectrometer. Zero-field Mössbauer spectra were recorded at 80 K by using a SeeCo constant acceleration spectrometer equipped with a temperature controller maintaining temperatures within ± 0.1 K and a 57 Co radiation source in a Rh matrix. Isomer shifts are referred to α -Fe at room temperature. Data were fit with a sum of Lorentzian quadrupole doublets by using a least-squares routine with the WMOSS program. Head space analysis of the gaseous components was performed utilizing a 7820A GC system from Agilent Technologies equipped with a methanizer from Joint Analytical Systems, a flame ionization detector (FID), and a thermal conductivity detector (TCD). The system is equipped with a HaysepQ and molesieve 5 Å column, and argon is used as the carrier gas. Quantification of formic acid was performed by HPLC on a C18 pyramid column applying 0.5 M H₃PO₄ as the mobile phase.

Computational Details. All calculations were performed using the ORCA program package.^{16,17} In the course of our computational study, multiple sets of calculations on different levels of theory were conducted. The first set comprises relaxed surface scans and geometry optimizations that employ the BP86 functional^{18,19} together with the def2-SVP double- ζ basis set.²⁰ These calculations helped to explore possible reaction pathways without investing immense computational resources. Final geometries for stable structures and transition states were computed using the B3LYP functional^{21,22} and the def2-TZVP(-f) basis set.²⁰ Integral generation was accelerated with the resolution of identity and chain of sphere (RIJCOSX) approximations in conjunction with the appropriate auxiliary basis set.^{23–28} Dispersion effects were accounted for using the semiempirical van der Waals

corrections with the Becke–Johnson damping (D3BJ) as implemented in ORCA. 29,30 While the same computational setup was utilized for the calculation of electronic absorption spectra, we have supplemented it with the zeroth order regular approximation (ZORA) and the scalar-relativistic recontractions of the same basis sets during the calculation of Mössbauer isomer shifts.^{31,32} In the case of electronic absorption spectra, the underlying electronic excitation energies and transition moments were evaluated within the framework of time-dependent linear response density functional theory (TD-DFT). Eventually, electronic energies were refined at high precision using the DLPNO-CCSD(T) method.³³⁻³⁶ The corresponding coupled cluster theory with single, double, and perturbative triple excitations CCSD(T) is considered as the "gold standard" owing to its high accuracy and reliability. Its domain based local pair natural orbital coupled cluster version DLPNO-CCSD(T) typically reproduces canonical CCSD(T) energies with chemical accuracy but comes at immensely reduced computational cost. The presented numbers were obtained from a two-point extrapolation to the complete basis set limit from the energies computed with the CC-PVTZ and CC-PVQZ basis sets.37

All geometries were fully optimized without symmetry constraints. Harmonic vibrational frequencies were computed to verify the nature of stationary points. Each of the intermediates reported is a local minimum on the potential energy surface, and therefore, the corresponding Hessian matrix has exclusively positive eigenvalues, whereas the Hessian matrices of transition states exhibit a single negative eigenvalue. Contributions from translational, rotational, and vibrational degrees of freedom to the molecular enthalpy and entropy were accounted for within the "particle in a box", "rigid rotor", and "harmonic" approximations.^{43,44}

A key factor in the observed reactivity is the influence of the solvent. In our calculations, it is modeled by a combination of implicit and explicit solvation: While unspecific interactions with the reactive site are evaluated with a polarizable continuum model (C-PCM,⁴⁵) specific interactions such as chemical bonding to Fe are taken into account by explicitly including solvent molecules in the model system (see discussion below). For intermediates immediately before binding or elimination of a solvent or CO2 molecule also unbound molecules had to be included in order to obtain a consistent picture of the reaction pathway. This inevitably leads to a considerable underestimation of the entropy contributions to the free energy, as the individual translational entropy of the ensemble of individual molecules is (wrongly) treated as translation of a single entity. Therefore, we compared our results for reaction steps that feature addition or elimination of a molecule with results from separate calculations for each of the reactants. In this way, an upper bound to the error is obtained (Table S17). To this end, it should be noted that for technical reasons the C-PCM model was only applied during final energy evaluations but not during geometry optimizations. However, a series of test calculations revealed that the neglect of implicit solvation does not alter geometries or energies significantly (Table S18). Moreover, the data presented in Tables S15 and S16 demonstrate that the computed structures closely agree with the available crystal structures, thus validating the chosen setup. A pressure correction value of 1.34 kcal mol⁻¹ per molecule of \overline{CO}_2 is added while plotting the free energy profile for the reactions with pressurized CO₂ (Supporting Information T1).

