ORGANOMETALLICS

Using CS₂ to Probe the Mechanistic Details of Decarboxylation of **Bis(phosphinite)-Ligated Nickel Pincer Formate Complexes**

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Supporting Information

ABSTRACT: The reaction of the formate complex $\{2,6-(R_2PO),C_6H_3\}$ -Ni(OCHO) (R = ^tBu, 5; R = ⁱPr, 6) with CS₂ shows first-order kinetics in nickel concentration and zero-order in $[CS_2]$ when CS_2 is used in large excess. Rate measurement at different temperatures gives activation parameters $\Delta H^{\ddagger} = 22.6 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -5.2 \pm 3.0$ eu for the decarboxylation of 5 and $\Delta H^{\ddagger} = 22.6 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -4.3$ \pm 3.2 eu for the decarboxylation of 6. Comparing the decarboxylation rate constants for 6 and {2,6-(ⁱPr₂PO)₂C₆H₃}Ni(OCDO) (6-d) yields KIE



values of 1.67-1.90 within the temperature range 30-45 °C. On the basis of these experimental results and DFT calculations, an ion pair mechanism has been proposed for the decarboxylation process. The CS₂ insertion products $\{2,6-(R_2PO)_2C_6H_3\}$ Ni-(SCHS) ($R = {}^{t}Bu$, 3; $R = {}^{i}Pr$, 4) have been characterized by X-ray crystallography.

INTRODUCTION

Decarboxylation of transition metal formate complexes (eq 1) is an important step in catalytic processes such as

decomposition of formic acid to H_2 and CO_{2} ,¹ transfer hydrogenation reactions using HCO_2H , HCO_2H-NEt_3 , or HCO_2^- as the hydrogen source,² and isomerization of methyl formate to acetic acid.³ It also constitutes a strategy to synthesize transition metal hydrides,⁴ provided that thermodynamics favor decarboxylation or the removal of CO₂ can drive the equilibrium to favor hydride formation. Double decarboxylation of bis(formato) complexes is a convenient way to generate low-valent metal species by taking advantage of the subsequent H₂ elimination.⁵ The reverse step of decarboxylation (i.e., insertion of CO_2 into metal hydrides) is often the key to the success of developing catalytic reduction of CO₂.⁶ Understanding the mechanistic details of decarboxylation reactions can thus shed light on how CO₂ insertion occurs because, according to the principle of microscopic reversibility, these two steps proceed via the same transition state.

Examples of decarboxylation of formate complexes are known for virtually every transition metal; however, very few systems have been subjected to in-depth analysis of this transformation.⁷ In particular, kinetic and mechanistic information pertaining to decarboxylation reactions is limited in the literature and relies mostly on density functional theory (DFT) calculations.⁸ For a thermodynamically favorable decarboxylation, direct measurement of the kinetics should be

straightforward, as demonstrated with CpRe(NO)(PPh₃)-(OCHO).^{7a} It is more challenging when decarboxylation is thermodynamically unfavorable. One solution is to study the exchange reaction between the formate complex and ¹³CO₂ as an indirect probe to the decarboxylation process. For instance, the isotopic exchange of trans- $(Cy_3P)_2M(H)(OCHO)$ (M = Ni, Pd)^{7b} or $[Cr(CO)_5(OCHO)]^{-7c}$ with excess ¹³CO₂ is first-order in formate concentration and independent of ¹³CO₂ pressure. The observed exchange rate is therefore equivalent to the rate of formate decarboxylation.

In this paper we investigate the reactions of formate complexes with CS₂ as an alternative but less expensive method to elucidate the mechanistic details of formate decarboxylation. We focus specifically on bis(phosphinite)-ligated nickel pincer formate complexes due to their involvement in nickel-catalyzed reduction of CO₂ with boranes.⁹ Our previous research has shown that decarboxylation of these formate complexes is kinetically accessible but thermodynamically unfavorable.9a,b Given the notion that CS_2 is more reactive than CO_2 ,¹⁰ we hypothesize that CS₂ will outcompete CO₂ for the insertion into the nickel hydride intermediates, leading to a kinetic scenario in which the decarboxylation step becomes rate determining.

