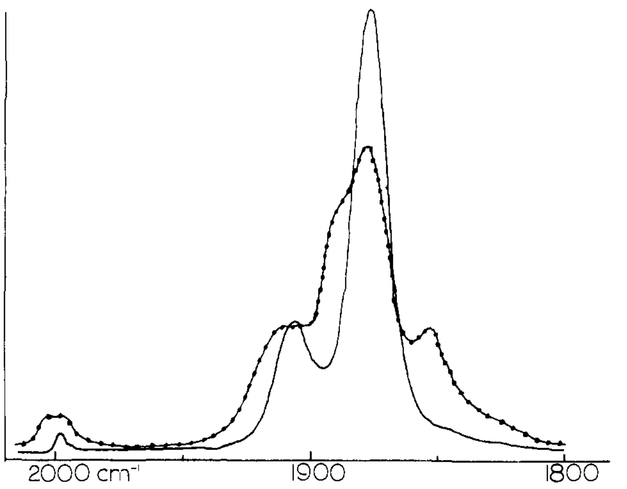
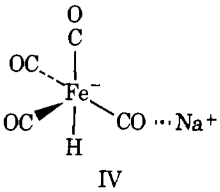


Figure 1. The ν(CO) infrared spectrum of THF solution of PPN$^+$HFe(CO)$_4^-$ (—) and of a PPN$^+$HFe(CO)$_4$ solution to which an eightfold excess of Na$^+$BPh$_4^-$ has been added (-•-•-•).

to move that carbonyl group, the M$^-$—C≡O···M$'^+$, to lower frequencies and the remaining CO groups on M to higher frequencies.[13] If the cation penetrates the coordination sphere, giving rise to metal-metal bonds[18-20] or to interaction with electron density pockets such as the Na$^+$ to allylic-like C—Fe—C in Na$^+$·(1.5dioxane)Fe(CO)$_4^{2-}$,[21] all CO frequencies are expected to be slightly raised with respect to the "free" anion. A symmetrical solvent or electronic environment about the anion produces a spectral pattern identical with that expected for the neutral metal carbonyl analogue. Barring some minor band width variations the spectra of all carbonylates in this study are indicative of a symmetrical field. That is, even though contact ion pairs are indicated by the conductance parameters, the charge delocalization of the cation is too great to induce any perturbation of the anion. For example, the ν(CO) for PPN$^+$HFe(CO)$_4^-$ displays three bands at 1998 cm^{-1} (w), 1905 (m), and 1876 (s), of intensity pattern expected for the distorted trigonal bipyramidal structure.[22] Upon addition of an excess of NaBPh$_4$ (K_D in THF = 8.52×10^{-5} M^{-1})[16] new bands at 2003, 1910, 1890, and 1854 cm^{-1} develop (Figure 1). Detailed assignments based on force constant correlations and intensity ratios will await the full report of this work; however, it is clear that the species produced is analogous to the Na$^+$Ph$_3$PMn(CO)$_4^-$ contact ion pair whose spectrum was fully analyzed previously.[13] Interaction of Na$^+$ with one of the "equatorial" carbonyl oxygens is indicated (IV).



IV

This perturbation has a dramatic effect on the reactivity of the HFe(CO)$_4^-$ toward O$_2$. The air sensitivity of cation-perturbed HFe(CO)$_4^-$, prepared by the metathesis of PPN$^+$HFe(CO)$_4^-$, may be quantitatively compared with that of the symmetrical HFe(CO)$_4^-$. Rigorously excluding air, THF solutions of PPN$^+$HFe(CO)$_4^-$ and NaBPh$_4$/PPN$^+$HFe(CO)$_4^-$ are stable under N$_2$ over extended periods. Upon introducing identical quantities of air, presumably saturating the solutions, a smooth decomposition of the carbonylate is observed, showing a first-order rate dependence on HFe(CO)$_4^-$. The half-lives of decomposition at 22 °C are 105 min for PPN$^+$HFe(CO)$_4^-$ and only 4.8 min for NaBPh$_4$/PPN$^+$HFe(CO)$_4^-$ (4:1 ratio, species IV clearly observable by IR).