[(Triphos^C)Fe(H)(BH₄)] (11). Triphos^CFeCl₂ (1 g, 1.33 mmol) was dissolved in dry THF (40 mL), and sodium borohydride (508 mg, 13.3 mmol) was added in one portion. The resulting dark red solution was stirred at room temperature for 2 d and subsequently filtered. The filtrate was then concentrated to 3 mL by slow evaporation in a vacuum, and addition of hexane (60 mL) afforded compound 11 as purple solid that was filtered off, washed with hexane, and dried in a vacuum (833 mg, 1.2 mmol, 90%). Purple crystals of 11 were obtained by slow diffusion of pentane into a solution of 11 dissolved in THF. ¹H NMR (250 MHz, CDCl₃): δ 7.59–7.19 (m, 30H, H_{Ar}), 5.89 (br s, 2H, terminal BH₄), 2.52 (s, 6H, CH₂), 1.90 (s, 3H, CH₃), -4.82 and -14.18 (s, 3H, hydride); IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3053, 2922, 2390, 2294, 2226, 1881, 1629, 1481,

1435, 1185, 1092. Mössbauer: $\delta = 0.11 (\pm 0.02) \text{ mm s}^{-1}$, $\Delta E_Q = 1.96 (\pm 0.02) \text{ mm s}^{-1}$. ESI-MS: calcd for $[C_{41}H_{44}BFeP_3]^+$, 696.22; found, 696.10. Anal. Calcd for $C_{41}H_{44}BFeP_3$: C, 70.72; H, 6.37. Found: C, 70.5; H, 6.2.

[(Triphos^C)FeD(BD₄)] (11-D). The deuterated complex 11-D was obtained following the same synthetic route as that described for complex 11 utilizing NaBD₄. Purple crystals of 11-D were obtained by slow diffusion of pentane into a solution of 11-D dissolved in THF.

[(Triphos^{Si})Fe(H)(BH₄)] (12). Triphos^{Si}FeCl₂ (1 g, 1.3 mmol) was dissolved in dry THF (40 mL) followed by the addition of sodium borohydride (493 mg, 13.0 mmol). The obtained dark red solution was then stirred for 2 d at room temperature. After filtration of the reaction mixture and concentrating the solution to 3 mL, complex 12 was precipitated by addition of Et₂O (60 mL). Filtration of the formed purple solid, washing with Et₂O, and drying in a vacuum yielded complex 12 in 19% yield (179 mg, 0.25 mmol). Crystals of 12 were obtained by slow diffusion of pentane into a THF solution of compound 12. ¹H NMR (CDCl₃, 250 MHz, ppm): δ 7.45-6.99 (m, $30H_1$, H_{Ar}), 1.60 (d, 6H, CH₂), 0.56 (s, 3H, CH₃), -12.97 (1H, s, hydride); IR (ATR, cm⁻¹): 3422, 3052, 2926, 2390, 2293, 2226, 1889, 1636, 1481, 1434, 1383, 1186, 1127, 1085, 1000, 820, 768, 744, 696. Mössbauer: δ = 0.14 (±0.02) mm s⁻¹, ΔE_Q = 1.90 (±0.02) mm s⁻¹. Anal. Calcd for C₄₀SiH₄₄BFeP₃: C, 67.43; H, 6.23. Found: C, 67.0; H, 6.1.

[(Triphos^C)Fe(CO)₂] (13). Compound 11 (350 mg, 0.503 mmol) was dissolved in dry THF (28 mL) in a 100 mL stainless-steel autoclave and pressurized with CO₂ to give an internal pressure of 7 bar at 70 °C. Subsequently, the mixture was stirred under such conditions for 2 d. After opening the pressurized bottle (ATTENTION: Instantaneous gas release should be avoided, and the autoclave should solely be opened under well-ventilated conditions), the obtained dark green solution was evaporated to dryness under the exclusion of air. The solid residue was then suspended in dry THF (5 mL), filtrated, and washed with hexane to yield 13 (290 mg, 0.387 mmol, 78%) as a dark green solid. Green crystals were obtained by slow diffusion of pentane into a THF solution of 13. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3053, 2959, 2925, 2386, 1907, 1796, 1742, 1580, 1513, 1425, 1091, 1059, 879. Mössbauer: $\delta = 0.13$ (± 0.02) mm s⁻¹, $\Delta E_Q = 0.26$ (± 0.02) mm s⁻¹. Anal. Calcd for C43H39FeO2P3: C, 70.12; H, 5.34. Found: C, 69.9; H, 5.4.

Samples of compound 13 can also be prepared from Triphos^C and $[(COT)Fe(CO)_3]$ following the route described by Lindner et al. earlier.⁴⁶

Generation of [(Triphos^C)Fe(H)(OOCH)] (14). Compound 11 (150 mg, 0.216 mmol) was dissolved in dry acetonitrile (20 mL). CO₂ was then purged through the solution, resulting in an instant color change from purple to bright orange. After additional stirring for 30 min at room temperature under a CO₂ atmosphere, the obtained mixture was filtrated and the solvent was removed in a vacuum to yield 80 mg of [(Triphos^C)Fe(H)(OOCH)]. ¹H NMR (250 MHz, CD₃CN) = 8.65 (s, OOCH), 7.30–6.96 (m, H_{Ar}), 2.36 (d, CH₂), 1.64 (s, CH₃), -12.07 (s, hydride). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3055, 2384, 1710, 1580, 1479, 1431, 1180, 1095, 1060, 995, 836, 735, 691. Mössbauer: δ = 0.09 (±0.02) mm s⁻¹, ΔE_Q = 1.33 (±0.02) mm s⁻¹. Despite repeated attempts, it was not possible to obtain satisfactory elemental analyses.