RESULTS AND DISCUSSION

Reactivity of Nickel Pincer Hydride Complexes toward CS₂. Although the insertion of CS₂ into metal hydrides is a well-known process,¹¹ examples for nickel complexes are

Received: September 27, 2016

surprisingly rare. Liaw and co-workers have used CS_2 to trap a transient Ni(III) hydride species bearing a tripodal $[P(C_6H_3-3-SiMe_3-2-S)_3]^{3-}$ ligand,¹² which, to our knowledge, is the only known case for inserting CS_2 into a Ni–H bond. To establish the insertion chemistry, nickel hydrides 1 and 2 were treated with excess CS_2 at room temperature (eq 2), which resulted in



an immediate color change from light yellow to golden yellow. The insertion products **3** and **4** were isolated in good yield and characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography. As expected for a dithioformate complex, **3** or **4** dissolved in CDCl₃ displays characteristic low-field ¹H and ¹³C resonances for the dithioformato group ($\delta_{\rm H}$ 11.50 and $\delta_{\rm C}$ 234.0 for **3**, $\delta_{\rm H}$ 11.55 and $\delta_{\rm C}$ 233.7 for **4**).

Our previous work on the analogous formate complexes $\{2,6-(R_2PO)_2C_6H_3\}$ Ni(OCHO) (R = ^tBu (5), ⁱPr (6), or cyclopentyl) shows that in the solid state the formato group prefers an in-plane conformation with respect to the coordination plane, unless the pincer ligand is sufficiently bulky (e.g., R = ^tBu).^{9a,c} The dithioformato group in both 3 (Figure 1) and 4 (Figure 2) adopts an almost perpendicular



Figure 1. ORTEP drawing of **3** at the 50% probability level. Selected bond length (Å) and angles (deg): Ni-C1 1.9051(19), Ni-P1 2.1955(6), Ni-P2 2.2119(6), Ni-S1 2.2203(6), C23-S1 1.694(2), C23-S2 1.638(2), P1-Ni-P2 163.44(2), C1-Ni-S1 166.41(6), Ni-S1-C23 120.47(8), S1-C23-S2 132.22(13). Interatomic Ni…S2 distance: 3.9841(6) Å.

conformation with a dihedral angle of $84.0(1)^{\circ}$ between the P1–P2–C1–Ni and SC(S)H planes. The S1 atom is displaced out of the least-squares plane defined by the P1, P2, C1, and Ni atoms; however, the long interatomic Ni…S2 distance suggests a κ^1 -coordination mode for the dithioformato ligand. Complex **3** displays a more bent C1–Ni–S1 angle but a longer interatomic Ni…S2 distance than **4**, further supporting that the displacement of S1 from the coordination plane is not due to Ni…S2 interaction.

Complexes 3 and 4 are moisture and air stable both as solids and in solution. No significant decomposition was observed



Figure 2. ORTEP drawing of 4 at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni–C1 1.8975(19), Ni–P1 2.1686(6), Ni–P2 2.1568(6), Ni–S1 2.2269(6), C23–S1 1.681(2), C23–S2 1.646(3), P1–Ni–P2 163.60(2), C1–Ni–S1 170.24(6), Ni–S1–C23 107.40(8), S1–C23–S2 128.65(14). Interatomic Ni…S2 distance: 3.4813(7) Å.

when a solid sample or a toluene/hexane solution was exposed to air for several weeks. Unlike nickel formate complexes **5** and **6**, which lose CO₂ readily under a dynamic vacuum while being heated at 60 °C, dithioformate complexes **3** and **4** show no sign of CS₂ deinsertion under the same conditions. Bubbling CO₂ through a solution of **3** or **4** in C₆D₆ for 2 h led to no change in NMR spectra, further illustrating that CS₂ insertion is irreversible or the dithioformate complex is more stable than the formate complex. Complex **3** underwent alkylation with allylic or benzyl bromide at 90 °C, producing the known {2,6-(^tBu₂PO)₂C₆H₃}NiBr¹³ and alkyl dithioformate^{11j} cleanly (eq **3**). In the latter case, the NMR yield for PhCH₂SCHS was



determined to be 74%. Had CS_2 deinsertion occurred, one would anticipate dehalogenation of the alkyl bromides by the nickel hydride intermediate **1**.

