Lewis Acid Assisted Reactions of *N*-Acylimidazoles with Transition-Metal Nucleophiles. A Route to Formyl Transition-Metal Complexes[1a]

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Lewis acid assisted acylations of $Na_2M(CO)_4$ complexes (M = Fe, Ru, Os) by *N*-acylimidazoles have been investigated, and *N*-formyl- (**1**), *N*-acetyl- (**6**), *N*-pivaloyl- (**7**), and *N*-benzoylimidazole (**8**) have been examined as acyl transfer agents. The yields of $NaFe(CO)_4CHO$ on treatment of $Na_2Fe(CO)_4$ with **1** were found to be dependent upon the types of solvent and Lewis acid employed. Optimum yields were obtained in HMPA by using 2 equiv of $(MeO)_3B$/equiv of **1**. THF and *N*-methylpyrrolidinone could also be employed as solvents. These reaction conditions enabled the in situ synthesis of the new anionic formylmetal complexes $NaRu(CO)_4CHO$ and $NaOs(CO)_4CHO$. The $NaM(CO)_4CHO$ complexes and $NaFe(CO)_4COPh$ were characterized in solution by NMR and infrared spectroscopy. $[PPN]Fe(CO)_4COCH_3$ and $[PPN]Fe(CO)_4CO$-*t*-Bu have been isolated by treatment of the $NaFe(CO)_4COR$ product mixtures with PPNCl. Acylations of $Na_2M(CO)_4$ complexes by **1** and **6** occurred only in the presence of a Lewis acid. In the absence of a Lewis acid, **1** was decarbonylated to afford $NaM(CO)_4H$ and sodium imidazolate and **6** underwent a Claisen-type condensation. Sodium imidazolate also caused the decarbonylation of **1** and the self-condensation of **6**. **7** and **8** acylated $Na_2Fe(CO)_4$ in both the presence and the absence of R_3B Lewis acids. The results of the study show that the Lewis acid scavenges the sodium imidazolate byproduct, prohibiting its promotion of the decarbonylation of **1** and the enolization of **6**. The Lewis acid also appears to increase the susceptibility of the *N*-acylimidazole to nucleophilic attack at the acyl carbon.

Introduction

Transition-metal formyl complexes have been proposed as reactive intermediates in the homogeneous hydrogenation of CO[2] and in ligand substitutions in transition-metal carbonyl hydrides.[3,4] Such postulations have led to syntheses of formylmetal complexes in efforts to study their structures and chemistry and to examine their relevance to these types of processes.

A convenient and efficient synthetic route to acyl transition-metal compounds is via attack of transition-metal nucleophiles on acyl halides.[5,6] This method is not useful for formyl group transfer reactions because of the thermal instability[7,8] and/or difficulty of synthesis and handling[9,10] of formyl halides. Prior to the initiation of this investigation, only one example of the synthesis of a formyl complex via nucleophilic attack on an organic substrate had been reported.[11] This method employed acetic formic anhydride as the organic substrate and provided the first kinetically stable formylmetal complex. Acetic formic anhydride is not a transition-metal formylating agent of general utility, and attempts to synthesize formyl complexes by reaction of this substrate with other nucleophilic transition-metal compounds have been unsuccessful.[12,13] Syntheses of well-characterized formyl transition-metal complexes via direct synthetic routes have included three other approaches: (1) hydride transfer to a metal-bonded carbonyl ligand;[12,14] (2) oxidative addition of formaldehyde to a transition-metal complex;[15] (3) insertion of CO into a metal–hydrogen bond.[16]

N-Acylimidazoles and their activated analogues efficiently transfer acyl groups to nucleophilic substrates.[17-20] The electrophilicity of this class of compounds has been ascribed to the electron-withdrawing effect of the imidazole ring.[17] Recent work in this laboratory[1a] has established that acyl group transfer can be accomplished by the reaction of certain *N*-acylimidazoles with disodium tetracarbonylferrate in the presence of Lewis acids. Background studies were conducted on disodium tetracarbonylferrate since the expected product complexes had previously been synthesized and characterized.[5,11,12] We have examined the acyl transfer reaction with a variety of *N*-acylimidazoles to provide a correlation between sub-

(1) (a) Taken from the Ph.D. dissertation of P. A. Kongshaug, University of North Dakota, 1984. Some of these results were reported in a preliminary communication: Kongshaug, P. A.; Haugen, K. R.; Miller, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 627. (b) Present address: Department of Chemistry, Wabash College, Crawfordsville, IN 47933. Send correspondence to this address.

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Table I. Comparative Data for the Formyl Complexes $NaM(CO)_4CHO$ (M = Fe (5a), Ru (5b), Os (5c))

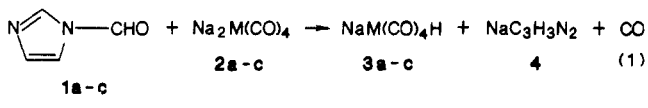
complex	% yield[a]	infrared,[b] cm^{-1} ligand CO	infrared,[b] cm^{-1} formyl CO	^1H NMR[c]	^{13}C NMR
5a	80	2017 (w) 1930 (s) 1903 (vs)	1577 (w)	14.72	257.1, 220.9[c]
5b	46	2072 (w) 1987 (s) 1952 (s)	1586 (w)	14.98	251.6, 212.6[d]
5c	79	2027 (w) 1938 (m) 1903 (s)	1581 (w)	16.25	227.4, 197.9[c]

[a] From reaction of $Na_2M(CO)_4$ (M = Fe, Ru, Os) with *N*-formylimidazole and 2 equiv of $(MeO)_3B$ in HMPA; yield calculated relative to added CH_2Cl_2 internal standard. [b] In THF, 0.1-mm NaCl solution cell. [c] In HMPA, ppm units relative to Me_4Si; recorded at 25 (^1H) and 34 °C (^{13}C). [d] In HMPA, recorded at 10 °C.

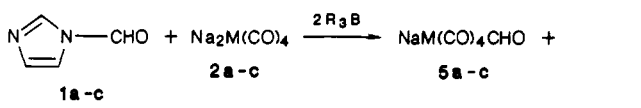
strate structure and reactivity. The effects of different Lewis acids on the extent of the formylation/acylation reactions have been examined, and the role of the Lewis acid in the determination of the outcome of these reactions has been sought.

Results

N-Formylimidazole[21] (1) reacts with compounds of the type $Na_2M(CO)_4$ (2) (M = Fe, Ru, Os) in THF and HMPA with immediate CO evolution to afford, in high yield, $NaM(CO)_4H$ (3) and sodium imidazolate (4) (eq 1). This



a, M = Fe
b, M = Ru
c, M = Os



a, M = Fe
b, M = Ru
c, M = Os

behavior differs markedly from that of carbocyclic aromatic and of aliphatic aldehydes. They have been shown to afford ester products and aldol condensation products, respectively, on treatment with $Na_2Fe(CO)_4$.[22] In addition to transition-metal anions, other bases such as 4 and lithium dimethylamide decarbonylate 1.