Generation of [(Triphos^C)Fe(OOCH)₂] (15). Compound 11 (1 g, 1.437 mol) was dissolved in dry acetonitrile (35 mL) in a 100 mL stainless-steel autoclave and pressurized with CO₂ to show an internal pressure of 7 bar at 75 °C. The mixture was then stirred under such conditions for 2 d. After opening the pressurized bottle (*ATTENTION: Instantaneous gas release should be avoided, and the autoclave solely being opened under well-ventilated conditions*), the obtained blue solution was evaporated to dryness. The solid residue was then suspended in dry acetonitrile (5 mL), filtrated, and washed with hexane to yield 780 mg of [(Triphos^C)Fe(OOCH)₂] as a blue solid material. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3050, 2988, 2379, 1696, 1588, 1479, 141, 1088, 832, 731, 691. Mössbauer: δ = 0.13 (±0.02) mm s⁻¹, $\Delta E_{\rm O}$ = 0.26 (±0.02) mm s⁻¹. ESI-MS: calcd for [C₄₃H₄₁FeO₄P₃ +

Na]⁺, 793.15; found, 793.36. Anal. Calcd for $C_{43}SiH_{41}FeO_4P_3$: C, 67.03; H, 5.36. Found: C, 66.6; H, 5.6.

RESULTS AND DISCUSSION

[(Triphos^{C/Si})Fe(H)(BH₄)]. The synthesis of [(Triphos^C)-Fe(H)(BH₄)] was previously reported via the reaction of Triphos^C with [Fe(H₂O)₆](BF₄)₂ and NaBH₄.^{13,47} In contrast, utilization of FeCl₂, FeBr₂, and [Fe(H₂O)₆](ClO₄)₂ salts was reported to afford [(Triphos)Fe(μ -H)₃Fe(Triphos)]^{+.48,49} Due to the dependence on the applied reaction conditions, we first focused on a straightforward reproducible synthetic method to generate [(Triphos^C)Fe(H)(BH₄)] (11) and its Si counterpart, [(Triphos^{Si})Fe(H)(BH₄)] (12), on the gram scale (Scheme 2).





We found that the reaction of $[(Triphos^{C})FeCl_{2}]$ (9) and 10 equiv of NaBH₄ exclusively leads to $[(Triphos^C)Fe(H)(BH_4)]$ (11) in 90% yield. The molecular structure (Figure S1) confirms the expected composition showing a κ^3 -coordinated Triphos ligand with iron as well as an additional hydride and a bidentate BH₄⁻ ligand. Notably, fast interchange between the Fe-H and the bridging hydrogen atoms of the BH₄⁻ moiety was previously reported on the basis of NMR spectroscopy, suggesting an overall similar reactivity of the terminal and bridging hydrides in 11. While the synthesis of the isostructural Si-derived compound 12 (Scheme 2, Figure S2) follows an identical reaction protocol, the desired complex is only obtained in 19% yield, with the major products being $[(Triphos^{Si})Fe(\mu-H)_3Fe(\mu-H)_3Fe(Triphos^{Si})]$ and [Tri $phos^{Si}(BH_3)_3$ (Figure S3) along with other hitherto unidentified Fe species. The respective C-analogues,

 $[(Triphos^{C})Fe(\mu-H)_{3}Fe(\mu-H)_{3}Fe(Triphos^{C})]$ and [Tri $phos^{C}(BH_{3})_{3}$ (Figure S4), were only observed when complex 11 was dissolved in polar solvents (e.g., acetonitrile) and stored over an extended period of time (>1 week). In dry and oxygen free nonpolar solvents (e.g., THF, hexanes), complex 11 did not show any spectroscopic changes (Figure S5a), although rapid decomposition is observed (Figure S5b) upon exposure to oxygen. The difference in reactivity of 11 and 12 can be explained by the altered electronics caused by the C/Si exchange and stems from a geometrical control of the ligand field splitting.^{12,50} This difference is best displayed by their Mössbauer parameters. While complex 11 reveals an isomeric shift of $\delta = 0.11$ mm s⁻¹ and a quadrupole splitting of $\Delta E_{\Omega} =$ 1.96 mm s⁻¹, compound 12 shows an isomeric shift of $\delta = 0.14$ mm s⁻¹ and a quadrupole splitting of $\Delta E_{\rm O}$ = 1.90 mm s⁻¹ (Figure S6). Here, the smaller isomer shift of 12 points at a slightly increased s-electron density at the Fe center and is in line with previous reports on Triphos^C/Triphos^{Si} derived iron complexes.¹² The change in the electron distributions caused by the different ligand platforms is further supported by the shifts of the Fe-H¹H NMR signals observed in CDCl₃. Here, the Fe-hydride resonance for 11 is observed at -14.18 ppm concomitant with an additional borohydride signal at -4.82 ppm (Figure S7a). Under identical conditions, the corresponding spectrum of 12 solely shows a Fe-H signal that is low field shifted to -12.97 ppm and further suggests an increased selectron density at the iron center (Figure S9).

