teresting to note that while peptide B displays considerable helical induction in the presence of Zn^{2+}, peptide A is Cd^{2+} selective and addition of Zn^{2+} has no effect on the helical content. In addition, helicity is independent of concentration of added NaF up to 250 mM for both peptide A (2.5 μM in 5 mM sodium borate, pH 8.0) and peptide B (2.0 μM in 5 mM sodium borate, pH 6.1). A and B show CD spectra independent of the peptide concentration in the presence and the absence of metal ions in the measured range of 0.5–70 μM, consistent with intramolecular helical structures.[11] Nonligated metal coordination sites are most likely occupied by water molecules, and addition of external ligands such as 5-nitro-1,10-phenanthroline or mercaptoethanol does not affect the stability of the helical conformation.

Support for the metal ion complexation site comes from NMR studies. Both of the histidine 2-H and 4-H resonances in peptide B (2.5 mM in D_2O, pH 6.6) occurring at δ 7.87 and 7.74 and δ 6.89 and 6.87 show upfield shifts upon addition of Zn^{2+} to δ 7.75 and 7.71 and δ 6.87 and 6.67, respectively. Similar results are obtained for peptide A (2.5 mM in D_2O, pH 6.5) in the absence (δ 7.91 and 6.95) and the presence of Cd^{2+} (δ 7.71 and 6.91). Of the 17 backbone amide protons in peptide A (3.0 mM, $CdCl_2$ 0.3 M in H_2O, pH 5.1), 11 have been sequentially assigned by using COSY and NOESY spectra.[12] Interestingly, amide resonances for N-terminal amino acid residues exhibit $^3J_{HN\alpha} < 5$ Hz, which is further evidence that helical structure extends to the N-terminus.

The above studies indicate that unprecedented levels of helicity can be induced in short monomeric peptides by taking advantage of selective metal ion complexation. Detailed structural characterization of these peptides using 2-D NMR techniques is currently in progress. We are also utilizing unnatural amino acid side chains as potential ligands as well as studying the feasibility of stabilizing proteins by this approach.

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Solution Structure of $(PPh_2Me)_2Fe(CO)(\eta^2\text{-}C(O)Me)I$. Direct DNMR Evidence for a Facile Alkyl ↔ η^2-Acyl Equilibrium

Chet Jablonski*

Department of Chemistry
Memorial University of Newfoundland
St. John's, Newfoundland A1B 3X7, Canada

Gianfranco Bellachioma, Giuseppi Cardaci, and Gustavo Reichenbach

Dipartimento di Chimica, Universitâdi Perugia
I-06100 Perugia, Italy

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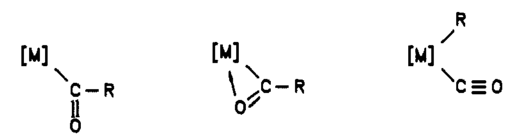
Transition-metal oxophilicity[1,2] and steric[3-6] factors have emerged as crucial parameters which determine the relative stability of mono- and bidentate acyl coordination modes **1** and **2** respectively. Although coordinatively saturated bidentate acyl



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structures have been *implicated* as intermediates in CO insertion chemistry,[7-12] little direct evidence[13] exists regarding the relative