Remarkably, the presence of certain Lewis acids diverts the course of the reaction toward formation of formylmetal complexes, at the expense of the decarbonylation reaction (eq 2). We report herein the details of our studies of these reactions and our extension of the investigation to other *N*-acylimidazoles.

Lewis Acid Assisted Reactions of *N*-Formylimidazole with $Na_2M(CO)_4$ Complexes. Treatment of solutions of $Na_2Fe(CO)_4$ (2) with *N*-formylimidazole (1) and trimethoxyborane ($(MeO)_3B$:1 = 2:1) afforded $NaFe(CO)_4CHO$ (**5a**) in yields of 80% (HMPA), 70% (NMP), and 55% (THF), most of the remaining iron product being present as $NaFe(CO)_4H$ (**3a**). The yields of **5a** were dependent upon the type of Lewis acid employed and on the 1:Lewis acid ratio, decreasing as the Lewis acid strength of the boron component increased. While triethylborane was moderately effective in promoting formation of **5a** from 1 and 2, $AlCl_3$, BF_3, and BBr_3 caused the decarbonylation of 1. Optimum yields of **5a** were obtained with a $(MeO)_3B$:1 ratio of 2:1.

The analogous reactions of ruthenium and osmium compounds **2b** and **2c**, respectively, with 1 and $(MeO)_3B$ (2:1:$(MeO)_3B$ = 1:1:2) were examined. NMR analyses of these product mixtures indicated, in each case, that the formylmetal complex **5b** or **5c** and the hydridometal compound **3b** or **3c** accounted for most of the transition-metal product species and the highest yields of **5b** and **5c** were afforded in HMPA (Table I). Conversely, THF solvent provided the lowest yields of **5b** and **5c** (14% and 24%, respectively).

The reactions of compounds 2 with 1 and $(MeO)_3B$ to generate 3 and 5 were complete within a few minutes at room temperature. The products 5 then gradually decarbonylated in solution to form products 3 and CO. To our knowledge, complexes of the type 5 possessing the Na^+ counterion have never been isolated, conversion of **5a** to the PPN salt being required.[11,12] Our attempts to isolate the PPN analogues of products 5 from HMPA have been unsuccessful. The presence of three anionic products in each experiment and the fact that the PPN salts of anionic formylmetal complexes have previously been isolated in experiments conducted in THF[12]—the solvent which has provided our lowest yields of 5—have contributed to product isolation problems. Our products, 5, have, however, been unambiguously characterized in solution by spectroscopic methods (Table I). Further support for our contention that $1/(MeO)_3B$ reacts with compounds 2 to afford acylmetal products is provided by experiments involving treatment of **2a** with other *N*-acylimidazoles, followed by isolation of the PPN^+ salts of the anionic products.

Reactions of Alkyl and Phenyl *N*-Acylimidazoles with 2a. Treatment of *N*-acetyl- (6), *N*-pivaloyl- (7), and *N*-benzoylimidazole (8) with **2a** in presence of $(MeO)_3B$ at room temperature resulted in the rapid formation of the corresponding acyliron products 9, 10, and 11. Solution samples of each product were prepared independently by treatment of 2 with the corresponding acyl chloride,[5] and the NMR and infrared spectral properties of the acyliron products were found to be essentially identical with those derived from the *N*-acylimidazole reactions. Products 9 and 10, prepared by treatment of 6 and 7, in the presence of $(MeO)_3B$, with **2a** in THF could be converted to the PPN salts on treatment with PPNCl and isolated as such (eq 3). Siegl and Collman reported the syntheses of 9 and 11 that were characterized only by infrared data without reference to the medium employed for the measurements.[5] The pivaloyliron compound 10 and its PPN analogue have not been previously reported. The PPN analogues of 9 and 10 were prepared independently by treatment of the acyl

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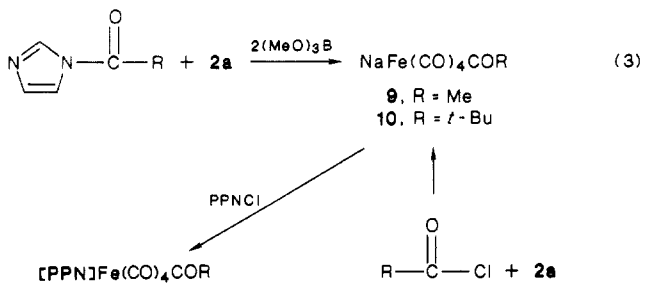

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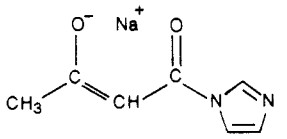
chloride–**2a** product in THF with PPNCl and isolation of the PPN acyliron salt. The NMR and infrared spectral properties of the isolated PPN salts derived from the *N*-acylimidazole and acyl chloride routes were the same.

When **2a** was treated with **6** in the *absence* of a Lewis acid, a condensation product, **12**, was formed (89% yield when **2a**:**6** = 1:2), accompanied by an equimolar mixture of **3a** and imidazole. Compound **12** could be prepared



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independently by treatment of 2 equiv of **6** with NaO-*t*-Bu in *tert*-butyl alcohol (55% yield) and with **4** in THF (95% yield).[17] The spectral properties of these samples compared favorably with the product isolated from the reaction of **6** with compound **2a**. Contrary to results from reactions of **2a** with *N*-formylimidazole and *N*-acetylimidazole, acyl transfer occurred with *N*-pivaloylimidazole (**7**) in the absence of a Lewis acid. Interference from enolization-type reactions was precluded, and a 90% yield of **10** was obtained during 24 h on treatment of **2a** with **7** in HMPA. This reaction time may be compared to the approximate quantitative formation of **10** during a few minutes when a **7**:$(MeO)_3B$:**2a** ratio of 1:2:1 in HMPA was employed. Disodium tetracarbonylferrate (**2a**) reacted with **8** in HMPA and THF, in both the presence and the absence of $(MeO)_3B$ to give the expected benzoyl complex $NaFe(CO)_4COC_6H_5$ (**11**),[5,23] the reaction occurring at a higher rate in the presence of the Lewis acid.

Lewis Acid Control Experiments. A large number of experiments were conducted in an effort to uncover the role of the Lewis acid in these reactions, and spectral evidence for the interaction of $(MeO)_3B$ and Et_3B with potential Lewis bases in the reaction system was sought.

Addition of 2 equiv of $(MeO)_3B$ to HMPA solutions of **2a** did not change the M–*CO* stretching frequency (1732 cm^{-1} (vs)) or the ^{13}C resonance position (δ 234.0). The ^1H and ^{13}C NMR resonances of $NaFe(CO)_4H$ were unshifted by the addition of 1 equiv of $(MeO)_3B$ (δ–8.87 and 222.0, respectively). The carbonyl absorption bands of $KFe(CO)_4H$ were similarly unaffected by the presence of 2 equiv of $(MeO)_3B$ (1882 (vs), 1906 (s), and 1997 cm^{-1} (m)).