Decarboxylation of Nickel Formate Complexes in the Presence of CS₂. The resistance of **3** and **4** against CS_2 deinsertion and the reversible nature of CO_2 insertion into **1** and **2** suggest that for the bis(phosphinite)-based nickel pincer system the formate complexes should react with CS_2 via decarboxylation. Indeed, such reactions were found to take place at room temperature, albeit slowly. At 80 °C with a large excess of CS_2 (~30 equiv), complexes **5** and **6** were fully converted to **3** and **4**, respectively, within 12 h and the dithioformate complexes were isolated in high yield (eq 4).



Kinetics for the aforementioned reactions in toluene- d_8 were studied by ¹H NMR spectroscopy using 1,4-dioxane as an

internal standard. The nickel formate complexes were first treated with 20 equiv of CS₂, and the initial formate concentration was kept at 0.013 M. Monitoring the disappearance of the nickel formate complexes at 30 °C showed a first-order decay with a rate constant of $(1.8 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ for 5 and $(3.7 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ for 6. Increasing the initial concentration or the equivalence of CS₂ accelerated the reaction of 5 until a plateau was reached at $[CS_2] \approx 0.8$ M, giving a saturation rate constant of $(2.5 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$. In contrast, the rate for the decarboxylation of 6 was not enhanced with increasing $[CS_2]$, suggesting that with 20 equiv of CS₂ the rate was already saturated.

The kinetics data can be rationalized by a reaction scheme involving reversible CO_2 deinsertion followed by CS_2 insertion (Scheme 1). The steady-state approximation applied to the

Scheme 1. Decarboxylation of Nickel Formate Complexes Assisted by CS_2



nickel hydride intermediate (which was not observed during the reaction) gives a rate law shown in eq 5. Saturation occurs when CO_2 insertion becomes negligible $(k_{-1}[CO_2] \ll k_2[CS_2])$, at which point the observed rate constant is for the decarboxylation step (eq 6).

$$\frac{-\mathrm{d}[\mathbf{NiOCHO}]}{\mathrm{d}t} = \frac{k_1 k_2 [\mathrm{CS}_2][\mathbf{NiOCHO}]}{k_{-1} [\mathrm{CO}_2] + k_2 [\mathrm{CS}_2]} \tag{5}$$

When $k_2[CS_2] \gg k_{-1}[CO_2]$,

$$\frac{-d[\mathbf{NiOCHO}]}{dt} \approx \frac{k_1 k_2 [CS_2][\mathbf{NiOCHO}]}{k_2 [CS_2]}$$
$$= k_1 [\mathbf{NiOCHO}]$$
(6)

The rate constants for the decarboxylation of **5** and **6** at higher temperatures were determined in a similar fashion (see Supporting Information). These data yielded activation parameters $\Delta H^{\ddagger} = 22.6 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -5.2 \pm 3.0$ eu for the decarboxylation of **5** and $\Delta H^{\ddagger} = 22.6 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -4.3 \pm 3.2$ eu for **6**. It should be noted that the errors provided here were derived from the standard least-squares procedures. The uncertainties in the activation parameters should be higher due to the very narrow temperature range applied (30 to 45 °C, limited by the NMR technique). Using the error propagation formulas described by Girolami et al.,¹⁴ the absolute errors in ΔH^{\ddagger} and ΔS^{\ddagger} were estimated to be 2.2 kcal/mol and 7.2 eu, respectively.¹⁵