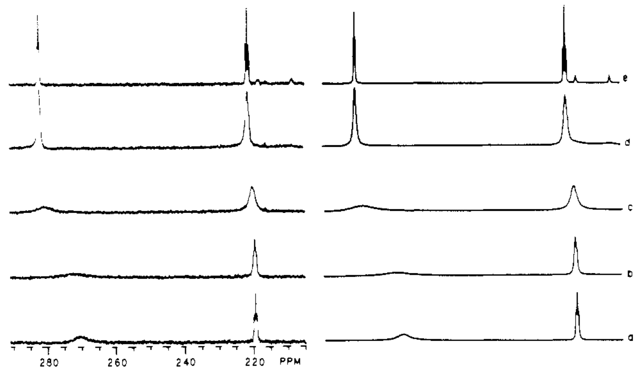
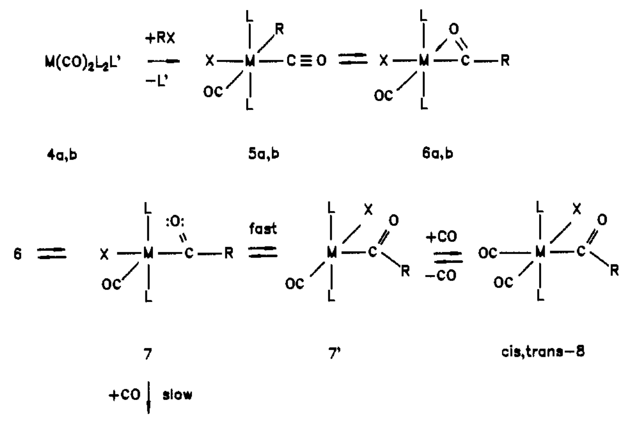


Figure 1. Variable-temperature ^{13}C NMR spectra in CD_2Cl_2 and DNMR simulations for **5b** ↔ **6b**: a, 309.5 K; b, 296.8 K; c, 270.0 K; d, 244.6 K; e, 220.0 K.

Scheme I[a]



[a] **a**: L = L′ = PPh_3, M = Ru, R = Me.[13] **b**: L = PPh_2Me, L′ = $MeCN$[4] or N_2,[6] M = Fe, R = Me.

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Table I. Kinetic and Thermodynamic Parameters for **5b** ↔ **6b**

temp,[a] K	k_{exch},[b] s^{-1}	k_f, s^{-1}	k_r, s^{-1}	K_{eq}
220.0 ± 0.3	≤1.0			9.0 ± 1[c]
244.6 ± 0.3	(1.0 ± 0.5) × 10^3	(1.7 ± 0.9) × 10^3	(2.6 ± 1.9) × 10^2	6.6 ± 1.8[d]
270.0 ± 0.3	(9.5 ± 2) × 10^3	(1.6 ± 0.4) × 10^4	(3.2 ± 0.8) × 10^3	5.0 ± 1.4[d]
296.8 ± 0.3	(5.5 ± 1.5) × 10^4	(8.8 ± 0.3) × 10^4	(2.2 ± 0.7) × 10^4	4.1 ± 1[d]
309.5 ± 0.3	≥7.5 × 10^4			3.8 ± 0.7[e]

[a] Calibrated by using methanol or ethylene glycol standards. [b] Calculated from manual line-shape fits using DNMR-3H.[19] [c] Determined by integration. [d] Calculated by using $\Delta H = -5.4 \pm 0.8$ kJ mol^{-1}, $\Delta S = -6.5 \pm 2$ J mol^{-1} K^{-1}, obtained from data at 220 K and 309 K (cf. text). [e] Determined from weighted average chemical shift data of **6b** and **5b**.

stabilities and reaction dynamics connecting the bidentate acyl structure **2** with its isomeric parent alkyl **3**. Herein we report variable-temperature DNMR evidence which unequivocally demonstrates a facile alkyl ↔ η^2-acyl migratory insertion/deinsertion **3** ↔ **2** and defines their relative thermodynamic and kinetic stabilities.