Hydride Transfer. Since $[(Triphos^{Si})Fe(H)(BH_4)]$ (12) rapidly rearranges to $[(Triphos^{Si})Fe(\mu-H)_3Fe(\mu-H)_3Fe(Triphos^{Si})]$, which lacks a reliable synthetic purification method, it evades being a potential platform for hydrogenation reactions. Therefore, we focused on the reactivity of complex 11 and first tested its potential to facilitate hydride transfer to simple organic molecules. Here, stoichiometric hydrogenation of nitrobenzene as well as benzophenone to aniline and diphenylmethanol, respectively, was achieved in quantitative yields (Supporting Information: Stoichiometric hydrogenation). A catalytic conversion, however, was not achieved, and addition of H₂ (1 atm), Et₃SiH, BH₃, NaBH₄, or N₂H₄ did not allow for more than one turnover.

CO₂ Reduction in THF. Inspired by the reactivity of 11 toward keto and nitro groups in organic molecules, we next tested the complexes' potential for the hydrogenation of CO₂. While 11 did not react with CO₂ in THF under atmospheric conditions, conversion of CO2 was readily observed at 7 bar and 70 °C visible by a distinct color change from purple to dark green. The UV/vis absorption bands change accordingly from 515 nm in complex 11 (Figure 1a) to afford an almost featureless spectrum with weak absorption bands at 612 and 805 nm upon reaction with CO₂. Crystallization of the product mixture from THF/pentane afforded green crystals which revealed a distinct IR band at 1907 cm^{-1} (Figure 1b). This characteristic CO stretching frequency suggests a conversion of CO₂ to afford metal-bound CO. Crystallographic analysis revealed the molecular structure of complex 13 (Figure 2, Table 1). Here, the Triphos^C ligand is bound to the central iron in a κ^3 -mode with equal P–Fe distances of 2.20 Å. Two additional CO ligands complete the coordination sphere. The Fe-CO distances were found to be 1.75 Å. According to the molecular structure, the Fe-center can be referred to as a Fe(0)species. This finding is also in line with the Mössbauer spectrum of complex 13 (Figure S15), revealing an isomer shift of 0.13 mm s⁻¹ with a quadrupole splitting of 0.26 mm s⁻¹.



Figure 2. Molecular structure of complex **13** with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms and ellipsoids of the phenyl rings are omitted for clarity). Gray, carbon; purple, phosphorus; blue, iron; red, oxygen.

Table 1. Selected Bond Lengths and Angles of Complex 13

	bond length (Å)
Fe1-P1	2.2015(6)
Fe1-P2	2.2007(6)
Fe1-P3	2.1940(6)
Fe1-C1	1.752(2)
Fe1-C2	1.756(2)
	bond angle (deg)
P1-Fe1-P2	86.34(2)
P1-Fe1-P3	92.78(2)
P2-Fe1-P3	94.19(2)
P1-Fe1-C1	89.69(8)
P1-Fe1-C2	156.50(9)
P2-Fe1-C1	110.62(9)
P2-Fe1-C2	152.63(8)
P3-Fe1-C1	86.75(8)
P3-Fe1-C2	112.57(8)
C1-Fe1-C2	86.22(11)

Notably, the synthesis of complex 13 was previously reported via reaction of Triphos^C and $(COT)Fe(CO)_3$, and the spectroscopic data obtained via this method are in good accordance with those of complex 13 generated via CO_2 reduction.⁴⁶ In addition, GC as well as HPLC analyses were performed to determine any potential CO_2 reduction products in the headspace or the reaction solution. Here, CO was solely detected in the headspace of as well as within the reaction mixture and thus highlights the specificity of the CO_2 reduction toward CO (Figure S15).

CO₂ Reduction in Acetonitrile. While stable in THF, complex 11 slowly converts into $[(Triphos)Fe(\mu-H)_3Fe(\mu$ $H_{3}Fe(Triphos)$ in acetonitrile over the course of 1 week. The different behavior of 11 in acetonitrile pointed our attention toward a potentially different reduction pathway of CO_2 in another solvent. Moreover, the solvent polarity was previously reported to influence the hydricity of transition metal hydrides⁵¹⁻⁵⁷ and an increase of the hydride donor strength of a metal complex corresponding with an increasing solvent polarity was shown. Along this line, a solventdependent CO₂ hydrogenation was reported for H₂Co-(dmpe)₂.⁵⁷ Herein, depending on the used solvent severe, alteration of the reaction pathway to afford HCO2⁻ was observed, while the product distribution was still the same. On the basis of such earlier reports, we anticipated that the solvent change will play a major role for the hydrogenation of CO_2 .