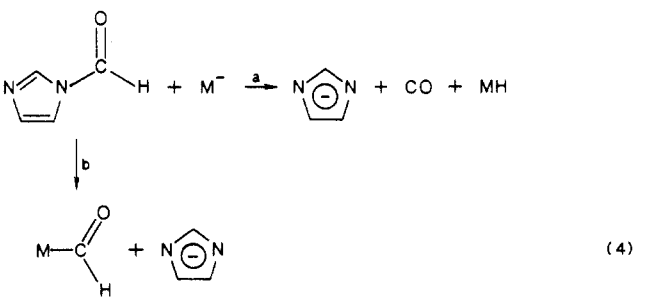
The absence of a variable-temperature dependence of the ^{13}C NMR resonances[2f,24] of $NaFe(CO)_4CHO$ in the presence of $(MeO)_3B$ indicated the noninteraction of $(MeO)_3B$ with the formyl complex under our reaction conditions. It was also observed that the various acyliron complexes exhibited identical NMR shifts and carbonyl stretching frequencies, whether $(MeO)_3B$ was present or not, and the spectral data were independent of whether the complexes were prepared by reaction of the tetracarbonylmetalate anion with the corresponding acid chloride or with the *N*-acylimidazole and $(MeO)_3B$.

A Lewis acid should complex with *N*-acylimidazoles either through the carbonyl oxygen or through the pyridinyl nitrogen[25] of the imidazole ring. Such Lewis acid–base interactions would be evidenced by shifts in NMR resonances and/or infrared carbonyl stretching frequencies. A large number of control experiments were performed to determine the extent of such interactions. Particular attention was given to $(MeO)_3B$ since this Lewis acid was the most effective in assisting acyl transfer reactions. Within the margin of experimental error, $(MeO)_3B$ did not induce any shift in the carbonyl stretching frequency of the *N*-acylimidazoles in THF. The stronger Lewis acid, Et_3B, did, however, induce *increases* in the carbonyl stretching frequencies ranging from 12 to 24 cm^{-1}. This implies that complexation of Et_3B was occurring primarily through the imidazole nitrogen and not with the carbonyl oxygen.[26,27] The ^1H and ^{13}C NMR chemical shifts of *N*-acylimidazoles in HMPA were unaffected by $(MeO)_3B$, while Et_3B caused downfield ^1H shifts.[28]

Sodium imidazolate (**4**) was the only imidazole species for which spectral data showed complexation with $(MeO)_3B$. By itself, **4** was insoluble in THF. However, it readily dissolved upon addition of either $(MeO)_3B$ or Et_3B, and an upfield shift in the $(MeO)_3B$ ^1H signal occurred. The signal was at δ 3.37, 3.10, and 3.00 for $(MeO)_3B$ alone, 1 equiv of $(MeO)_3B$ with **4**, and 2 equiv with **4**, respectively. The adducts that formed between **4** and either Et_3B or $(MeO)_3B$ were both relatively stable.

Discussion

Our results are consistent with an interpretation in which the tetracarbonylmetalate anion acts as both a base and as a nucleophile in its reactions with *N*-acylimidazoles. In the absence of an appropriate Lewis acid, nucleophilic substitution cannot compete with the acid–base reactions that lead to decarbonylation of **1** and enolate formation in **6**. Clearly, bases other than compounds **2** can participate in these acid–base reactions. It seems reasonable, however, that the strongest base in the system should be most effective and the quantitative reaction of **2a** with imidazole to afford **3a** and **4**[1a] has demonstrated that **2a** is the strongest base in our iron-based system. The competing reaction paths for **1** and transition metal base/nucleophiles are described in eq 4. The driving force for path



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a would be the generation of the resonance-stabilized imidazolate ion and the stable CO molecule. We believe that the role of the Lewis acid in diverting the course of the reaction from decarbonylation of **1** to nucleophilic substitution, route b, is twofold. (1) The Lewis acid acts as a scavenger of the imidazolate anion that has been dem-

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onstrated to catalytically decarbonylate 1.[1a] It is interesting that the few previous reports of nucleophilic substitution reactions of 1 employed protionucleophiles such as H_2O, CH_3OH, and primary and secondary amines.[17,21] Imidazole would be the leaving group in these reactions, thus avoiding the generation of imidazolate ion and the subsequent catalytic decarbonylation of 1. (2) The Lewis acid enhances the susceptibility of *N*-acylimidazoles to nucleophilic attack. Evidence for this conclusion is found in the large observed rate enhancement by $(MeO)_3B$ in the reactions of *N*-pivaloylimidazole and *N*-benzoylimidazole with **2**, reaction systems where an acid–base option is precluded.

Experimental Section

General Techniques. All experimental manipulations were performed either in a Vacuum Atmospheres drybox or by standard Schlenk techniques under an argon atmosphere. All transition-metal complexes were stored under argon. Solvents were deoxygenated by either three freeze–pump–thaw cycles or distillation under an inert-gas atmosphere. Liquids were transferred via syringe or transfer-needle through rubber septa or three-way stopcocks.

Materials. Tetrahydrofuran (Aldrich) was used as received (Gold Label 99.9%) or was distilled from $LiAlH_4$ and degassed prior to use (Gold Label 99.5%). Diethyl ether, pentane, and hexane were dried over $LiAlH_4$ and distilled. Methylene chloride and acetonitrile were distilled from phosphorus pentoxide. Benzene, toluene, and dioxane were purified by distillation from sodium benzophenone ketyl. Hexamethylphosphoramide, HMPA, and *N*-methylpyrrolidinone, NMP, were purified by heating 2 days over CaH_2 followed by distillation into 4A molecular sieves under reduced pressure.

Potassium hydride was purchased from Aldrich as a 35% dispersion in mineral oil. Sodium hydride, triethylborane, and lithium dimethylamide were obtained from Ventron Division of Alfa Products and were used as received. Trimethoxyborane and boron tribromide were purified by distillation under dry Ar. Acetyl chloride and benzoyl chloride were distilled and degassed prior to use. Pivaloyl chloride was prepared from pivalic acid according to the method in Beilstein.[29] Formic acid and bis(triphenylphosphine)nitrogen(1+) chloride were purchased from Aldrich and used as received. *N,N'*-Carbonyldiimidazole (Aldrich) was used as received while imidazole and benzophenone were sublimed twice. Other imidazole derivatives, *N*-acetyl,[30,31] *N*-pivaloyl,[28,32] and *N*-benzoyl,[33,34] and the sodium salt[35] were synthesized according to published procedures and were characterized by their infrared and NMR spectra.

