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$$\sqrt{\left[ \sum \left( \frac{\Delta}{\sigma} \right)^2 (n_{\text{obs}} - n_{\text{var}}) \right]}$$

- where  $\Delta$  is the observed deviation between observed and calculated values,  $\sigma$  is the standard deviation of the observation,  $n_{\text{obs}}$  is the number of independent observations, and  $n_{\text{var}}$  is the number of variables optimized in the refinement.  
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## Preparation and Characterization of Organoiron Secondary Alkoxycarbene Complexes

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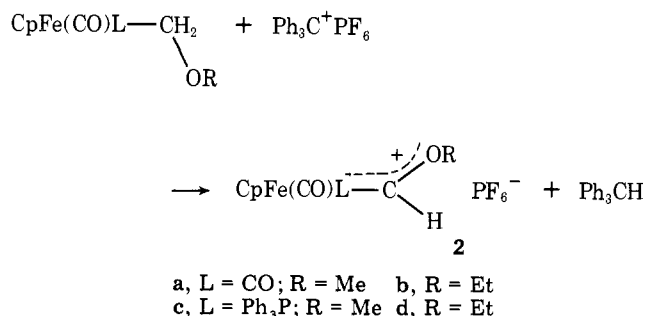
**Abstract:** A series of organoiron secondary alkoxycarbene salts,  $\text{CpFe}(\text{CO})\text{L}\{\text{C}(\text{OR})\text{H}\}^+\text{PF}_6^-$  ( $\text{L} = \text{CO}, \text{Ph}_3\text{P}$ ;  $\text{R} = \text{Me}, \text{Et}$ ) (**2a-d**) has been synthesized by hydride abstraction from the requisite alkoxymethyl complexes (**1a-d**) with a trityl salt. The dealkylation of **2** with iodide was investigated as a synthetic approach to  $\eta^1$ -formyl complexes,  $\text{CpFe}(\text{CO})\text{L}(\text{CHO})$  (**3**). One equivalent of iodide dealkylated **2a-c** to mixtures of  $\text{CpFe}(\text{CO})_2\text{L}^+$  (**6a,b**), **1a-c**, and alkyl iodide, by a reaction sequence involving hydride transfer from a transient **3** to **2**. The hydride acceptor properties of **2** were also investigated by their reactions with borohydride. The observed reduction of coordinated alkoxycarbenes to alkoxymethyl and methyl ligands is of possible relevance to the catalytic fixation of carbon monoxide (e.g., Fischer-Tropsch processes) to hydrocarbons, since surface-bound secondary hydroxycarbene ligands have been postulated in forming the initial C-H bonds.

The Fischer-Tropsch synthesis and related processes<sup>1</sup> for fixing  $\text{CO}/\text{H}_2$  mixtures to methane, methanol, and higher homologues with transition metal containing heterogeneous catalysts are regaining importance as a major area of catalysis research.<sup>2</sup> Impetus for this research activity derives from the possible use of coal, a source of these  $\text{CO}/\text{H}_2$  mixtures of "synthesis gas", as a future source of petrochemicals. Although little is known about the mechanism of CO fixation, plausible intermediates in forming initial C-H bonds often are represented as surface-bound secondary hydroxycarbene [ $\text{M}=\text{CH}(\text{OH})$ ] or formyl [ $\text{M}-\text{C}(\text{O})\text{H}$ ] ligands.

Development of homogeneous analogues to this synthesis and ascertaining the role of formyl and secondary hydroxycarbene complexes in the fixation of CO correspond to recent research directions. Homogeneous hydrogenation of coordinated CO with mononuclear organometallic compounds of early transition metals may involve transitory formyl intermediates.<sup>3,4</sup> Carbonyl ligands are also hydrogenated stoichiometrically with borohydride reagents. Thus, cationic carbonyl compounds reduce to neutral methyl<sup>5a</sup> and hydroxymethyl<sup>5b</sup> complexes, and neutral carbonyl compounds reduce to anionic  $\eta^1$ -formyl<sup>6</sup> complexes. Neutral  $\eta^1$ -formyl complexes may be intermediates in the former borohydride reactions, but such compounds<sup>7</sup> have not been detected as a result of intermolecular hydride transfer (or intramolecular hydride ligand transfer)<sup>8</sup> to a coordinated carbonyl. Secondary hydroxy- or alkoxycarbene complexes have not been reported, although many tertiary examples exist.<sup>9</sup> Information on the reactions of coordinated secondary hydroxy- and alkoxycarbene ligands clearly would be useful in probing the reaction paths available

during CO fixation with homogeneous or heterogeneous catalysts.