Oxidative addition of alkyl halides to "dissociatively activated" d^8 Ru[13] (**4a**) and Fe[4,6] (**4b**) substrates proceeds readily even when the ligand sphere is sterically demanding (Scheme I). In contrast with oxidative addition to less hindered d^8 substrates,[14] structural evidence[4,6] shows that the isolated product in these cases is a bidentate acyl, **6**, rather than a six-coordinate octahedral alkyl, **5**, respectively. Clearly a delicate balance exists between the isomeric alkyl and bidentate acyl structures, with increasing steric demands favoring the latter.[4,6]

Examination of the ^{13}C NMR spectrum[15] of the bidentate acyl **6b** (M = Fe, L = PPh_2Me, R = Me) in dichloromethane-d_2 reveals that its solution structure differs markedly from that observed in the solid state.[4] At ambient temperature, the phosphine methyls as well as the diastereotopic $P(C_6H_5)_2$ groups appear as sharp triplets, virtually coupled to two isochronous, trans ^{31}P atoms. At the same temperature, however, the signals for the carbonyl and especially the acyl methyl are curiously broad. Furthermore, no resonance appropriate to the bidentate acyl carbon was detected at ambient temperature (293 K). These ambiguities were resolved by recording the ^{13}C NMR spectrum of isotopically enriched **6b** at low temperature. Figure 1 shows partial, temperature-dependent ^{13}C DNMR spectra recorded for a sample of **6b** specifically enriched at FeC*O and Fe(C*(O)CH_3).[16] A rather large solubility temperature coefficient of **6b** in dichloromethane restricted the low-temperature limit to 203 K.[17] On cooling, the broad carbonyl resonances at 270.0 and 220.0 ppm resolve into sharper signals at 282.3, 221.4, 218.2, and 208.5 ppm,[18] cf. Figure 1. The observed changes are completely reversible. We interpret the variable-temperature ^{13}C NMR spectra of Figure 1 in terms of the rapid equilibrium OCFeMe ↔ η^2-FeC(O)Me, **5b** ↔ **6b**. The intense resonances at 282.3 and 221.4 ppm can be assigned to the acyl and carbonyl groups, respectively, for the bidentate acyl isomer, **6b**.[4] Low-intensity carbonyl resonances at 218.2 and 208.5 ppm are assigned to a smaller equilibrium concentration of the isomeric alkyl complex **5b**.

Equilibrium constants (cf. Table I) for **5b** ↔ **6b** were obtained by integration of the low-temperature-limiting ^{13}C NMR spectrum (203 K) and from DNMR-3H[19] fits at the high-temperature limit (309.5 K) in CD_2Cl_2. The enthalpy change, ΔH, for **5b** → **6b** was determined to be −5.4 kJ mol^{-1}, indicating that the bidentate acyl is only slightly more stable than its alkyl isomer. The low-temperature-limiting spectrum shows two, nonisochronous carbonyl triplets (δ = 218.2 ppm (J = 20.8), 208.5 ppm (J = 16.2)), which can be confidently assigned[20] to the carbonyls trans to I and trans to Me, respectively, for the cis structure **5b**. ^{13}C magnetization transfer experiments at 223 K demonstrated that the acyl site of **6b** *specifically* exchanged with the 218.2 ppm CO site of **5b**, which is, vide supra, cis to the methyl group. Consistent with these results is the observation that the diastereotopic o-C_6H_5 resonances are *not* averaged even at the fast-exchange limit. Thus, if the phosphorus ligands remain mutually trans, the insertion cannot pass through any intermediate having an axial symmetry plane.

Line-shape calculations[19] of the exchanged-broadened ^{13}C NMR spectra incorporated the specific site exchange of eq 1 demonstrated by magnetization transfer and allowed for the temperature dependence of the equilibrium constant. Good fits of the experimental data were then obtained by using the exchange rate as the only variable (cf. Figure 1). The temperature dependence of the ^{13}C DNMR exchange rates established activation parameters, $\Delta H^{\ddagger}$ = 41.9 ± 4 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −28 ± 15 J mol^{-1} K^{-1}, for the insertion (cf. Table I).