Disodium tetracarbonylferrate(II)–sesquidioxane[36] was purchased from Ventron and used as received or was synthesized by the method of Fink and Sorrell.[37] Iron pentacarbonyl (Ventron) was stored at 5 °C and filtered prior to use. Triosmium and triruthenium dodecacarbonyls (Strem) were used as received. Disodium tetracarbonylruthenate and -osmate were synthesized according to published procedures.[38]

Equipment. ^1H and ^{13}C NMR spectra were recorded on Varian EM-390 and JEOL FX-60 instruments, respectively. All resonances are reported in δ (ppm) relative to Me_4Si internal standard. ^{13}C NMR samples in nondeuteriated solvents were run in coaxial NMR tubes, the inner tube of which was sealed and contained D_2O. A Nicolet MX-S FT spectrometer was used to record infrared spectra. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Product Yields. Yields of $NaM(CO)_4CHO$ and $NaM(CO)_4H$ products were determined in situ by comparisons of ^1H resonance integrations with those of CH_2Cl_2 or $CHClCCl_2$ internal standards, introduced after the reactions were complete. Control experiments established that neither the $NaM(CO)_4CHO$ nor the $NaM(CO)_4H$ products reacted with these internal standards in the product solutions during time periods well in excess of the intervals required for peak integrations. The sum of the ^1H integrations of $NaMCHO(CO)_4$ plus $NaM(CO)_4H$ and that of the CH_2Cl_2 or $CHClCCl_2$ remained constant for several hours. Material balances could also be verified internally. Since product mixtures in HMPA and NMP were homogeneous, it could be determined from ^1H and ^{13}C spectra that the reactants were completely consumed. Integrations of the MCHO and MH resonances relative to the product imidazolate ring ^1H resonances afforded yield values similar to those from use of CH_2Cl_2 or $CHClCCl_2$ internal standards.

***N*-Formylimidazole (1).**[21] Addition of a THF solution (60 mL) of formic acid (2.0 mL, 53 mmol) to a stirred solution of *N,N'*-carbonyldiimidazole (6.61 g, 41 mmol) in 100 mL of THF afforded gradual evolution of carbon dioxide. Solvent was removed under reduced pressure after stirring 2 h, and sublimation onto a cold-finger probe afforded the product as white needles. Two additional sublimations gave a crystalline product with an imidazole impurity of 3–10%. A product with an imidazole impurity of ca. 0.8% was obtained by extraction of the sublimed material with hexane and subsequent recrystallization in a −20 °C bath: ^1H NMR ($CDCl_3$) δ 9.18 (s, 1), 8.17 (s, 1), 7.51 (s, 1), 7.15 (s, 1); ^{13}C NMR ($CDCl_3$) δ 157.2, 137.2, 132.1, 115.1; IR (THF) 1740 cm^{-1} (s) (acyl C=O).

In addition to its moisture sensitivity, the material was found to be somewhat thermally unstable as well. Slight decarbonylation was observed to occur in samples stored at room temperature under argon for more than 1 week at a time. For this reason, samples of 1 were stored at −5 °C under a dry inert atmosphere and were generally repurified by sublimation after approximately 3-month storage.

Reactions of 1 with Disodium Tetracarbonylferrate(II)–Sesquidioxane (2a) in the Presence of $(MeO)_3B$. An HMPA solution (1.5 mL) of **2a** (244 mg, 0.710 mmol) was treated with a mixture of freshly sublimed 1 (68 mg, 0.71 mmol, containing ca. 3% imidazole impurity) and $(MeO)_3B$ (161 μL, 1.42 mmol) in HMPA (0.5 mL). The orange-brown solution turned red-brown on stirring 10 min. There was no visible gas evolution. ^1H NMR integration relative to a CH_2Cl_2 internal standard (91 μL, 1.42 mmol; δ 5.83) indicated a yield of **5a** (δ 14.72) of 81%, the remainder of the iron being present as **3a** (^1H NMR δ −8.85; ^{13}C NMR δ 222.0). In separate identical experiments employing 1 with up to 10% imidazole impurity, yields of **5a** were determined to be 74% and 75% relative to internal integration standards $ClCHCCl_2$ (δ 7.90) and CH_2Cl_2, respectively. The imidazolate product resonance peaks appeared at δ 7.70, 7.55, 6.92, and 6.73. Off-resonance decoupling converted the **5a** formyl ^{13}C resonance into a doublet. Experiments in NMP and THF were conducted in an analogous manner.

Spectral Comparison of an Authentic Sample of Formyliron Complex. A sample of $[PPN]Fe(CO)_4CHO$ (270 mg, 0.370 mmol), prepared by the method of Winter et al.[39] (^1H NMR (HMPA) δ 14.68 (s, 1); ^{13}C NMR (HMPA) δ 257.1, 220.9) was treated with sodium imidazolate (33 mg, 0.37 mmol) and Et_3B (52 μL, 0.37 mmol) in HMPA (1.5 mL), and the solution was analyzed: ^1H NMR δ 14.72 (FeCHO), −8.79 (FeH from partial decarbonylation of FeCHO); ^{13}C NMR δ 257.1, 220.9, 222.0 (FeH).

Reactions of 1 with Disodium Tetracarbonylosmate(II) (2c) in the Presence of $(MeO)_3B$. (a) Treatment of an HMPA solution (1 mL) of **2c** (247 mg, 0.710 mmol) with an HMPA solution (1 mL) of 1 (68 mg, 0.71 mmol) and $(MeO)_3B$ (161 μL, 1.42 mmol) caused the greenish yellow solution to quickly turn

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yellow. The reaction mixture was stirred 30 min and CH_2Cl_2 (91 μL, 1.42 mmol) added. ^1H NMR analysis indicated the formation of $NaOs(CO)_4CHO$ (**5c**) in 79% yield and $NaOsH(CO)_4$ in 18% yield (−10.22 ppm). The ^{13}C NMR sample of **5c** was subjected to off-resonance decoupling, and the low-field ^{13}C resonance (227.4 ppm) was split into a doublet.

(b) Treatment of an orange NMP solution (0.5 mL) of **2c** (125 mg, 0.360 mmol) with an NMP solution (0.25 mL) of **1** (35 mg, 0.36 mmol) and $(MeO)_3B$ (82 μL, 0.72 mmol) resulted in the solution gradually turning yellow over a period of 15 min. Methylene chloride (46 μL, 0.72 mmol) was added, and the solution was analyzed by ^1H NMR. Integration revealed that **5c** was formed in 56% yield (δ 16.25) and $NaOs(CO)_4H$ in 19% yield (δ −10.22).