To further understand the decarboxylation process, deuterium-labeled nickel formate complex 6-*d* was prepared from protonation of hydride 2 with formic acid-*d*₂. Its decarboxylation in the presence of 20 equiv of CS₂ was markedly slower than the protio species 6. Comparing their rate constants ($k_{\rm H}$ / $k_{\rm D}$) revealed a kinetic isotope effect (KIE) of 1.90 ± 0.12 at 30 °C and 1.85 ± 0.19 at 45 °C. Rate measurements for 6-*d* at different temperatures gave activation parameters $\Delta H^{\ddagger} = 23.4 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -2.9 \pm 1.2$ eu. The absolute errors $\sigma \Delta H^{\ddagger}$ (2.3 kcal/mol) and $\sigma \Delta S^{\ddagger}$ (7.4 eu) again are higher than the errors obtained from fitting the Eyring equation.^{14,15} **Transition State for the Decarboxylation Reaction.** We have previously proposed a four-membered-ring transition state featuring axial hydride abstraction by the nickel, first based on DFT calculations^{9b} and more recently from a reactivity study of P-stereogenic nickel formate complexes as shown in Figure 3.¹⁶



Figure 3. Reactivity difference between *meso* and *racemic* isomers of nickel formate complexes.

The current work provides additional experimental evidence supporting the transition-state structure. The experimentally determined ΔH^{\ddagger} value (22.6 kcal/mol) for **5** is in good agreement with the computed value (24.0 kcal/mol),^{9b} especially considering the absolute error in ΔH^{\ddagger} (2.2 kcal/mol). The measured ΔS^{\ddagger} values for **5**, **6**, and **6**-**d** are slightly negative, comparable to the ΔS^{\ddagger} value ($-6.3 \pm 1.3 \text{ eu}$) determined for the decarboxylation of CpRe(NO)(PPh₃)-(OCHO).^{7a} However, the absolute errors in ΔS^{\ddagger} are too large to discern the gain or loss of degrees of freedom. Nevertheless, the sterically less demanding nickel formate complex **6** loses CO₂ at a rate consistently faster than **5** (by 30–60%) and appears to be controlled by the entropy term.

Darensbourg and co-workers have reported a small KIE ($k_{\rm H}$ / $k_{\rm D}$ = 1.13 at 15 °C) for the decarboxylation of [Cr- $(CO)_5(OCHO)$ ⁻ and have accordingly proposed an early transition state.^{7c} Creutz et al. have shown a similarly small KIE $(k_{\rm H}/k_{\rm D} = 1.15 \pm 0.10$ at 25 °C) for the limiting rate at which formate ion binds to $[(\eta^6-C_6Me_6)Ru(bipy)(H_2O)]^{2+}$ and have used it as the rate for the decarboxylation of $[(\eta^6-C_6Me_6)Ru-$ (bipy)(OCHO)^{+.17} The KIE values (1.67–1.90 at 30–45 °C) obtained in this work are larger but comparable to the KIE $(k_{\rm H}/$ $k_{\rm D}$ = 1.55 ± 0.19 at 112 °C) reported for the decarboxylation of CpRe(NO)(PPh₃)(OCHO).^{7a} Our results suggest that at the transition state 5 or 6 has a more elongated formate C-H bond than $[Cr(CO)_5(OCHO)]^-$. The larger KIE values are likely due to $[\{2,6-(R_2PO)_2C_6H_3\}Ni]^+$ and $[CpRe(NO)(PPh_3)]^+$ being better hydride acceptors than the neutral $Cr(CO)_{s}$ fragment. Compounds 5 and 6 are 16-electron complexes and therefore can undergo β -hydrogen elimination directly as the decarboxylation mechanism. Coordinatively saturated complexes, on the other hand, would require ligand dissociation prior to β -hydrogen elimination.¹⁸ Alternatively, decarboxylation of these complexes may proceed via an ion pair mechanism involving the dissociation of HCO2⁻ accompanied by H⁻ transfer from carbon to metal, as proposed for CpRe(NO)- $(PPh_3)(OCHO)^{7a}$ and $(^{R}PN^{H}P^{R})Fe(CO)H(OCHO)$ $(^{R}PN^{H}P^{R} = HN(CH_{2}CH_{2}PR_{2})_{2})^{.8b}$ On the basis of DFT calculations, Catlow, Xiao, and co-workers have proposed a similar mechanism for the decarboxylation of Cp*Ir(iminoaryl)(OCHO).^{8e} Their experimental data on Cp*Ir(iminoaryl)-catalyzed transfer hydrogenation of imines with HCO₂H-NEt₃ have suggested that the decarboxylation step is rate limiting with a $k_{\rm HCO2H}/k_{\rm DCO2D}$ value of about 1.9 (at 60 °C). For our system, the calculated transition state for the decarboxylation of 5 (Figure 4) shows a relatively short Ni… H distance (1.757 Å) between nickel and the formate