Upon change of the solvent from THF to acetonitrile, the main absorption band of complex 11 shifts from 515 to 525 nm (Figure 1a). While this shift might be due to implicit solvent effects (e.g., change in electric field, etc.), we believe that it originates from coordination of an additional solvent molecule to the Fe center (see the computational section below). ¹H NMR spectroscopy further supports an altered electronic distribution. Here, the hydride signal at -14.18 ppm in nonpolar solvents (CDCl₃ and THF- d_8 , Figure S7a,b) shifts to -10.06 ppm in CD₃CN (Figure S7c). Notably, a significant increased broadening of the borohydride ¹H NMR signal was observed in acetonitrile. Notably the line width significantly varies as a function of temperature (Figure S8) and suggests a change of the binding of the H atoms as well as a likely coordination of the solvent. Similar line broadenings were previously reported for $(PNMeP)Fe(H)BH_4$ (PNP = HN- $\{CH_2CH_2(PR_2)\}$ and suggest an overall alteration of the binding mode of this ligand from κ^2 to a κ^1 bound BH₄^{-.5}

While the reaction of 11 and CO₂ under ambient pressure and room temperature did notably not proceed in THF solutions, the analogous reaction in acetonitrile instantly led to a color change of the reaction mixture from purple to orange along with a shift of the band from 525 to 464 nm (Figures 1a and S15). Whereas a faster reaction with CO₂ might be expected in acetonitrile due to the significantly increased solubility of CO_2 in acetonitrile versus THF,⁵⁹ the CO_2 reduction product was likewise altered visibly by a new IR band at 1710 cm⁻¹ in the reaction mixture as well as isolated complex 14 (Figure 1b). This band is indicative for the formation of formate in acetonitrile under ambient conditions. Notably, GC and HPLC analysis (Figure S18) confirmed the sole formation of formate under such conditions and thus shows a significantly different product formation as observed in THF. While we were not able to obtain single crystals suitable for X-ray structure determination, Mössbauer spectroscopy gave additional evidence for the formation of complex 14. The isomer shift of 0.09 mm s^{-1} together with a quadrupole splitting of 1.33 mm s^{-1} is in accordance with the formation of a low spin Fe(II) complex (Figure S19). In addition, the ¹H NMR spectrum of complex 14 in acetonitrile- d_3 revealed a signal at -12.07 ppm, indicating that the Fe center is potentially coordinated by an additional hydride ligand as well as a formate ligand (Figure S20).

H/D Exchange. The formation of formate from CO_2 was further supported by utilizing the deuterated complex, $[(Triphos^{C})Fe(D)(BD_{4})]$ (11-D), during the reduction experiments. While the results were comparable to the IR pattern of 14, the band at 1710 cm^{-1} (14) was shifted to 1684 cm^{-1} (Figure S21), which is in accordance with the expected H/D exchange in the formate ligand. The high stretching frequency of the C=O group as well as the appearance of the C-H_{formate} resonance at 8.65 ppm furthermore supports the formation of an iron bound formate molecule (Figure S20).⁵⁸ Thus, the formate formed is clearly a result of CO₂ reduction facilitated by complex 11. Notably, while the neat reaction of CO2 and NaBH4 in acetonitrile was previously reported to afford $[HB(OCHO)_3]^-$ and $[H_2B(OCHO)_2]^-$,^{60,61} neither ¹¹B NMR nor IR spectroscopy revealed the typical signals for such species. Furthermore, to investigate the possibility of a direct CO₂ reduction by dissociated BH₄⁻ followed by rapid formate interception by the Fe complex, the reaction of 11 with formate was attempted but neither agrees with the





^aAll spectroscopically characterized species (see text) are boxed. Note that, in the case of species **B**, only two isomers are observed experimentally (see Scheme 4 and the corresponding text).

spectrum of 15, 14, nor compound B (Scheme 3) and thus further suggests a purely metal centered reduction process.

The Importance of Pressure. To exclude the different pressure conditions as the reason for the varied product formation, the reaction of 11 with CO₂ in acetonitrile was repeated at 7 bar/70 °C. Although a different product formation can be observed, no CO could be detected. Instead of the IR pattern of 14, the spectrum of the reaction mixture of 11 with CO₂ in acetonitrile at 7 bar/70 $^{\circ}$ C reveals two bands at 1696 and 1589 cm⁻¹ that can be reasoned by the formation of compound 15 (Figure 1b). Furthermore, when a solution of sodium borohydride in acetonitrile was purged with CO₂ under otherwise identical experimental conditions as those used for the formation of 14, the IR spectrum of the formed colorless solid clearly differs from the one observed for complexes 14 and 15 (Figure S22). This finding furthermore shows that an iron centered reaction mechanism for the formate formation has to be considered and not the reduction of CO_2 by free BH_4^- due to decomposition of 11.

Computational Studies. In order to rationalize the unique solvent-controlled CO_2 reduction, the different reactions were investigated by means of quantum chemical calculations. In the course of this investigation, a large number of possible reaction pathways were simulated. For the sake of clarity, we herein constrain the discussion to the energetically most favorable pathways as well as some particularly relevant alternatives and refer the reader to the Supporting Information (Supporting Information: T3) for additional information. The most favorable mechanisms are shown in Scheme 3.

