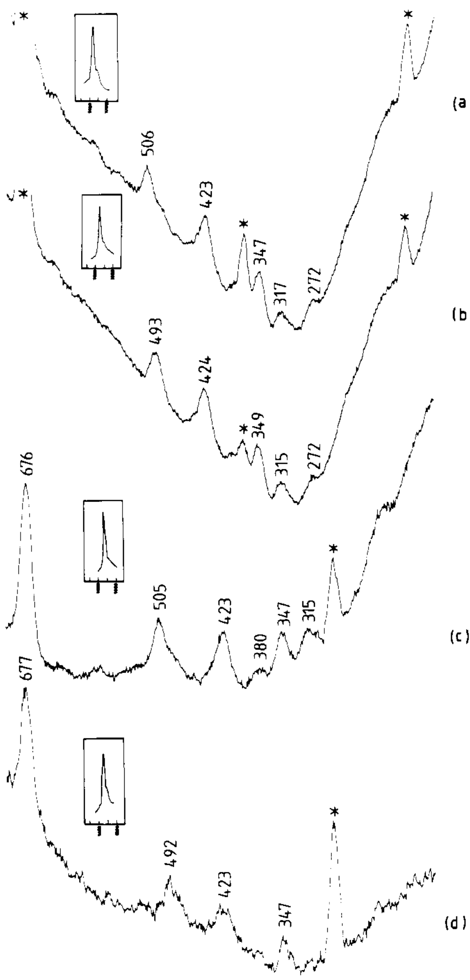

Figure 2. Resonance Raman spectra of CO-leghemoglobin (0.3 mM). (a) $Lb^{12}C^{16}O$—457.9 nm; (b) $Lb^{13}C^{18}O$—457.9 nm; (c) $Lb^{12}C^{16}O$—441.6 nm; (d) $Lb^{13}C^{18}O$—441.6 nm. Typical conditions were 15 (457.9 nm) and 10 mW (441.6 nm) at sample; 0.2-cm^{-1} s^{-1} scan; 5-s time constant; 12-cm^{-1} resolution; 4 scans accumulated. Insets show 1300-cm^{-1} region which was used to monitor extent of photodissociation. A He–Cd laser was used to provide irradiation at 441.6 nm. Asterisk denotes plasma line.

consequence of this defocusing. In Raman spectra of LbCO and MbCO reported earlier using 488.0- and 514.5-nm excitation it was also necessary to defocus the incident beam and to use low laser power (12 mW).[14] It is thus apparent that photodissociation is reduced as excitation is moved into the Soret absorption band. Spectra recorded in this laboratory show that the intensity of the Fe–CO stretch is strong with 413.1-nm irradiation and absent with 514.5-nm irradiation. Thus we conclude that the absorption band which is responsible for resonance enhancement of the ν_{Fe-CO} Raman band is distinct from that which is most favorable for photodissociation.

Acknowledgment. We thank Dr. C. A. Appleby for supply of leghemoglobin, Drs. G. L. D. Ritchie and G. H. Atkinson for the use of a He–Cd laser and a Kr^+ laser, respectively, and the Chemistry Department, Syracuse University, for access to their Raman spectrometer. The work was supported by a grant from the Australian Research Grants Committee and a University of Sydney Travel Grant to M. J. Irwin.

Registry No. CO, 630-08-0; Fe, 7439-89-6.

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Lewis Acid Assisted Reaction of *N*-Formylimidazole with a Transition-Metal Complex. Formyl Group Transfer

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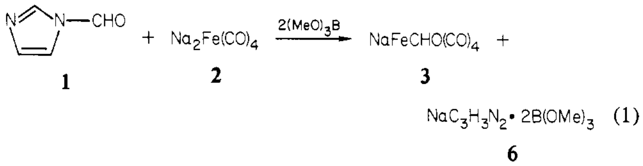
A very common route for syntheses of acyl transition-metal compounds has involved attack of transition-metal nucleophiles on acyl halides. This method has apparently not been used for formyl group transfer reactions because of the thermal instability[1] and/or difficulty of synthesis and handling[2] of formyl halides. To our knowledge, the only example of the synthesis of a stable formylmetal complex via a nucleophilic displacement reaction on an organic X–CHO substrate involved the use of acetic formic anhydride.[3] With few exceptions,[3,4] most preparations of mononuclear formylmetal complexes have utilized hydride attack on carbonyl ligands bound to the metal.[5,6]