Figure 4. Calculated transition state for the decarboxylation of 5 (for clarity, methyl groups on the pincer ligand are not shown).

hydrogen.9b By comparison, the calculated Ni-H distance of nickel hydride 1 (1.535 Å) is about 0.22 Å shorter.^{9b} In contrast, going from the ground state of 5 to the decarboxylation transition state, the Ni-O bond is significantly stretched from 1.934 to 2.492 Å. Thus, the decarboxylation pathway is best described as an ion pair mechanism. The boundary to the β -hydrogen elimination mechanism could be blurred, as with the mechanistic scenarios for the insertion of CO₂ into pincer-ligated group 10 metal hydride complexes. Hazari, Kemp, and co-workers have shown in a palladium system that varying the central donor of the pincer ligand could shift the mechanism from typical 1,2-insertion to nucleophilic attack on CO_2 by the metal hydride.¹⁹ The ion pair mechanism implicates that increasing the polarity of the solvent or adding salts may enhance the rate of decarboxylation or CO₂ insertion, as observed in a number of cases.²⁰

CONCLUSIONS

Through this study, we have demonstrated that CS_2 is an effective mechanistic probe for the decarboxylation of transition metal formate complexes, particularly when the decarboxylation process is thermodynamically unfavorable. Because CS_2 is more reactive than CO_2 toward insertion, the limiting rates for the reactions of formate complexes and CS_2 are in fact the rates for the decarboxylation reactions. We believe that the method developed here can be applied to a wide variety of formate complexes, thus providing the opportunity to study the mechanistic details of decarboxylation reactions. Our ongoing efforts focus on identifying factors that promote this transformation.

EXPERIMENTAL SECTION

General Comments. All air-sensitive compounds were prepared and handled under an argon atmosphere using standard Schlenk line and glovebox techniques. Dry and oxygen-free solvents were collected from an Innovative Technology solvent purification system and used throughout the experiments. Toluene- d_8 was distilled from Na and benzophenone under an argon atmosphere. NMR spectra were recorded on a Bruker Avance-400 MHz NMR spectrometer. {2,6-(^tBu₂PO)₂C₆H₃}NiH (1),²¹ {2,6-(ⁱPr₂PO)₂C₆H₃}NiH (2),²¹ {2,6-(^tBu₂PO)₂C₆H₃}Ni(OCHO) (5),^{9a} and {2,6-(ⁱPr₂PO)₂C₆H₃}Ni-(OCHO) (6)^{9c} were prepared as described in the literature.

Synthesis of {2,6-(^t**Bu**₂**PO)**₂**C**₆**H**₃**Ni(SCHS) (3).** *Method A from* **1.** Under an argon atmosphere, **1** (200 mg, 0.44 mmol) was dissolved in 20 mL of toluene, followed by the addition of CS_2 (0.53 mL, 8.80 mmol). The resulting mixture was stirred at room temperature for 2 h. The volatiles were then removed under vacuum, and the yellow residue was subjected to recrystallization from toluene/hexane (1:1) to produce orange crystals of 3 (207 mg, 88% yield).

Method B from 5. Under an argon atmosphere, 5 (150 mg, 0.30 mmol) was dissolved in 20 mL of toluene, followed by the addition of CS_2 (0.54 mL, 8.98 mmol). The resulting mixture was stirred at 80 °C for 12 h. The volatiles were then removed under vacuum, and the