Before giving a detailed description of the full reaction mechanisms, we start with a brief characterization of the starting material 11 and focus the discussion on the initial step of the reaction that is responsible for the different product selectivity in different solvents. According to our results, 11 has a closed shell singlet electronic ground state with a central Fe(II) ion. Close agreement between experimentally obtained data and calculated values for key structural parameters (Table S16) and Mössbauer isomer shifts (Table S15) as well as good agreement between the experimental and calculated UV/vis spectra (Figures S23 and S24) indicate that our electronic structure calculations adequately describe the investigated system. The facial coordination of the Triphos ligand in 11 imposes a favorable geometrical arrangement such that all observed reactions occur at the borohydride face of the

molecule. Importantly, the bulky phenyl groups form a shielded cavity in which all reactions take place. In contrast to previous findings for structurally related compounds in different solvents,¹² a change of the binding mode of the Triphos ligand was found to be unfavorable (Figure S40). The abundance of hydrides in 11 in principle opens up possibilities for the formation of H₂ and for several low energy pathways during the course of the reaction. However, the reactivity of the Fe-bound hydride is limited by its poorly accessible position within the cavity, while the two peripheral hydrides are bound to the electron-deficient boron. Accordingly, a direct insertion in the Fe-H or B-H bonds of 11 by CO_2 is associated with prohibitively large reaction barriers (Figure \$39). Instead, the reaction in acetonitrile is initiated by binding of a solvent molecule to a Fe(II) center, resulting in A. Experimental support for this finding is provided by the good agreement between the UV/vis spectrum of 11 after dissolution in acetonitrile and the calculated spectrum of A (Figures S23 and S25) as well as a broadening of the ¹H NMR (vide supra). Concomitant to the binding of acetonitrile to Fe, the borohydride changes its coordination mode from κ^2 to κ^1 which increases the number of peripheral hydrides from two to three and renders each of them more nucleophilic. This effectively reduces the barrier for an electrophilic attack by CO_2 to $\Delta G^{\ddagger}(TS-A-B) = 11.6$ kcal mol⁻¹, and accordingly, the formate containing **B** is readily formed (Scheme 3). An analogous reaction in THF is prevented by steric factors. Owing to its relatively large size, a THF molecule cannot enter the cavity of 11 and consequently no activation of the peripheral hydrides occurs. If, however, the temperature and pressure are increased, CO₂ acts as a nucleophile and attacks the boron before binding to the Fe via its carbon (Scheme 3) which is a prerequisite for CO formation.^{2,62-64}

The first step of the reaction in acetonitrile corresponds to one solvent molecule binding to the Fe(II) center in complex 11, resulting in **A**. As depicted in Figure 3, this step is associated with a barrier of $\Delta G^{\ddagger}(\mathbf{TS-11-A}) = 8.4 \text{ kcal mol}^{-1}$ and by $\Delta G(\mathbf{A}/\mathbf{11}) = 6.4 \text{ kcal mol}^{-1}$ endothermic. Nevertheless, the abundance of acetonitrile together with the following irreversible and exothermic addition of a CO₂ molecule to **A** act as a driving force for this step. The reduction of CO₂ by one of the peripheral hydrides in **A** results in the formation of a metastable intermediate with a κ^2 -bound borohydride and an unbound formate anion.



Figure 3. Calculated free energy profile for the reaction of **11** with CO_2 in acetonitrile at ambient temperature and pressure (r.t./1 atm of CO_2). All values are given in kcal mol^{-1} and were obtained at the DLPNO-CCSD(T)/CBS level of theory (see the Computational Details section).

Due to the prior activation of the peripheral hydrides, this step has a relatively low barrier of $\Delta G^{\ddagger}(\mathbf{TS}\cdot\mathbf{A}\cdot\mathbf{B}) = 11.6$ kcal mol⁻¹ as compared to the addition of CO₂ to unactivated 11. The metastable intermediate with an unbound formate further undergoes a geometrical reorganization where the formate binds to the Fe(II) center while breaking one Fe-H-B bond in a concerted fashion, which yields the stable product **B** ($\Delta G(\mathbf{B}/\mathbf{11}) = -6.5$ kcal mol⁻¹). The predicted low barriers for the formation of **B** are in agreement with the experimental findings of a facile reaction. Under the given reaction conditions, **B** may eliminate the Fe-bound acetonitrile to give **B2** (Scheme 4), which is more stable by $\Delta G(\mathbf{B2}/\mathbf{B}) =$

Scheme 4. Structures of Possible Isomers of Compound B Together with Their Calculated Relative Stability in kcal mol⁻¹