In 1962, Staab and Polenski reported the facile synthesis of *N*-formylimidazole (**1**) by treatment of carbonyldiimidazole with formic acid.[7] A search of the subsequent literature has revealed that little chemistry of **1** has been explored although the reactivities of a variety of alkyl and aryl *N*-acylimidazoles toward non-transition-metal nucleophiles have been examined.[8] We describe herein what we believe to be the first study of the reactivities of *N*-acylimidazoles toward a transition-metal nucleophile. In preliminary studies, we have examined the reactivity of **1** toward $Na_2Fe(CO)_4$ (**2**), since the expected product of a nucleophilic displacement, $NaFeCHO(CO)_4$ (**3**), has been characterized and shown to be kinetically stable in solution.[3]

We have found that certain Lewis acids promote the reaction of **1** with **2** to produce formyliron complex **3** in high yields. When mixtures of **1** and triethylboron or trimethoxyboron were treated with **2** in HMPA and THF (1:**2** molar ratio = 1) at 25–27 °C, the immediate formation of product mixtures which contained **3** and Lewis acid–imidazole anion adducts were observed (reaction 1).[9] The highest yields of **3**, and a near quantitative overall



$$\mathbf{1} + \underset{\mathbf{2}}{Na_2Fe(CO)_4} \xrightarrow{2(MeO)_3B} \underset{\mathbf{3}}{NaFeCHO(CO)_4} + \underset{\mathbf{6}}{NaC_3H_3N_2 \cdot 2B(OMe)_3} \quad (1)$$

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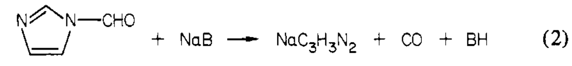
material balance,[10] were achieved when $(MeO)_3B$ was employed as Lewis acid. The yields were affected by the $(MeO)_3B$:**1** molar ratio employed. Optimum yields of **3** ranging from 70 to 80% were achieved at a $(MeO)_3B$:**1** ratio of 2:1 in HMPA (55% yield in THF). Triethylboron and BF_3 were less effective as promoters of **3** formation. For instance, a 46% yield of **3** was afforded when a Et_3B:**1**:**2** ratio of 2:1:1 was employed in HMPA, and yields of **3** were <20% when BF_3 was used. Boron trifluoride caused some decarbonylation of **1** in the absence of **2**.

The production of **3** was accompanied by varying amounts of $NaFeH(CO)_4$ (**4**), the yield of the latter being determined by the nature of the Lewis acid and the BR_3:**1** ratio. The half-life for the conversion of **3** to **4** in product mixtures from experiments employing a $(MeO)_3B$:**1**:**2** ratio of 2:1:1 in HMPA at 27 °C was ca. 72 h. Thus, it could be determined that the **4** in these product mixtures did not derive primarily from **3**.

The formation of **3** in these experiments could be monitored by following the appearance of the ^1H and ^{13}C resonances at δ 14.73 (FeC*H*O) and 220.9 (Fe*C*O) and 257.0 (Fe*C*HO) (HMPA), respectively, and the disappearance of the resonances due to **1** and **2**. Compound **4** was determined to be the only other iron carbonyl product since its δ 221.9 ^{13}C resonance was the only other ^{13}C resonance found in the δ 200–300 region. Authentic samples of **4**[11] and the bis(triphenylphosphine)iminium (PPN) analogue of **3**[12] were synthesized independently. The ^1H and ^{13}C spectra of these samples were recorded in HMPA and were found to be identical with the corresponding compounds derived from the **1**–R_3B–**2** reactions. The presence of Et_3B or $(MeO)_3B$ had little effect upon the ^1H and ^{13}C resonance positions of **3** and **4**.