Reactions of 1 with Disodium Tetracarbonylruthenate(II) (2b) with $(MeO)_3B$ Present. Rapid addition of an HMPA solution (0.25 mL) of **1** (35 mg, 0.36 mmol) and $(MeO)_3B$ (82 μL, 0.72 mmol) to a solution (0.5 mL) of **2b** (93 mg, 0.36 mmol) resulted in rapid gas evolution. The red solution lightened in color upon stirring 20 min. Methylene chloride (46 μL, 0.72 mmol) was added as an internal integration standard. ^1H NMR integration revealed the formation of $NaRu(CO)_4CHO$ in 46% yield as well as $NaRu(CO)_4H$ (δ −7.88) in 52% yield. Due to the short lifetime of the ruthenium formyl species at 35 °C ($t_{1/2}$ = 0.9 h) the ^{13}C NMR spectra were recorded at 10 °C. Off-resonance decoupling split the formyl carbon resonance into a doublet.

An analogous experiment in THF afforded products with ^1H NMR: δ 14.96, −7.93.

Syntheses of Independent Samples of Hydridotetracarbonylmetal Complexes. $[PPN]Fe(CO)_4H$, prepared by the method of Darensbourg et al.,[40] exhibited the following spectra: ^1H NMR (HMPA) δ −8.78; ^{13}C NMR (HMPA) δ 222.0; IR (THF) 2005 (m, sh), 1905 (m), 1876 cm^{-1} (s).

The sodium salt of the hydridoiron tetracarbonyl complex was prepared by protonation of **2a** with glacial acetic acid. A stirred solution of **2a** (346 mg, 1.00 mmol) in 2 mL of HMPA was treated with glacial acetic acid (57 μL, 1.00 mmol). The reaction mixture was stirred 10 min and analyzed by NMR spectroscopy. The NMR resonances were unaffected by an added equivalent of $(MeO)_3B$: ^1H NMR (HMPA) δ −8.87; ^{13}C NMR (HMPA) δ 221.9.

$NaRu(CO)_4H$ and $NaOs(CO)_4H$ were prepared by careful protonation of **2b** and **2c**, respectively, with glacial acetic acid in either HMPA or THF. $NaOs(CO)_4H$: ^1H NMR (HMPA) δ −10.22, (THF) −10.23, ^{13}C NMR (HMPA) δ 195.4; IR (HMPA) 2010 (s), 1946 (s), 1883 cm^{-1} (vs), (THF) 2012 (m), 1954 (s), 1883 (vs), 1850 cm^{-1} (m) (lit.[41] ^1H NMR (THF) δ −10.24; IR (THF) 2010, 1949, 1881, 1848 cm^{-1}). $NaRu(CO)_4H$; ^1H NMR (HMPA) δ −7.96, (THF) −7.96; ^{13}C NMR (HMPA) δ 201.7, IR (HMPA) 2004 (m), 1927 (s), 1888 cm^{-1} (vs), (THF) 2006 (w), 1930 (s), 1888 (vs), 1860 cm^{-1} (m, sh) (lit. $[PPN]Ru(CO)_4H$:[42] ^1H NMR (acetone-d_6) δ −7.77; IR (THF) 2003, 1925, 1885 cm^{-1}).

Characterization of the Sodium Imidazolate–Trimethoxyborane Adduct. The $(MeO)_3B{\cdot}NaC_3H_3N_2$ adduct afforded in the reactions of **2** with *N*-acylimidazoles and $2(MeO)_3B$ was identified by its ^1H and ^{13}C spectra by comparison with an authentic sample, prepared by treatment of **4** (0.500 g, 5.46 mmol) with 2 equiv of $(MeO)_3B$ (10.92 mmol) in THF (12 mL). The latter product (white solid) could be isolated after removal of solvent in vacuo: ^1H NMR (HMPA) δ 7.66 and 6.88 in 2:1 ratio with minor peaks at δ 7.51 and 6.73, major to minor in 6:1 ratio; ^{13}C (HMPA) δ 138.2, 121.4. $(MeO)_3B$ component: ^1H NMR δ 3.05; ^{13}C NMR δ 48.5. THF component: ^1H NMR δ 3.60, 1.80; ^1H integration (Me_2SO-d_6) showed the $(MeO)_3B{:}C_3H_3N_2{:}$THF ratio to be 2:1:0.5. Warming the solid at 52 °C (0.1 mm) for 15 h caused most of the THF to be released. All of the $(MeO)_3B$ was retained. Anal. Calcd for $C_9H_{21}N_2O_6B_2Na$: C, 36.27; H, 7.12; N, 9.40; B, 7.26. Found: C, 36.62; H, 7.13; N, 9.29; B, 7.45.

Reactions of 6 with 2a in the Presence of $(MeO)_3B$. A solution of **6** (156 mg, 1.42 mmol) and $(MeO)_3B$ (324 μL, 2.84 mmol) in HMPA (0.5 mL) was added to a stirred solution of **2a** (491 mg, 1.42 mmol) in HMPA (2 mL). The red-brown solution was stirred for 20 min and then analyzed: ^{13}C NMR (HMPA) δ 258.3 (acyl CO), 221.6 (FeCO), 222.0 ($NaFe(CO)_4H$ byproduct), 138.2, 130.8, 121.3, 119.1 (imidazolate) 51.3 (CH_3), 48.6 ($(MeO)_3B$). Consistent with the formation of $NaFe(CO)_4COCH_3$ and supported by analysis of an HMPA solution (2 mL) of $[PPN]Fe(CO)_4COCH_3$ (vide infra) (532 mg, 0.710 mmol), sodium imidazolate (64 mg, 0.71 mmol), and $(MeO)_3B$ (161 μL, 1.42 mmol): ^{13}C NMR (HMPA) δ 258.0 (acyl CO), 221.6 (FeCO), 134.3, 133.0, 132.6, 132.2, 131.0, 130.6, 129.7, 123.9 (PPN), 51.2 (CH_3), 49.3 $(MeO)_3B$. These data established that the acyl CO and FeCO chemical shifts in HMPA were independent of the counterion.

A suspension of **2a** (244 mg, 0.710 mmol) in THF (1 mL) was treated with a THF solution (1 mL) of **6** (78 mg, 0.71 mmol) and $(MeO)_3B$ (161 μL, 1.42 mmol). The suspension turned brown upon stirring 20 min. The mixture was then filtered, and CH_2Cl_2 (91 μL, 1.42 mmol) was then added to the filtrate. Integration of the ^1H NMR spectrum δ 2.57 (s, CH_3) relative to the CH_2Cl_2 indicated a 77% yield of $NaFe(CO)_4COCH_3$. Other ^1H resonances: δ 6.99, 7.90 (imidazolate in 2:1 ratio), 5.48 (CH_2Cl_2), −8.81 ($NaFe(CO)_4H$, 13% yield); IR (THF) 1582 cm^{-1} (w) (acyl CO).