-8.9 kcal mol⁻¹. Furthermore, we assume that evaporation of the solvent prior to the spectroscopic characterization of the reaction product effectively leads to the elimination of both, acetonitrile and BH₃ (as an acetonitrile adduct), since the experimental isomer shift (Figure S19) and CO stretching frequency (1710 cm⁻¹) only match the calculated values for intermediate **B4** (Scheme 4, Tables S7–S9, and Table S14). Interestingly, **B4** features a 5-fold coordinated Fe(II) center

with a κ^1 bound formate while according to our calculations changing the binding mode to κ^2 would lead to the more stable 14 ($\Delta G(14/B4) = -7.5$ kcal mol⁻¹). In contrast to the Mössbauer and IR spectra, the UV/vis spectrum was recorded after the produced solid was again dissolved in acetonitrile. Therefore, it is not unexpected that the calculated spectrum of B3 fits the experimental spectrum best (Figures S26 and S29). Thus, we believe that, although B2 is more stable than B, the latter is the predominant species in an acetonitrile solution. Moreover, for the same reason as that discussed above for 11 and A, B is more reactive toward a nucleophile attack than B2.

Upon applying a CO_2 pressure of 7 bar and increasing the temperature to 70 °C, **B** reacts with a second molecule of CO_2 . The corresponding reaction profile is presented in Figure 4. It



Figure 4. Calculated free energy profile for the reaction of 11 with CO_2 in acetonitrile at 70 °C and a pressure of 7 bar. All values are given in kcal mol⁻¹ and were obtained at the DLPNO-CCSD(T)/CBS level of theory (see the Computational Details section).

must be noted that, although both the final point in Figure 3 and the first point in Figure 4 correspond to compound **B**, their absolute energies differ by 10.0 kcal mol⁻¹, as they correspond to a calculation including the second CO_2 molecule ($\Delta G(\mathbf{B}/\mathbf{11}) = 3.5$ kcal mol⁻¹, Figure 4) and two separate calculations of complex and substrate ($\Delta G(\mathbf{B}'/\mathbf{11}) =$ -6.5 kcal mol⁻¹, Figure 3).

The difference between the two free energies largely originates from differences in the translational entropy (see the Computational Details section). Starting from the former, our calculations indicate that the second CO₂ approaches the singly bound borohydride and reacts in an S_N2 fashion to increase the electropositive character of the carbon. Subsequently, this carbon inserts into the just formed Fe–H bond to give C (Figure 4). Despite intense efforts, the optimization of the transition state **TS-B-C** did not quite meet the convergence criteria. Nevertheless, the energy during optimization steps only changes marginally ($\Delta E \approx 0.1 \text{ kcal mol}^{-1}$) and the highest imaginary harmonic frequency for the partially converged configuration is associated with a symmetric mode of the S_N2 fashioned reaction with boron being the central



Figure 5. Calculated free energy profile for the reaction of 11 with CO₂ in THF at 70 °C and 7 bar of CO₂. All values are given in kcal mol⁻¹.

atom. Therefore, we strongly believe that the obtained structure resembles the true transition state and the calculated barrier for the same is an upper bound to the true reaction barrier. Even though the partial formation of the C-H bond stabilizes the transition state, the associated activation barrier is comparably large ($\Delta G^{\ddagger}(\mathbf{TS}\text{-B}\text{-C}) = 27.1 \text{ kcal mol}^{-1}$), consequently making TS-B-C a kinetically inaccessible conformation at ambient temperature and pressure. In an alternative pathway that would feature a direct insertion of CO₂ in the B-H bond, no stable product could be located (Figure S38). We attribute this observation to the reduced nucleophilic character of the peripheral hydrides in B as compared to the extremely electron-rich compound A. Importantly, only after elimination of acetonitrile and BH₃ (as an acetonitrile adduct) from C to obtain 15, the total reaction free energy becomes negative $(\Delta G(15/B) = -8.9 \text{ kcal})$ mol^{-1}). Good agreement between the experimental and calculated CO stretching frequencies (exptl 1589/1696 cm⁻¹ vs calcd 1605/1707 cm⁻¹, Table S11) as well as the UV/vis spectrum (Figures S31 and S32) support the identity of 15 as the final reaction product.

While the reduction of CO_2 by 11 in acetonitrile is predicted to proceed through "normal" insertion into B-H and Fe-H bonds, our results indicate that the reaction in THF follows a different route. The Triphos ligand scaffold offers steric protection to the Fe(II) center, leaving only the BH_4^- moiety chemically active. Our calculations indicate that cleaving one of the Triphos-Fe bonds is highly energetically unfavorable (Figure S40). Therefore, the Triphos does not actively participate in the reaction. On the other hand, THF, being a comparably bulky solvent, cannot bind to the Fe center in a fashion similar to acetonitrile. Consequently, no reaction between 11 and CO_2 is observed at ambient temperature and pressure. Only at an elevated temperature of 70 °C and a pressure of 7 bar the final product 13 is immediately formed. In contrast to the above-discussed reaction, no spectroscopic evidence for stable intermediates was found, leaving only theory-based arguments to elucidate the most probable