It is quite remarkable that **3** can be formed in such high yields. Independent treatment of **1** with **2** and sodium imidazolate (**5**) caused its decarbonylation. Treatment of **1** with an equimolar amount of **5** in HMPA produced immediate and copious gas evolution to afford a 1:1 mixture of imidazole and **5** (reaction 2), identified by comparison of its ^1H NMR spectrum with that of an independently prepared mixture of the authentic compounds.



$$\mathbf{1} + NaB \longrightarrow \underset{\mathbf{5}}{NaC_3H_3N_2} + CO + BH \quad (2)$$

$$B^- = C_3H_3N_2^-,\ NaFe(CO)_4^-$$

The decarbonylation of **1** by **5** was found to be catalytic in **5**, a turnover of 9 being achieved during ca. 30 min when a **1**:**5** reactant ratio of 20:1 was employed. Treatment of **3** with **5** caused no decarbonylation of **3** or any other detectable reaction. Compound **1** reacted instantaneously with an equimolar amount of **2** in THF and HMPA solutions at 25–27 °C to afford, in near quantitative yield, **4**, CO, and sodium imidazolate (**5**).[13] The behavior of **1** toward **2** differed markedly from that of carbocyclic aromatic and aliphatic aldehydes. They have been shown to afford ester dismutation and aldol condensation products, respectively.[15]

Products **4** and **5** were produced quantitatively when imidazole was treated with an equimolar amount of **2** in HMPA at room temperature (reaction 3). Thus, any imidazole impurity in **1** employed in reactions with **2** could provide an additional base which decarbonylates **1**. Samples of **1** which contained <1% imidazole impurity by ^1H NMR integration were rapidly decarbonylated when treated with **2**. Although some of the ensuing decarbonylation undoubtedly was caused by the primary product **5**, it would appear that **2** initiated the process by reaction with **1**.

$$\text{imidazole} + \underset{\mathbf{2}}{Na_2Fe(CO)_4} \longrightarrow \underset{\mathbf{4}}{NaFeH(CO)_4} + \underset{\mathbf{5}}{NaC_3H_3N_2} \quad (3)$$

N-Acetylimidazole[16] (**7**) reacted with **2** in the presence of $(MeO)_3B$ [$(Meo)_3B$:**7**:**2** = 2:1:1] in THF and HMPA at 25–27 °C to afford $NaFeCOCH_3(CO)_4$[3] (**8**). A yield of 77% was afforded in THF, determined by comparison of the CH_3CO ^1H resonance integration at δ 2.54 (THF) with that of a dichloromethane internal standard, introduced after the reaction was complete. Compound **8** was characterized by its conversion to the PPN salt. The ^{13}C NMR (HMPA) spectrum [δ 258.4 (Fe*C*OCH$_3$), 221.5 (Fe*C*O), 51.2 (FeCO*C*H$_3$)] was essentially identical with that of an authentic sample prepared by reaction of acetyl chloride with **2** in THF, followed by treatment of the product with PPNCl, isolation, and spectral characterization in HMPA. Compound **8** was not detected as a product when **7** was treated with **2** in THF in the absence of a R_3B Lewis acid.

Our results indicate that the formation of **3** is not derived from a Lewis acid mediated transfer of hydride[17] from **4** to an iron-bound carbonyl ligand present in the reaction mixture. Control experiments demonstrated that the formation of **3** was not aided by the presence of **4**. Significantly, an acyl transfer reaction was demonstrated when **7** was the *N*-acyl substrate, a case where hydride transfer would not be involved. The results demonstrate that $(MeO)_3B$ is very effective in preventing the decarbonylation