Synthesis of $[PPN]Fe(CO)_4COCH_3$ from Acetyl Chloride and 2a.[5] A solution of 210 μL (2.95 mmol) of acetyl chloride in THF (5 mL) was added during 17 min to a stirred suspension of **2a** (0.982 g, 2.84 mmol) in THF (10 mL). The reaction mixture gradually turned red-brown upon stirring 1 h. Solid bis(triphenylphosphine)nitrogen(1+) chloride (1.63 g, 2.84 mmol) was then added in small portions. The solvent was removed in vacuo after the solution was stirred for 2 h. The light brown solid residue was dissolved in CH_2Cl_2 (5 mL), the mixture was filtered, and the filtrate was treated with Et_2O (2–3 mL) and then cooled to −20 °C for 12 h. The resultant orange-brown crystals were dried in vacuo for 8 h: 1.348 g, 63% yield; ^1H NMR (THF) δ 7.35–7.70 (m), 2.35 (s); ^{13}C NMR (HMPA) δ 257.6 (acyl CO), 221.6 (FeCO), (134.3, 133.0, 132.6, 132.2, 130.6, 130.2, 129.7, 123.9, PPN), 51.2 (CH_3); IR (THF) 1610 (w) (acyl), 2004 (w), 1909 (m) 1892 (s), 1876 cm^{-1} (s). For comparison, a sample of $[PPN]Fe(CO)_4CHO$ prepared by the method of Winter et al.[39] exhibited the following: ^{13}C NMR (HMPA) δ 257.1, 220.9, 134.2, 133.0, 132.6, 132.1, 131.0, 130.5, 130.0, 129.6, 123.9, 119.3.

Isolation of $[PPN]Fe(CO)_4COCH_3$ from Reaction of 6. A stirred suspension of **2a** (982 mg, 2.84 mmol) in THF (10 mL) was treated with a THF solution (5 mL) of **6** (313 mg, 2.84 mmol) and $(MeO)_3B$ (645 μL, 5.68 mmol) over a 30-min period. The light tan suspension gradually darkened to a reddish brown upon stirring 3.5 h. Solid bis(triphenylphosphine)nitrogen(1+) chloride (3260 mg, 5.68 mmol) was then slowly added in small portions. The solvent was removed in vacuo after stirring overnight. The residue was dissolved in CH_2Cl_2 (6 mL) and filtered into a recrystallizing Schlenk. Ethyl ether (3 mL) was added, and overnight refrigeration at −5 °C induced the formation of small light brown crystals. Further addition of Et_2O (4 mL), at −20 °C, in 1-mL aliquots over a 4-day period, led to the formation of yellowish brown crystals which were washed twice with 10-mL aliquots of 6:7 (v/v) CH_2Cl_2 in Et_2O and dried in vacuo: yield 0.985 g, 46%; ^1H NMR (THF) δ 2.36 (CH_3), 7.35–7.70 (m, PPN); ^{13}C NMR (HMPA) δ 221.5 (FeCO), 134.2, 132.9, 132.1, 130.9, 130.4, 129.5, 123.9 (PPN), 51.0 (CH_3); IR (THF) 2004 (w), 1909 (m), 1892 (m), 1876 (s), 1610 cm^{-1} (w). The acyl CO ^{13}C resonance for this sample was too weak to detect. The infrared spectrum was virtually identical with that of the product from the acetyl chloride route.

Acylation Reactions of 2a with *N*-Pivaloylimidazole (7). **(a)** An HMPA solution (1.5 mL) of **2a** (244 mg, 0.710 mmol) was rapidly treated with **7** (108 mg, 0.710 mmol) in HMPA (0.5 mL). The solution immediately turned a very dark brown. An ^1H NMR sample was taken and intermittently monitored over a period of 24 h. Percent formation of $NaFe(CO)_4COC(CH_3)_3$ (**11**) was calculated from the relative integrations of the methyl resonances of **11** and **7**, the sum of which remained constant. The product yield gradually increased from 20% at a reaction time of 16 min to 90% after 24 h.

(b) An immediate color change, from orange-brown to a dark reddish brown, occurred upon addition of an HMPA solution (0.5 mL) of **7** (108 mg, 0.710 mmol) and $(MeO)_3B$ (161 μL, 1.42 mmol) to a solution (1.5 mL) of **2a** (244 mg, 0.710 mmol). ^1H NMR integration indicated quantitative formation of $NaFe(CO)_4CO$-$C(CH_3)_3$ within 20 min.

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Isolation of [PPN]Fe(CO)$_4$COC(CH$_3$)$_3$. A stirred suspension of **2a** (982 mg, 2.84 mmol) in THF (10 mL) was treated with a solution of **7** (432 mg, 2.84 mmol) and (MeO)$_3$B (645 μL, 5.68 mmol) in THF (5 mL). Upon being stirred overnight, the tan suspension had reacted to afford a brown solution. Bis(triphenylphosphine)nitrogen(1+) chloride (3260 mg, 5.68 mmol) was then slowly added from a solid addition funnel. After the solution was stirred approximately 6 h, the solvent was removed in vacuo and the residue dissolved in excess CH_2Cl_2 (8 mL) and filtered into a recrystallizing Schlenk. The product was precipitated with Et_2O, filtered, redissolved in a minimal amount of CH_2Cl_2 (3 mL), and refrigerated while Et_2O (17 mL) was slowly introduced over a period of 2 weeks. The product (1.993 g, 89% yield), as yellowish brown crystals, had been washed with 30% CH_2Cl_2 in Et_2O and dried in vacuo. The dry salt was moderately stable to air, decomposing only slightly after approximately 3 days: ^{1}H NMR (THF) δ 1.01 (s, 9, CH_3), 7.39–7.63 (m, 30, PPN); ^{13}C NMR (THF) δ 269.5 (acyl CO), 222.3 (FeCO), 134.5, 133.2, 132.8, 131.7, 130.8, 130.4, 129.9, 124.6 (PPN); 56.4 (C), 28.9 (CH_3); IR (THF) 2002 (m), 1909 (s), 1888 (s), 1871 (s), 1597 cm^{-1} (m). These values may be compared to those for [PPN]Fe(CO)$_4$COEt;[5] IR 2005 (m), 1905 (s), 1887 (vs), 1870 (vs), 1612 cm^{-1} (w/m). See data from the acyl chloride synthesis below.