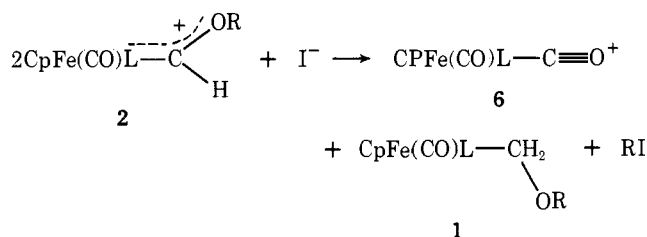
We now report preparation of secondary organoiron alkoxycarbene complexes and present preliminary observations of their reactivity that may be relevant to CO fixation. Previous workers demonstrated that alkoxide abstraction from the methoxymethyl iron complexes,  $\text{CpFe}(\text{CO})\text{L}(\text{CH}_2\text{OCH}_3)$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), generated transient methylene iron compounds,  $\text{CpFe}(\text{CO})\text{L}(\text{CH}_2)^+$  ( $\text{L} = \text{CO}, \text{Ph}_3\text{P}$ ).<sup>10,11</sup> We find that  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  abstracts hydride quantitatively from alkoxy-methyl iron complexes (**1a-d**) in methylene chloride to give the alkoxycarbene salts (**2a-d**).<sup>12,13</sup>



All four products were isolated at room temperature in 80-90% yields as stable, yellowish solids, although **2a,b** were hydrolyzed slowly in air. Spectroscopic data, particularly the diagnostic <sup>1</sup>H NMR carbene proton absorptions at low downfield positions,<sup>9a,11</sup> and analytical evidence agree with

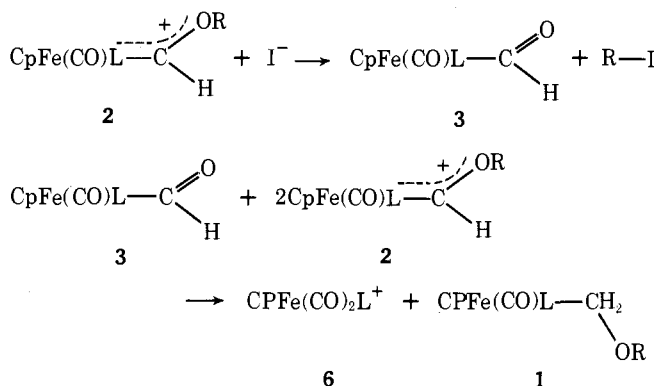
the proposed structures.<sup>14,15</sup> The phosphine alkoxy-carbene salts (**2c,d**) are stable as solutions in dry acetone, nitromethane, methylene chloride, and trifluoroacetic acid; whereas solutions of the dicarbonyl analogues **2a,b** decompose rapidly in acetone and slowly in nitromethane to mixtures of  $\text{CpFe}(\text{CO})_3^+$  and  $\text{CpFe}(\text{CO})_2\text{CH}_3$ . Similar replacement of a carbonyl ligand by a phosphine enhances the stability of iron benzylidene complexes,<sup>11</sup>  $\text{CpFe}(\text{CO})\text{L}(\text{CHPh})^+$ , and tertiary iron hydroxy- and alkoxy-carbene salts,<sup>16</sup>  $\text{CpFe}(\text{CO})\text{L}\{\text{C}(\text{OR})\text{CH}_3\}^+$  (R = H, Me, Et).

Dealkylation of the alkoxy-carbene salts (**2**) with iodide was investigated as a synthetic approach to  $\eta^1$ -formyl complexes,  $\text{CpFe}(\text{CO})\text{L}(\text{CHO})$  (**3**). The control for this approach was the iodide displacement of iron acetyl complexes,  $\text{CpFe}(\text{CO})\text{L}(\text{COCH}_3)$  (**5a,b**), from the tertiary methoxy-carbene salts,  $\text{CpFe}(\text{CO})\text{L}\{\text{C}(\text{OCH}_3)\text{CH}_3\}^+\text{PF}_6^-$  (**4a,b**).<sup>16</sup>  $\text{Ph}_3\text{PMe}^+\text{I}^-$  in methylene chloride at room temperature cleanly converts, as demonstrated via IR and  $^1\text{H}$  NMR monitoring, **4** to **5** plus methyl iodide. Analogous treatment of **2**, however, affords equimolar mixtures of an iron carbonyl compound (**6**), an alkoxy-methyl complex (**1**), and an alkyl iodide. Excess iodide