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(9) In a typical experiment, 0.244 g (0.710 mmol) of $Na_2Fe(CO)_4 \cdot 1.5$ dioxane in 1.5 mL of HMPA was treated with a solution containing 0.068 g (0.71 mmol) of **1** and 161 μL (1.42 mmol) of $(MeO)_3B$ in 0.5 mL of HMPA at 27 °C. The $(MeO)_3B$-**1** solution was added rapidly to the stirred solution of **2**, and the resulting yellow-brown solution was stirred for 10 min. Spectra recorded immediately thereafter showed that **1** and **2** had been completely consumed. The solvent was dried and deoxygenated prior to use, and all operations were conducted under argon. The $Na_2Fe(CO)_4 \cdot 1.5$ dioxane employed was either reagent purchased from Ventron or was synthesized in our laboratory from $Fe(CO)_5$ and sodium in dioxane. It was desirable that $NaFeH(CO)_4$ impurity be maintained at a minimum. Samples of **1**[7] containing only 3% of imidazole could be obtained after two sublimations. The yields of **3** were not particularly sensitive to the presence of minor amounts of imidazole, yields >70% being consistently achieved when the imidazole impurity in samples of **1** ranged from 3–10%. Extremely pure samples of **1** with <1% imidazole impurity were obtained by recrystallization of twice-sublimed samples of **1** from hexane.

(10) The material balance was established by integrations of the FeC*H*O resonance in **3**, the Fe*H* resonance in **4**, and the product imidazolate ring ^1H and $(MeO)_3B$ ^1H resonances. Since the product mixtures in HMPA were homogeneous, it could be determined from ^1H and ^{13}C spectra that the reactants were completely consumed, and no significant amounts of other products were present. The yields were verified by use of trichloroethylene and dichloromethane as internal PMR standards, introduced after the reactions were complete. Product **6** was identified by its ^1H and ^{13}C NMR spectra by comparison with those of an authentic sample, prepared by treatment of **5** with 2 equiv of $(MeO)_3B$ in THF. The latter product could be isolated after removal of solvent in vacuo to afford a white solid. NMR (HMPA): Imidazole ring, ^1H, δ 7.66, 6.88 ppm in 2:1 ratio with minor peaks at δ 7.51 and 6.73, major to minor components in 6:1 ratio; ^{13}C, δ 138.2, 121.4; $(MeO)_3B$ component, ^1H, δ 3.05; ^{13}C, 48.5; THF component, ^1H, δ 3.60, 1.80. ^1H integration (Me_2SO-d_6) showed the $(MeO)_3B$:$C_3H_3N_2$:THF ratio in the material to be 2:1:0.5. Warming the solid at 52 °C in vacuo (0.1 mm) for 15 h caused 20% of the THF to be released. All of the $(MeO)_3B$ was retained. The analogous compound containing units of **5**, $(MeO)_3B$, and THF in 1:1:0.5 ratio was also synthesized and isolated after treatment of **5** with 1 equiv of $(MeO)_3B$ in THF.

(11) Prepared by treatment of $Na_2Fe(CO)_4 \cdot 1.5$ dioxane with an equivalent of acetic acid. ^{13}C and ^1H NMR spectra (HMPA): δ 221.9 and −8.87, respectively.

(12) An authentic sample of $KFeCHO(CO)_4$ was prepared from $KHB(OMe)_3$ and $Fe(CO)_5$.[5c] The PPN salt[3] was then prepared from this potassium derivative; NMR (HMPA); ^{13}C, δ 220.9, 257.1; ^1H, δ 14.68.

(13) The course of the reaction was monitored by observing the disappearance of the resonances of **1** (^1H, δ 9.73, 8.56, 7.68, 7.10; ^{13}C, δ 160.8, 139.2, 131.74, 114.73, HMPA) and **2** (^{13}C, δ 234.7) and the appearance of the resonances of **4** (^1H, δ −8.84; ^{13}C, 221.9). The amount of evolved gas (0.75 equiv) was determined volumetrically, GLC retention time identical with that of CO on a 60–80 mesh 5-Å molecular sieve column operated at 95 °C. The quantitative yields of **4** and **5** were determined by ^1H NMR integration relative to a dimethyl formamide internal standard, introduced after gas evolution ceased. The integrations of the Fe*H* and imidazole ring proton resonances in products **4** and **5** were in 1:3 ratio. No other products were present. Compound **5** could be separated from **4** in product mixtures dervied from experiments conducted in THF due to the marginal solubility of **5** in this solvent. The ^1H and ^{13}C spectra of the isolated material were nearly identical with those of an authentic sample prepared by treatment of imidazole with NaH in THF[14]: ^1H, δ 7.08 and 6.63 in 1:2 ratio; ^{13}C, δ 143.9, 124.6 (imidazole ring) (HMPA).