Synthesis of [PPN]Fe(CO)$_4$COC(CH$_3$)$_3$ from Pivaloyl Chloride and 2a. Pivaloyl chloride (350 μL, 2.840 mmol) in THF (5 mL) was gradually added to **2a** (982 mg, 2.84 mmol, in 10 mL of THF) and the reaction mixture stirred 1 h. Bis(triphenylphosphine)nitrogen(1+) chloride (3.260 g, 5.680 mmol) was then slowly added to the dark brown mixture. After being stirred an additional hour, the mixture was filtered into a recrystallizing Schlenk, and the solvent was removed under reduced pressure to yield an oily dark brown residue. This residue was dissolved in a minimal amount of CH_2Cl_2 (5 mL), enough Et_2O added (10 mL) to cause a slight haziness, and the mixture cooled to −20 °C. Additional Et_2O (10 mL) was introduced over the next 3 days to afford clumps of reddish brown crystals, which were washed with fresh Et_2O and vacuum dried 8 h: ^{1}H NMR (THF) δ 1.01 (s, 9, CH_3), 7.40–7.80 (m, 30, PPN); ^{13}C NMR (THF) δ 269.7 (acyl CO), 222.4 (FeCO), 134.5, 133.5, 133.1, 132.8, 131.8, 130.8, 130.3, 129.9, 124.6 (PPN), 56.4 (C), 29.0 (CH_3). Anal. Calcd for $C_{45}H_{39}FeNO_5P_2$: C, 68.27; H, 4.98; Fe, 7.05; N, 1.77. Found: C, 68.01; H, 5.07; Fe, 7.00; N, 1.75.

Acylation Reactions of 2a with *N*-Benzoylimidazole (8). **(a)** A THF solution (1.5 mL) of **8** (122 mg, 0.710 mmol) was slowly added to a stirred suspension of **2a** (244 mg, 0.710 mmol) in THF (1.5 mL). The mixture was stirred for 6 h and filtered and the reddish orange filtrate analyzed. The data indicated the formation of NaFe(CO)$_4$COC$_6$H$_5$ (**11**):[5] ^{1}H NMR δ 7.69 (m, 2), 7.15 (m, 3); ^{13}C NMR δ 276.5 (acyl CO), 220.9 (FeCO), 153.9, 129.4, 127.7; IR (THF) 1560 cm^{-1} (m).

(b) An analogous experiment when (MeO)$_3$B (1.61 μL, 1.42 mmol) was present afforded the following data after 2.5-h reaction time: ^{13}C NMR δ 275.6, 220.9, 154.1, 129.1, 127.5, 48.7 ((MeO)$_3$B); IR 2016 (s), 1925 (s), 1896 (vs, br), 1553 cm^{-1} (m). A sample of **2a** (244 mg, 0.710 mmol) in THF (1.5 mL) was treated with benzoyl chloride (82 μL, 0.710 mmol) in THF (0.5 mL), the mixture was stirred for 1 h and filtered and the filtrate analyzed: ^{1}H NMR δ 7.19, 7.71 (m); ^{13}C NMR δ 277.0, 220.9, 154.1, 129.5, 127.8, 127.6; IR 2015 (s), 1928 (m), 1898 (s, br), 1550 cm^{-1} (m). (An analogous experiment in HMPA afforded: ^{13}C NMR δ 258.9, 221.0.)

Percent Yield of 11 by ^{13}C NMR Integration. Reaction yields of **11** were determined by integration of ^{13}C NMR spectra. Difficulties arise in integrating ^{13}C spectra since metal-bonded carbonyl carbons have unusually long T_1 relaxation times.[43] Small amounts of added paramagnetic compounds can, however, effectively reduce spin-lattice relaxation times without adversely affecting signal resolution.[44] The spectrometer was operated in the "without NOE" pulse mode in order to ensure accurate intensity ratios. Chromium(III) acetylacetonate, Cr(acac)$_3$, was present in 0.5 M concentration. Preliminary integration experiments were conducted on benzophenone alone, benzophenone and acetone, and benzophenone and **11** (from **2a** and benzoyl chloride). The average experimental error in these control experiments was 2.4%. An HMPA solution (0.5 mL of **8** (122 mg, 0.710 mmol)) and (MeO)$_3$B (161 μL, 1.42 mmol) was introduced into a stirred suspension of **2a** (244 mg, 0.710 mmol) in HMPA (0.5 mL). The dark reddish brown solution was stirred 20–30 min and then combined with an HMPA solution (1.0 mL) of benzophenone (129 mg, 0.710 mmol) and Cr(acac)$_3$ (26 mg, 0.075 mmol). The yield was calculated from the relative integrations of the benzophenone acyl resonance and either the acyl or carbonyl resonances of the benzoyliron product. The values from four independent experiments were 57%, 54%, 67%, and 66%, resulting in an average yield of 61%.

Reaction of 1 with 2a in the Absence of a Lewis Acid. A stirred solution (1.5 mL) of **2a** (244 mg, 0.710 mmol) in HMPA was rapidly treated with an HMPA solution (0.5 mL) of **1** (68 mg, 0.71 mmol). The reaction mixture turned black immediately upon addition. This black coloration persisted 2–4 s, after which there was copious gas evolution as the reaction mixture turned light brown. The solution was analyzed after stirring 10 min: ^{1}H NMR δ 7.16, 6.69, −8.84; ^{13}C NMR δ 221.9 (HFeCO), 143.8 and 124.7 (imidazolate). The ^{1}H NMR integration (DMF internal standard) indicated complete decarbonylation and overall material balance. The gaseous product had a GLC retention time identical with that of CO on a 60–80 mesh 5A molecular sieve column operated at 95 °C.

A sample of **1** (30 mg, 0.31 mmol) containing <1% imidazole impurity (by ^{1}H NMR) in HMPA solution (0.5 mL) was added very rapidly to a stirred solution (1.5 mL) of **2a** (107 mg, 0.310 mmol) in HMPA. The reaction mixture immediately turned black. This lasted 15–20 s, after which the color faded to light brown accompanied by vigorous gas evolution. The solution was stirred 10 min and analyzed: ^{1}H NMR δ 7.19, 6.71, −8.85. The relative integrations confirmed that there was quantitative decarbonylation of **1**. Analogous procedures were employed in experiments in which **2b** and **2c** were treated with **1** in HMPA.

The following experiment was conducted to isolate and identify the sodium imidazolate product from the decarbonylation of **1**. A THF solution (1 mL) of **1** (136 mg, 1.42 mmol) was added to a suspension of **2a** (491 mg, 1.42 mmol) in THF (3 mL). Gradual gas evolution accompanied the transition of the reaction mixture to a deep reddish brown. The material was filtered after being stirred 1 h to afford a burgundy-red filtrate and a pale tan residue, which was washed twice with THF (2 mL). This residue was vacuum dried 30 min, dissolved in HMPA, and analyzed: ^{1}H NMR δ 7.13, 6.68; ^{13}C NMR δ 144.1, 124.7. Analysis of the filtrate by ^{1}H NMR indicated the presence of **3a** (−8.80 ppm). Product **4** could be isolated due to its insolubility in THF. The material was unambiguously identified by spectral comparison with an authentic sample independently prepared from imidazole and NaH.[35]