It is possible that the asymmetric PPN$^+$ exercises a physical, covering type of protection toward its associated anion, even in solution. Preliminary results on studies of the air-sensitivity of Et$_4$N$^+$HFe(CO)$_4^-$, i.e., the counterion of HFe(CO)$_4^-$ here is a large symmetrical cation, incapable of either a "covering" effect or perturbation, lead us to suggest that the instability of Na$^+$HFe(CO)$_4^-$ results from cation distortion, producing steric and/or electronic sites more susceptible to reaction.

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Metalation and Carboxylation of Activated Carbon–Hydrogen Bonds by Complexes of Iridium and Rhodium

Sir:

Metalation of carbon–hydrogen bonds has been of interest as a means of activating these bonds for subsequent reactions.[1] Recent activity in CO$_2$ coordination chemistry has afforded examples of adduct formation[2] and of CO$_2$ insertion reactions.[3] We report both metalation and carboxylation reactions of activated hydrocarbons (A-H) such as acetonitrile, acrylonitrile, and phenylacetylene, by the complexes ML$_4^+$, M = Rh, Ir; L= trialkylphosphine or -arsine (eq 1 and 2).

$$\mathrm{M(L)_4^+ + A\text{-}H \overset{K_1}{\rightleftharpoons} M(A)(H)(L)_4^+} \quad (1)$$

$$\mathrm{M(L)_4^+ + A\text{-}H + CO_2 \overset{K_2}{\rightleftharpoons} M(O_2CA)(H)(L)_4^+} \quad (2)$$

{Ir[(C$_2$H$_5$)$_2$PCH$_2$CH$_2$P(C$_2$H$_5$)$_2$]$_2$}Cl ([Ir(depe)$_2$]Cl, **1**) was

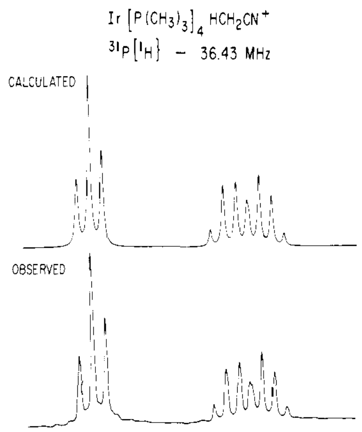

Figure 1. The $^{31}P\{^1H\}$ 36.43-MHz spectrum of $Ir[P(CH_3)_3]_4(H)(CH_2CN)^+Cl^-$ in acetonitrile at 30 °C. The calculated spectrum is constructed with δ_A 53.8 ppm, δ_B 59.6 ppm, δ_C 61.1 ppm, $J_{AB} = J_{AC} = J_{BC} = 19$ Hz.

prepared by addition of the bidentate phosphine to a benzene solution of $Ir_2Cl_2(C_8H_{14})_4$.[4] Stable red acetonitrile solutions of **1** showed ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra consistent with a four-coordinate structure.[5] Pressurization of this solution with 1 atm of CO_2 yielded a colorless solution in hours; this color change was reversed by evacuation at 80 °C. The CO_2 addition and evacuation cycle are repeatable.

^{31}P NMR spectra of **1** were recorded in the presence of either broad band proton decoupling radiation ($^{31}P\{^1H\}$) or CW aliphatic proton decoupling irradiation ($^{31}P\{CW^1H\}$). The latter type of decoupling allowed the identification of hydride containing species through the phosphorus-hydride spin-spin coupling. The ^{31}P NMR spectrum of **1** in CH_3CN showed a singlet (δ −56.6 ppm) under both decoupling conditions. After pressurizing with CO_2, the now colorless solution displayed a singlet (δ −26.9 ppm) in the $^{31}P\{^1H\}$ spectrum and a doublet in the $^{31}P\{CW^1H\}$ spectrum. The same experiments performed in CD_3CN showed only singlets.[6] These results indicate that all phosphorus nuclei in **2** (vide infra) are equivalent on the NMR time scale and are coupled to a single hydridic proton which arises from the acetonitrile solvent. ^1H NMR spectra showed a hydride quintet at δ −22.2 ppm ($J_{P-H} = 13$ Hz) in CH_3CN and no hydride resonance in CD_3CN.[7] The NMR spectra of **2** indicate it to be trans or fluxional cis; work on similar species[8,9] suggests that a trans structure is the likely choice.