yellow residue was subjected to recrystallization from toluene/hexane (1:1) to yield pure 3 (155 mg, 97% yield). ¹H NMR (CDCl₃, 400 MHz, δ): 11.50 (t, $J_{P-H} = 2.0$ Hz, SCHS, 1H), 7.00 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 6.48 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 1.45 (vt, $J_{P-H} = 7.2$ Hz, CH₃, 36H). ¹H NMR (C₆D₆, 400 MHz, δ): 11.70 (t, $J_{P-H} = 2.4$ Hz, SCHS, 1H), 6.87 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 6.55 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 1.34 (vt, $J_{P-H} = 7.2$ Hz, CH₃, 36H). ¹³C{¹H} NMR (CDCl₃, 101 MHz, δ): 234.0 (s, SCHS), 168.8 (t, $J_{P-C} = 8.7$ Hz, ArC), 129.7 (s, ArC), 128.2 (t, $J_{P-C} = 18.9$ Hz, ArC), 104.9 (t, $J_{P-C} = 5.8$ Hz, ArC), 40.1 (t, $J_{P-C} = 7.8$ Hz, C(CH₃)₃), 28.4 (t, $J_{P-C} = 2.5$ Hz, CH₃). ³¹P{¹H</sup> NMR (CDCl₃, 162 MHz, δ): 190.5 (s). Anal. Calcd for C₂₃H₄₀NiO₂P₂S₂: C, 51.80; H, 7.56. Found: C, 51.96; H, 7.45.

Synthesis of $\{2,6-(Pr_2PO)_2C_6H_3\}$ Ni(SCHS) (4). Method A from 2. Under an argon atmosphere, 2 (200 mg, 0.50 mmol) was dissolved in 20 mL of toluene, followed by the addition of CS₂ (0.60 mL, 9.98 mmol). The resulting mixture was stirred at room temperature for 2 h. The volatiles were then removed under vacuum, and the yellow residue was subjected to recrystallization from toluene/hexane (1:4) to yield pure 4 (157 mg, 66% yield).

Method B from **6**. Under an argon atmosphere, **6** (100 mg, 0.22 mmol) was dissolved in 20 mL of toluene, followed by the addition of CS₂ (0.41 mL, 6.82 mmol). The resulting mixture was stirred at 80 °C for 12 h. The volatiles were then removed under vacuum, and the yellow residue was subjected to recrystallization from toluene/hexane (1:4) to yield pure **4** (96 mg, 90% yield). ¹H NMR (CDCl₃, 400 MHz, δ): 11.55 (s, SCHS, 1H), 7.00 (t, $J_{H-H} = 7.6$ Hz, ArH, 1H), 6.71 (d, $J_{H-H} = 7.6$ Hz, ArH, 2H), 2.29–2.26 (m, CH(CH₃)₂, 4H), 1.38–1.32 (m, CH₃, 12H), 1.26–1.20 (m, CH₃, 12H). ¹³C{¹H} NMR (CDCl₃, 101 MHz, δ): 233.7 (t, $J_{P-C} = 3.3$ Hz, SCHS), 168.2 (t, $J_{P-C} = 9.3$ Hz, ArC), 129.8 (s, ArC), 129.7 (t, $J_{P-C} = 19.8$ Hz, ArC), 105.1 (t, $J_{P-C} = 6.2$ Hz, ArC), 29.6 (t, $J_{P-C} = 11.9$ Hz, CH(CH₃)₂), 17.5 (s, CH₃), 16.9 (s, CH₃). ³¹P{¹H} NMR (CDCl₃, 162 MHz, δ): 190.7 (s). Anal. Calcd for C₁₉H₃NiO₂P₂S₂: C, 47.84; H, 6.76. Found: C, 48.03; H, 6.88.