Isolation and Characterization of Enolate 12. (a) From 2 and 6. A THF solution (5 mL) of **6** (313 mg, 2.84 mmol) was slowly added to a stirred suspension of **2a** (491 mg, 1.43 mmol) in THF (4 mL) with gradual formation of a fine white precipitate. The suspension was stirred 3 h, filtered, washed three times with THF (6 mL), and dried in vacuo. The off-white product was obtained in 89% yield; ^{1}H NMR (Me$_2$SO-d_6) δ 8.05 (s, 1 H), 7.43 (s, 1 H), 6.86 (s, 1 H), 5.18 (s, 1 H), 1.83 (s, 3 H); ^{13}C NMR (Me$_2$SO-d_6) δ 190.9 (acyl CO), 159.9 (enolic C), 135.0, 128.2, 116.1 (imidazole ring C's), 82.8 (vinylic C), 29.4 (CH_3); IR (Nujol) 1672 (s), 1660 (s sh, acyl C=O), 1226 (s, C=C). ^{1}H NMR of the THF filtrate: δ 7.26, 6.81, −8.77 (s, 1). An analogous reaction employing **2b** afforded the same condensation product. The THF filtrate contained NaOsH(CO)$_4$ (δ −10.24) and imidazole (δ 11.23 (s, br), 7.58 (s, 1), 7.00 (s, 2)) in equal amounts.

(b) From 4 and 6. A THF solution (10 mL) of **6** (510 mg, 4.61 mmol) was introduced to a stirred suspension of **4** (205 mg, 2.27 mmol) in THF (5 mL) over a period of 65 min. A dense milky white suspension gradually formed. The material was filtered after being stirred overnight, washed three times with THF (25 mL), and dried 2 days under reduced pressure. The off-white product was obtained in 95% isolated yield: ^{1}H NMR (Me$_2$SO-d_6) δ 8.04 (s, 1 H), 7.44 (s, 1 H), 6.84 (s, 1 H), 5.17 (s, 1 H), 1.83 (s,

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3 H); ^{13}C NMR (Me_2SO-d_6) 191.0 (acyl CO), 159.8 (enolic C), 135.0, 128.3, 116.1 (imidazole ring C's), 82.8 (vinylic C), 29.5 (CH_3); IR (Nujol) 1670 (s), 1660 (s, acyl C=O), 1230 cm^{-1} (s, C=C). Anal. Calcd for $C_7H_7N_2NaO_2$: C, 48.27; H, 4.06; N, 16.09. Found: C, 48.11; H, 4.14; N, 16.09. The filtrate was analyzed by ^1H NMR and found to contain imidazole.

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Phosphine-Functionalized Phosphazene Precursors: Synthesis and Metal Carbonyl Complexes[1]

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Direct bromination of the benzyl- and allyl-substituted (silylamino)phosphines $(Me_3Si)_2NPRR'$ (**1a**, R = Ph, R' = CH_2Ph; **1b**, R = R' = CH_2Ph; **1c**, R = Ph, R' = $CH_2CH{=}CH_2$; **1d**, R = R' = $CH_2CH{=}CH_2$) affords the *P*-bromophosphoranimines $Me_3SiN{=}P(Br)RR'$ (**2a–d**) which, upon treatment with CF_3CH_2OH/Et_3N or $LiOCH_2CF_3$, are easily converted to the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines $Me_3SiN{=}P(OCH_2CF_3)RR'$ (**3a–d**). The latter compounds, as well as the simpler analogues $Me_3SiN{=}P(OCH_2CF_3)(R)Me$ (**4**, R = Me; **5**, R = Ph), are smoothly deprotonated by *n*-BuLi in ether solution at −78 °C. Quenching of the resulting anions with Ph_2PCl or $(Me_2N)_2PCl$ yields the title compounds $Me_3SiN{=}P(OCH_2CF_3)(R)CH(R')PPh_2$ (**6**, R = Me, R' = H; **7**, R = Ph, R' = H; **8a**, R = R' = Ph; **8b**, R = CH_2Ph, R' = Ph), $Me_3SiN{=}P(OCH_2CF_3)(R)CH{=}CHCH_2PPh_2$ (**8c**, R = Ph; **8d**, R = $CH_2CH{=}CH_2$), and $Me_3SiN{=}P(OCh_2CF_3)(Me)CH_2P(NMe_2)_2$ (**9**). The phosphine derivatives **6–9** as well as their new precursors **3a–d** are obtained as distillable liquids, fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analyses. Some rearrangements involving the C=C double bonds are noted for the allyl-substituted phosphoranimines **3c,d** and their Ph_2P derivatives **8c,d**. The phosphine ligands **6**, **7**, **8a**, **8b**, and **9** all react quantitatively with $Fe_2(CO)_9$ at room temperature to give the corresonding (phosphine)$Fe(CO)_4$ complexes **10–12**, **14**, and **15** as viscous liquids, characterized by NMR spectroscopy. Likewise, treatment of ligand **6** with $Cr(CO)_6$ in refluxing diglyme affords the chromium pentacarbonyl complex **13**. These complexation reactions, which proceed cleanly without affecting the $Me_3SiN{=}POCH_2CF_3$ framework of the precursors, are viewed as model reactions for possible derivative chemistry of the poly(alkyl/arylphosphazenes).

Introduction

The synthesis of poly(alkyl/arylphosphazenes), $[NPRR']_n$, has been accomplished by the thermal condensation polymerization of appropriate *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)RR'$, where R = R' = Me, Et, and Ph.[3] Having characterized these simple polymers,[4] we are currently investigating synthetic approaches to related systems with more diverse substituents attached to the backbone via phosphorus–carbon bonds. These new polymers could possess many useful characteristics including higher thermal stability and improved mechanical properties and, with the introduction of suitable ligating sites (e.g., $-CH_2PPh_2$) might also serve as supports for transition-metal catalysts.[5]

Toward these goals, we are studying three general methods of altering the substituents at phosphorus: (1) the synthesis of new (silylamino)phosphines, $(Me_3Si)_2NPRR'$, and *N*-silylphosphoranimines, $Me_3SiN{=}P(X)RR'$, containing more complex alkyl and/or aryl groups, (2) the functionalization of the substituents (R, R') in the phosphazene precursors $Me_3SiN{=}P(OCH_2CF_3)RR'$ via deprotonation/substitution reactions,[6] and (3) the application of similar derivative chemistry to the preformed poly(alkyl/arylphosphazenes). We have recently reported the preparation of a series of silylated derivatives of the poly(alkyl/arylphosphazenes) by the latter approach.[7]

This paper is based on our initial results related to the first two of the above methods. Sepcifically, we report here: (a) the synthesis of several new *N*-silylphosphoranimines containing various combinations of phenyl, benzyl, and allyl substituents on phosphorus; (b) the incorporation of phosphine substituents [Ph_2P or $(Me_2N)_2P$] into the *N*-silyl-*P*-(trifluoroethoxy)-phosphoranimines by the second method; and (c) the coordination of the phosphine sites to simple metal carbonyls.

Results and Discussion

***N*-Silylphosphoranimines.** The (silylamino)phosphines **1a–d** used in this study were prepared as described

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