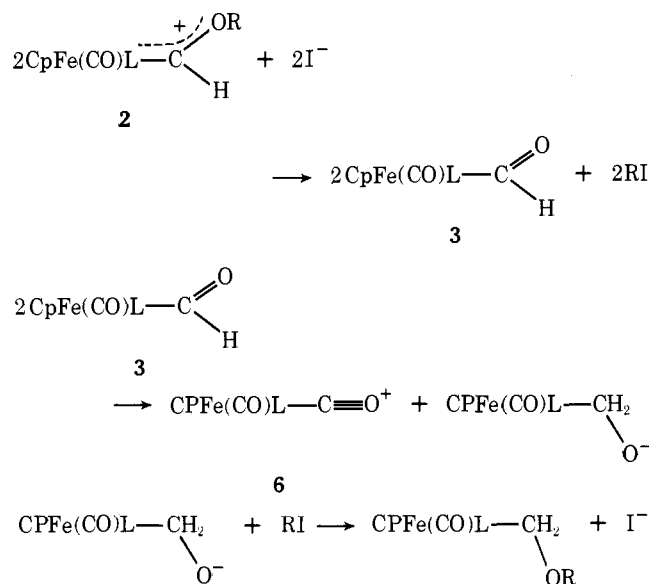
consumes **2a-c** within 1 h, but **2d** has a half-life of at least 12 h. Iodide also undergoes reaction with  $\text{CpFe}(\text{CO})_3^+$  (**6a**), but not **6b** (L =  $\text{Ph}_3\text{P}$ ), to produce  $\text{CpFe}(\text{CO})_2\text{I}$ <sup>17</sup> in a slower step. Accordingly, only 0.5 equiv of iodide was necessary to consume the phosphine methoxy-carbene salt (**2c**).

Formyl complexes (**3**) initially derived by iodide displacement from alkoxy-carbene salts (**2**) may be responsible for the dealkylation products. Rapid hydride transfer from these formyl complexes (**3**)<sup>18</sup> to unaltered **2** then accounts for the observed products.



An alternative mechanism requiring quantitative dealkylation of **2** to its formyl complex (**3**), followed by **3** both donating and accepting hydride,<sup>18</sup> was eliminated.

This mechanism also agrees with the limiting stoichiometry observed for the iodide reaction with **2c**, but it is inconsistent with the general lack of reactivity of acetyl complexes (**5a,b**) toward nucleophilic hydride donors.<sup>19</sup> Two other observations also favor alkoxy-carbene salts (**2**) rather than formyl complexes (**3**) as hydride acceptors: (1) An equimolar mixture of **2c** and **2d** undergoes a reaction with excess iodide, under conditions where **2d** does not dealkylate, and produces a mixture of the alkoxy-methyl complexes, **1c** (29%) and **1d** (71%). (2) Treatment of the ethoxy-carbene salt (**2b**) with  $\text{Ph}_3\text{PMe}^+\text{I}^-$  and excess methyl iodide affords the ethoxymethyl complex



(**1b**) in 93% yield, with no trace of the methoxymethyl complex (**1a**).

The hydride-accepting capability of the alkoxy-carbene salts (**2**) was investigated further by examining their reactions with 1 equiv of  $\text{Ph}_3\text{PMe}^+\text{BH}_4^-$  in methylene chloride. Thus, **2b** gives a 3:1 mixture of the ethoxymethyl (**1b**) and methyl,  $\text{CpFe}(\text{CO})_2\text{CH}_3$ , complexes, and **2c** quantitatively affords the corresponding methyl complex,  $\text{CpFe}(\text{CO})(\text{Ph}_3\text{P})\text{CH}_3$ . Diborane derived as a byproduct from the borohydride reduction of **2** to **1** presumably converts the alkoxy-methyl groups to methyl ligands, since 2 equiv of  $\text{BH}_3\cdot\text{SMe}_2$  in dichloromethane quantitatively transforms **1c** into its methyl complex,  $\text{CpFe}(\text{CO})\text{Ph}_3\text{P}(\text{CH}_3)$ . A similar dichotomy of products from treatment of the tertiary alkoxy-carbene salt (**4b**) with borohydride has been reported.<sup>16c</sup> In agreement with our proposed mechanism, alkoxy-carbene salts (**2**) serve as more efficient hydride acceptors than the corresponding carbonyl compounds (**6**). Equimolar mixtures of **2b** or **2c** and its corresponding carbonyl compound **6a** or **6b** react with up to 1 equiv of borohydride exclusively at **2b** or **2c**. Additional borohydride subsequently reduces **6a** or **6b** to their reported products,  $\text{CpFe}(\text{CO})_2\text{H}/\{\text{CpFe}(\text{CO})_2\}_2$  or  $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_2\text{Ph}_3\text{P}$ , respectively.<sup>20</sup>