Reaction of 3 with Allylic or Benzyl Bromide. In a glovebox, 3 (8.0 mg, 15 μ mol) and alkyl bromide (30 μ mol) were mixed in ~0.6 mL of toluene- d_8 . The resulting mixture was heated by a 90 °C oil bath, and the progress of the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. The reaction was complete in 8 h (for benzyl bromide) or 10 h (for allylic bromide). The organic product was also confirmed by GC-MS. ¹H NMR (toluene- d_8 , 400 MHz, δ) of {2,6-(¹Bu₂PO)₂C₆H₃}NiBr: 6.83 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 6.48 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 1.43 (vt, $J_{P-H} = 6.8$ Hz, CH_3 , 36H). ³¹P{¹H} NMR (toluene- d_8 , 400 MHz, δ) of {2,6-(¹Bu₂PO)₂C₆H₃}NiBr: 189.4 (s). ¹H NMR (toluene- d_8 , 400 MHz, δ) of CH₂=CHCH₂SC(S)H: 10.66 (s, SCHS, 1H), 5.51–5.40 (m, CH₂=CH, 1H), 4.94–4.90 (m, CH₂=CH, 1H), 4.85–4.82 (m, CH₂=CH, 1H), 3.50 (d, $J_{H-H} = 7.2$ Hz, CH_2 , 2H). ¹H NMR (toluene- d_8 , 400 MHz, δ) of PhCH₂SC(S)H: 10.67 (s, SCHS, 1H), 6.97–6.91 (m, ArH, 5H), 4.13 (s, CH₂, 2H).

Synthesis of {2,6-(ⁱPr₂PO)₂C₆H₃}Ni(OCDO) (6-*d***). Under an argon atmosphere, 2 (80 mg, 0.20 mmol) was dissolved in 20 mL of toluene, followed by the addition of formic acid-d_2 (0.02 mL, 0.53 mmol). The resulting mixture was stirred at room temperature for 2 h. The volatiles were then removed under vacuum, and the resulting residue was subjected to recrystallization from toluene/hexane (1:4) to yield pure 6-***d* **(79 mg, 88% yield). ¹H NMR (toluene-d_8, 400 MHz, \delta): 6.84 (t, J_{H-H} = 7.9 Hz, ArH, 1H), 6.48 (d, J_{H-H} = 7.9 Hz, ArH, 2H), 2.34–2.27 (m, CH(CH₃)₂, 4H), 1.38–1.17 (m, CH₃, 24H). ²H NMR (toluene, 61 MHz, \delta): 8.25 (s, NiOCDO). ³¹P{¹H} NMR (toluene-d_8, 162 MHz, \delta): 182.6 (s).**

Rate Constant Measurement for the Reactions of Nickel Formate Complexes with CS₂. In a typical experiment, a 0.6 mL solution of complex 5, 6, or 6-*d* in toluene- d_8 (13 mM) was transferred into a resealable NMR tube. For the kinetic studies of 5 or 6, 2 μ L of 1,4-dioxane was added as an internal standard. For 6-*d*, a sealed capillary tube containing P(OEt)₃ was inserted into the solution as an external standard. To each solution was added 20 to 100 equiv of CS₂. The sealed NMR tube was immediately placed into an NMR probe that was precalibrated to the desired temperature (using 100% ethylene glycol). The first ¹H NMR (for 5 or 6) or ³¹P{¹H} NMR (for 6-*d*) spectrum was recorded within 5 min, and spectra were taken

every 5-30 min for 3-5 half-lives. The integration for the NiOCHO resonance of **5** or **6** was compared to that of the internal standard, whereas the integration for the phosphorus resonance of **6**-*d* was compared to that of the external standard.

X-ray Structure Determination. Single crystals of **3** and **4** were obtained from recrystallization in toluene/*n*-hexane. Crystal data collection and refinement parameters are provided in the Supporting Information. Intensity data were collected at 150 K on a standard Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu K α radiation, $\lambda = 1.54178$ Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multiscan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares on F^2 for reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were either located or calculated and subsequently treated with a riding model. No solvent of crystallization is present in the lattice for both structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00759.

Kinetic data, plots of these data, NMR spectra of the nickel pincer complexes, and crystallographic details (PDF)

Crystallographic data (CIF)

Optimized Cartesian coordinates for compounds 3 (XYZ) and 4 (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (No. 21571052), the Key Science and Technology Project of Henan Province (No. 152102210085), and the U.S. National Science Foundation (CHE-1464734) for support of this research. We also thank Prof. Gregory Girolami (University of Illinois–Urbana–Champaign) for sharing the method of calculating absolute errors in activation parameters. Crystallographic data were collected on a Bruker SMART6000 diffractometer, which was funded by an NSF-MRI grant (CHE-0215950).

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