reaction mechanism. According to our results, the first step of the reaction involves the insertion of CO_2 in one of the two electron-deficient three-center-two-electron B-H-Fe bonds to give intermediate E that features a stable six-membered ring (Scheme 3). As expected, this endothermic ($\Delta G(E/11) = 10.6$ kcal mol⁻¹) step has a high barrier of $\Delta G^{\ddagger}(TS-11-E) = 37.3$ kcal mol⁻¹ and is hence only proceeded through high temperatures and pressures (Figure 5). After its formation, E isomerizes to a $Fe(0)-H_2$ species with a short H-H bond of 0.83 Å. This change in oxidation state at the Fe is critical for the observed overall reaction, as it allows the Fe to act as a nucleophile and form a Fe-C bond (F). Despite the considerable free energy gain during this step $(\Delta G(\mathbf{F}/\mathbf{E}) =$ -11.9 kcal mol⁻¹), no transition state could be localized, since the corresponding part of the potential energy surface calculated with the setup used for geometry optimizations is extremely flat $(\Delta G^{\text{DFT}}(\mathbf{F}/\mathbf{E}) = -1.1$ kcal mol⁻¹). We are thus convinced that this reaction barrier is readily surpassed under the given reaction conditions. The next step of the reaction is initiated by an intramolecular proton transfer via heterolytic cleavage of the coordinated H₂ which leads to a simultaneous cleavage of one C-O bond and formation of an O-H bond. As a result, water and Fe-bound CO are formed while BH₂OH is eliminated, resulting in complex G. Although the formation of **G** is exothermic by $\Delta G(\mathbf{G}/\mathbf{F}) = -24.3 \text{ kcal mol}^{-1}$, it is associated with a barrier of $\Delta G^{\ddagger}(\mathbf{TS}\text{-}\mathbf{F}\text{-}\mathbf{G}) = 24.7 \text{ kcal mol}^{-1}$ due to the breaking and formation of multiple bonds. Analogous to E, G isomerizes to a $Fe(0)-H_2$ species and subsequently binds a second CO₂ through the carbon to generate H. Intermediate H in turn eliminates water with a barrier of $\Delta G^{\ddagger}(\text{TS-H-13}) = 39.0 \text{ kcal mol}^{-1}$ to give the final product 13, which has been characterized by X-ray crystallography. As expected, 13 constitutes the lowest point on the potential energy surface $(\Delta G(13/11) = -41.3 \text{ kcal})$ mol^{-1}). To this end, we would like to point out that the high barriers on the way to 13 can only be overcome because of the applied reaction conditions that favor the thermodynamic product and, to a lesser degree, the considerable gain in free

energy associated with some of the previous steps. Furthermore, since the produced BH_2OH is only metastable, it is likely to further react with water, BH_2OH , or other boron containing degradation products. Even though the ultimate boron containing degradation product could not yet be characterized, the concomitant gain in free energy adds to the driving force of the observed total reaction.

CONCLUSION

In conclusion, a unique example of a solvent-controlled CO_2 reduction is reported. While the reduction of CO_2 is facilitated by $[(Triphos^C)Fe(H)(BH_4)]$ in stoichiometric conversions, our results show that the solvent also plays a significant role in the reduction pathway of CO_2 and needs to be investigated. By performing comparative spectroscopic and quantum chemical studies, we provide reasonable pathways for the different reactions observed. Here, the solvent coordination controls if a $Fe(0)-(H_2)$ or a $Fe(II)-(H^-)$ intermediate is formed, leading either to a C- or O-coordinated formate intermediate, respectively. Thus, the reaction either leads to the formation of CO or formic acid in a highly selective manner. These results could clearly stimulate the further investigation of the role of solvents in organometallic catalysis and provides valuable information on the control of CO_2 conversion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00711.

Methods, additional calculations and experimental details, and supportive spectroscopic data (PDF)

Accession Codes

CCDC 1871381–1871387 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Fonds der Chemischen Industrie (Liebig grant to U.-P.A.) and through the Deutsche Forschungsgemeinschaft (Emmy Noether grant to U.-P.A., AP242/2-1, and Cluster of Excellence RESOLV EXC1069), the Fraunhofer Internal Programs under Grant No. ATTRACT 097-602175 as well as the Max Planck Gesellschaft (M.v.G.). F.W. thanks the Studienstiftung des deutschen Volkes for a Ph.D. fellowship. M.R. and A.K. gratefully acknowledge funding by the Otto-Hahn program of the Max-Planck Gesellschaft. The presented quantum chemical calculations were partially conducted on computers provided by the Zentrum für molekulare Spektroskopie und Simulation solvensgesteuerter Prozesse (ZEMOS). We thank R. Miller and M. Reback for support in language polishing.

ABBREVIATIONS

COT, cyclooctatetraen; DFT, density functional theory; DLPNO-CCSD(T), coupled cluster theory with singles doubles and perturbative triples in its domain-based pair natural orbital implementation; CC-PVXZ (X = TQ), correlation consistent polarized valence triple (T) or quadruple (Q) zeta basis sets; def2-SVP, split-valence polarized basis set; def2-TZVP, triple- ζ valence polarized basis set; PCM, polarizable continuum model; TDDFT, time-dependent linear response density functional theory

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