Addition of HCl then BF_3/CH_3OH to the colorless solution of **1** and CO_2 in acetonitrile afforded methyl cyanoacetate, identified mass spectrometrically. The above data are consistent with the scheme:

$$\underset{\mathbf{1}}{[Ir(depe)_2]Cl} + CH_3CN \underset{}{\overset{K_1'}{\rightleftharpoons}} [Ir(H)(CH_2CN)(depe)_2]Cl$$

$$[Ir(depe)_2]Cl + CH_3CN + CO_2 \overset{K_2'}{\rightleftharpoons} \underset{\mathbf{2}}{[Ir(H)(O_2CCH_2CN)(depe)_2]Cl}$$

$$K_2' \gg K_1'$$

The corresponding rhodium complex, $[Rh(depe)_2]Cl$, does not react with acetonitrile even in the presence of CO_2. $[Rh(Me_2PC_2H_4PMe_2)_2]Cl$ does not metalate acetonitrile or nitromethane detectably. However, CO_2 addition reversibly results in carboxylation of nitromethane, analogous to the chemistry of $[Ir(depe)_2]Cl + CH_3CN + CO_2$.

Acetonitrile is also readily metalated (and carboxylated) by $[Ir(PMe_3)_4]Cl$ (**3**). This species is much more reactive than **1** as is illustrated by its reactions with acetonitrile and CO_2. The reaction of **3** with acetonitrile at room temperature is quite rapid ($\tau_{1/2} \simeq 10$ min) and the K_1 is sufficiently large that only *cis*-$[Ir(H)(CH_2CN)(PMe_3)_4]Cl$ (**4**) (Figure 1) is observable via $^{31}P\{^1H\}$ NMR. Addition of CO_2 at room temperature to an equilibrated solution of **3** in acetonitrile (e.g., **4**) affords no observable reaction; however, immediate addition of CO_2 to a solution of **3** in acetonitrile (i.e., **3**) yields $[Ir(H)(O_2CCH_2CN)(PMe_3)_4]Cl$ (**5**). These results indicate that **4** is not the species whose reaction with CO_2 yields **5.** In this case at least, the carboxylation is not CO_2 insertion into the metal-carbon bond formed in eq 1.[10]

The metalation and carboxylation reactions have been observed with a range of ML_4^+ complexes and activated hydrocarbons. As illustrated above, Rh complexes are less reactive than the corresponding Ir species, and bulkier ligands attenuate reactivity. The observed correlation of extent of reaction with metal basicity (Ir > Rh) and C-H bond acidity suggests electrophilic attack at the metal. Work is in progress to elucidate the mechanisms of the metalation and carboxylation reactions.

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(7) ^{31}P spectra at 36.43 MHz were recorded in FT mode using 10-mm tubes on a Bruker HFX-90 with Digilab FTS-3 data system; negative chemical shifts are downfield from external 85% H_3PO_4. ^1H spectra were recorded at 220 MHz in CW mode, using 5-mm tubes on a Varian HR 220; positive chemical shifts are downfield from internal tetramethylsilane.

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Asymmetric Induction in Catalytic Allylic Alkylation

Sir:

Catalytic processes for forming C-H bonds with creation of chirality have progressed almost to the limit in some cases.[1] Such reactions have been much less successful in forming C-C bonds.[2] The most successful is in an olefin oligomerization system developed by Wilke.[2b] We wish to report that optical yields in the range of 35-45% can be obtained in a catalytic allylic alkylation without resorting to impractically low temperatures.