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of **1**, diverting the course of the reaction toward formation of **3**.[18] It is clear that one function of the Lewis acid is to react with **5**, thus preventing the decarbonylation of **1** by **5**. However, this does not appear to be its only task. An understanding of the detailed role(s) of the Lewis acid is being sought.

The importance of formylmetal complexes as intermediates in homogeneous Fischer–Tropsch processes has recently been underscored.[4,5,19] *N*-Acylimidazole–transition-metal reactions provide a potential route to a variety of acyl transition-metal complexes, including formylmetal derivatives. We are currently examining the synthetic scope and mechanistic aspects of the transition-metal–*N*-acylimidazole reactions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE-76-01786) for support of this research.

Registry No. 1, 3197-61-3; **2**, 14878-31-0; **3**, 80327-81-7; **4**, 53558-55-7; **5**, 5587-42-8; **7**, 2466-76-4; **8**, 64867-63-6; BF_3, 7637-07-2; triethylboron, 97-94-9; trimethoxyboron, 121-43-7.

Supplementary Material Available: A table of ^1H and ^{13}C chemical shift data for imidazole, *N*-formylimidazole, and sodium imidazolate in the presence and absence of Lewis acids (1 page). Ordering information is given on any current masthead page.

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[18] While Et_3B and BF_3 were less effective in this regard, they appeared to form stronger complexes with imidazole and **1** than did $(MeO)_3B$. The complexes were detectible by shifts in the ^1H and ^{13}C resonance positions. No analogous shifts were observed in the $(MeO)_3B$ case.

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Some Structural Effects on Triplet Biradical Lifetimes. Norrish II and Paterno–Buchi Biradicals

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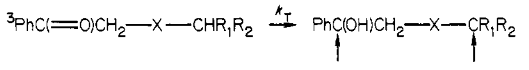
Norrish II biradicals provide remarkably good model systems for the study of triplet biradical properties in general, especially in cases for which the triplet ketone precursor is quite short lived.[1] Scaiano[1] has shown that the lifetime generally observed in hydrogen-bonding solvents for valerophenone-derived biradicals is about 100 ns and is largely independent of alkyl substitution at the terminus; typical lifetimes in hydrocarbon solvents are 35–40 ns. We now report that the effect of γ-aryl substituents is to increase the lifetime modestly and that the effect of replacing β-CH_2- by β-O- is to shorten the lifetime dramatically. The latter substitution affords a lifetime similar to that for Paterno–Buchi (preoxetane) biradicals.

The well-known mechanism[1,2] for the Norrish II process is given in eq 1–3. We prepared benzhydryl phenacyl ether expecting that it would afford a Norrish II biradical with convenient spectroscopic properties. The conventional photochemistry is unexceptional. The principal products are benzophenone and acetophenone (initially of course via the enol) in quantum yields of 0.70 ± 0.05 and 0.76 ± 0.06, respectively; the same values are obtained in both methanol and benzene. A secondary product, 1,2-dibenzoylethane, is absent at 8% conversion but is found in 46% yield at completion. Its formation is readily rationalized by excitation of the product Ph_2CO and eq 4–6.

$$\mathrm{PhC({=}O)CH_2{-}X{-}CHR_1R_2} \xrightarrow{h\nu} \xrightarrow{\mathrm{isc}} \mathrm{{}^3PhC({=}O)CH_2{-}X{-}CHR_1R_2} \quad (1)$$



$$\mathrm{{}^3PhC({=}O)CH_2{-}X{-}CHR_1R_2} \xrightarrow{k_T} \mathrm{Ph\dot{C}(OH)CH_2{-}X{-}\dot{C}R_1R_2} \quad (2)$$