With the availability of secondary alkoxy-carbene compounds (**2**), a detailed investigation of the reactivity associated with the alkoxy-carbene ligands has been implemented. Thus far, coordinated alkoxy-carbenes have been reduced to alkoxy-methyl and methyl ligands under a variety of conditions. A similar sequence of coordinated ligand reactions may be involved on some metal surfaces or homogeneous catalysts, in which secondary hydroxy-carbene ligands (formed by hydrogenation of bound CO)<sup>2</sup> are further hydrogenated to methanol or methane via hydroxymethyl or methyl ligands. Results of this study are also consistent with the intermediacy of neutral  $\eta^1$ -formyl complexes (**3**) during the iodide dealkylation of **2a-c**, although we have been unable to find appropriate low-temperature conditions at which the formyl complexes can be simultaneously generated and detected. These formyl complexes decompose to carbonyl compounds (**6**), evidently by transferring hydride to alkoxy-carbene compounds (**2**) present. Iron hydride complexes,  $\text{CpFe}(\text{CO})\text{L}(\text{H})$ , which would have resulted from an anticipated CO elimination from the formyl complexes, were not detected.<sup>8a</sup> Work is in progress on preparing secondary alkoxy-carbene complexes of the heavier transition metals.

**Acknowledgment.** Support from the Research Corporation and Wesleyan University is gratefully acknowledged.

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- (14) **2a**: IR (CH<sub>3</sub>NO<sub>2</sub>)  $\nu_{C=O}$  2085, 2043 cm<sup>-1</sup>; <sup>1</sup>H NMR (CF<sub>3</sub>CO<sub>2</sub>H)  $\delta$  12.88 (s, 1, FeCH), 5.55 (s, 5, Cp), 4.73 (s, 3, CH<sub>3</sub>). **2b**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{C=O}$  2082, 2042 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>)  $\delta$  13.24 (s, 1, FeCH), 5.65 (s, 5, Cp), 4.97 (q, J = 7.0 Hz, 2, CH<sub>2</sub>), 1.59 (t, J = 7.0 Hz, 3, CH<sub>3</sub>). Anal. Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>FePF<sub>6</sub>: C, 31.61; H, 2.92. Found: C, 31.82; H, 3.12. **2c**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{C=O}$  1995 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  13.50 (br s, 1, FeCH), 7.65 (s, 15, Ph<sub>3</sub>P), 5.28 (d, J = 1.5 Hz, 5, Cp), 4.09 (s, 3, CH<sub>3</sub>). Anal. Calcd for etherate C<sub>30</sub>H<sub>34</sub>O<sub>3</sub>FeF<sub>6</sub>P<sub>2</sub>: C, 53.43; H, 5.08. Found: C, 53.13; H, 4.81. **2d**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{C=O}$  1990 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  13.67 (d, J = 1.5 Hz, 1, FeCH), 7.70 (s, 15, Ph<sub>3</sub>P), 5.32 (d, J = 1.5 Hz, 5, Cp), 4.40 (m, 2, CH<sub>2</sub>), 1.06 (t, J = 7.0 Hz, 3, CH<sub>3</sub>). Anal. Calcd for C<sub>27</sub>H<sub>26</sub>O<sub>2</sub>FeF<sub>6</sub>P<sub>2</sub>: C, 52.79; H, 4.27. Found: C, 53.02; H, 4.49.
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## Water-Soluble Polyphosphazenes as Carrier Molecules for Iron(III) and Iron(II) Porphyrins<sup>1,2</sup>

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**Abstract:** The water-soluble poly(aminophosphazenes) [NP(NHCH<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**1**) and [NP(NHCH<sub>3</sub>)<sub>x</sub>(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>y</sub>]<sub>n</sub> (**2**) (containing the 3-(1-imidazolyl)propylamino group) have been investigated as polymeric "carrier" ligands for iron(III) and iron(II) protoporphyrin IX. In the presence of aqueous polymer **1**, hemin or heme exists as hematin-hemin hydroxide or bisaquoheme, respectively, with only weak (probably acid-base) binding between the polymer and the metalloporphyrin. However, polymer **2** binds strongly to both heme and hemin via the imidazole residues. In aqueous solution or as solid films, the presence of the polymeric ligands did not prevent the irreversible oxidation of heme on contact with oxygen. Polymer-heme complexes of polymers **1** and **2**, including the CO and oxidized complexes, were characterized by electronic absorption and Mössbauer spectroscopy. Although the Mössbauer data confirmed that Fe(II) oxidation occurred on contact with O<sub>2</sub>, the electronic spectra were compatible with reversible dioxygen binding. The apparent "dioxygen cycling" in the solid state was attributed to oxidation of Fe(II) by dioxygen, followed by reduction of the Fe(III) by the polymer or, in some cases, by residual reducing agent.

In this paper we report the synthesis of a new, high polymeric, water-soluble carrier molecule (**2**) for the binding of metalloporphyrins, and the behavior of this polymer as a

coordination ligand for hemin and heme in aqueous solution and in the solid state. The behavior of polymer **2** as a ligand is compared to that of the related macromolecule, **1**. The re-