1a–g

$$\mathbf{1} \xrightarrow{\tau_{BR}^{-1}} \mathrm{PhC(OH){=}CH_2} + \mathrm{R_1R_2C{=}X} \quad (3)$$

(+ cyclobutanols, starting material)

$$\mathrm{{}^3Ph_2CO + PhC({=}O)CH_2OCHPh_2 \rightarrow Ph_2\dot{C}OH + PhC({=}O)CH_2O\dot{C}Ph_2} \quad (4)$$

$$\mathrm{PhC({=}O)CH_2O\dot{C}Ph_2 \rightarrow Ph_2CO + PhC({=}O)CH_2} \quad (5)$$

$$\mathrm{2PhC({=}O)CH_2\cdot \rightarrow PhC({=}O)CH_2CH_2C({=}O)Ph} \quad (6)$$

Quenching by isoprene afforded $k_Q\tau$ for the triplet ketone of 0.63 M^{-1} in benzene and 0.62 M^{-1} in methanol, leading to triplet lifetime estimates of approximately 120–130 ps. There is ample precedent[3] for very rapid γ-hydrogen abstraction in other phenacyl ethers, and the presence of two γ-Ph groups should further increase the rate.[2] The very short triplet lifetime and the expectation that the well-known and easily detected benzophenone ketyl radical[4] would be a good model for the absorption spectrum of the biradical prompted a study of the transient spectroscopy in the system.

We were initially chagrined to find that, utilizing nitrogen laser excitation (3371 Å, ca. 5 mJ, 8-ns fwhm), the only detectable transient was benzophenone triplet, λ_{max} 525 nm,[4] $\tau \sim 300$ ns in CH_3OH,[5] $\phi \sim 0.03$, which we expect is largely or exclusively the result of a biphotonic process. However, using a mode-locked Nd:YAG laser pulse extended to ca. 100 ps (fourth harmonic, 2662 Å, ca. 0.5–10 mJ) and a Tektronix 7912 transient digitizer, we have detected transient absorption in the UV region ($\lambda > 3000$ Å) with lifetime of the order of a few nanoseconds. The fwhm of the combined excitation/response function for the system is ca. 1.75 ns; a (highly reproducible) ringing of modest but nonnegligible intensity requires deconvolution for any transient with $\tau \lesssim 10$ ns.

Table I lists lifetimes and λ_{max} values in the UV region for the Norrish II biradicals. Our lifetime for the valerophenone derived biradical **1f** is in excellent agreement with the literature value;[1] λ_{max} in the UV region has not been previously reported. Its extinction coefficient is at least tenfold larger than that at its λ_{max} in the visible region.[6]

The transient **1a** from benzhydryl phenacyl ether is clearly not the corresponding triplet, especially since it is unaffected by 0.5 M isoprene and since the triplet lifetime from steady-state quenching is so short. It can only be assigned as the biradical **1a**. The observed spectrum is consistent in that the rather broad shape may reflect overlapping absorptions of the termini, **1f** being a model for one and benzophenone ketyl[4] (λ_{max} 330 nm) being a model for the other. The lifetime is remarkably short when compared to previously reported valerophenone-derived biradicals;[1] **1b**, with one phenyl replaced by H, is even more short lived. Lifetimes for **1a** and **1b** were obtained as deconvolution fits to the equation $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ by using the scattered laser light detected by the same system as the combined excitation/response function. The two exponential fit assumed a τ_1 of 10 μs, and was required by an observed small increase in base-line absorption (presumably due to absorbing products or unknown biphotonic transients). The ratio A_1/A_2 was always <0.1 and decreased with decreasing laser power.

The biradicals **1c** and **1d** prove that the short lifetime for **1a** is not related to the phenyl groups. Note the monotonic increase in lifetime in both protic and nonprotic solvent in the order of

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[5] The decay produced the spectrum of benzophenone ketyl, λ_{max} 550 nm, as expected.

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