At 211 K, the bidentate acyl **6b** rapidly and quantitatively coordinates carbon monoxide to give the monodentate acyl *cis,-trans*-$Fe(CO)_2(PPh_2Me)_2(C(O)Me)I$ (**8**), which slowly isomerizes to afford *trans,trans*-**8** as the sole thermodynamic product. Similar stereochemical results have been reported for the carbonylation of other related *cis,trans*-$Fe(CO)_2L_2(Me)X$[6,20,21] alkyls and bidentate acyls.[6] Although a bimolecular mechanism involving back-side attack of CO concerted with η^2-acyl → η^1-acyl interconversion can in principle account for the observed stereochemistry, we believe that a dissociative mechanism is more likely. Opening of the bidentate acyl **6b** gives the 16e⁻ η^1-acyl intermediate **7**, which is to some degree "protected" from external nucleophilic attack at the vacant site by the adjacent acyl oxygen. Thus **7** is not intercepted by CO and facile isomerization occurs, affording an "unprotected" 16e⁻ intermediate **7′** with apical acyl. Intermediate **7′** rapidly captures CO to give the observed cis,trans kinetic product.[22] We note here that exchange of the R and O positions via rotation of the monodentate acyl-metal bond in **7** followed by alkyl migration provides a stereospecific route to **5b**.

If we accept the proposal that coordination of an external ligand by the η^2-acyl is not concerted but rather a two-step process, our results imply that although coordinatively saturated bidentate acyls

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(15) The 60-MHz ^1H NMR spectrum of **6b** has been reported; cf. ref 4. We have reexamined the ^1H NMR spectrum at 300 MHz at ambient temperature and find that while the gross features remain, the resonance assigned to η^2-C(O)CH_3 is a slightly broadened triplet.

(16) Unlabeled **6b** was prepared by using the method of Cardaci et al.; cf. ref 4. The specifically enriched **6b** used in this study was prepared from labeled $(PPh_2Me)_2Fe(C^*O)_3$ by using a modification of the photochemical procedure reported by Berke; cf. ref 6. Its structure was verified by comparison of ^1H and ^{13}C NMR spectra with those determined from an authentic sample.

(17) The low-temperature solubility of **6b** is appreciably greater in THF. At 203 K, both carbonyl resonances were well-resolved triplets. Similar dynamic behavior occurred on warming.

(18) **6b**: 75-MHz $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 220 K) δ *C*(O)Me, 282.3 (t, J = 17.3); CO, 221.4 (t, J = 38.0); *ipso*-C_6H_5, 136.4 (t, J = 23.1), 135.4 (t, J = 24.7); *o*-, *m*-C_6H_5, 133.9 (t), 131.7 (t), 130.7 (t), 130.2 (t); *p*-C_6H_5, 128.7 (m); C(O)*Me*, 13.5 (t, J = 14); PMe, 13.6 (t, J = 14.0). **5b**: 75-MHz $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 220 K) δ CO, 218.2 (t, J = 20.8), 208.5 (t, J = 16.2); C_6H_5 135.1, (t, J = 21.4), 133.1, 130.5, 130.5; PMe, 18.1 (t, 16.5). The ^{13}C NMR spectrum of specifically labeled **6b** was identical except for intensity increases of the carbonyl resonances; cf. Figure 1. The chemical shifts reported for the carbonyl groups of **5b** were measured by using an enriched sample. Coupling constants reported for the carbonyl resonances of **5b** were determined in THF-d_8 at 203 K.

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(22) Isotopic labeling studies to test this point are currently underway.

are both thermodynamically and kinetically accessible from their isomeric alkyl structures, they are not *required* intermediates in CO insertion chemistry. Bidentate acyl coordination reversibly traps the intermediate, producing an observable species in sterically conjested systems.[23] Reversion to a monodentate coordination mode precedes conversion to the six-coordinate product in a manner analogous to the "dissociative trapping" mechanism demonstrated by Halpern[24] for nucleophilic catalysis of migratory CO insertion.

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(23) We thank a referee for pointing out that other factors such as solvation may also be important in determining the position of the methyl ↔ η^2-acyl equilibrium, particularly when the energy change is very small. Examination of **6b** in THF shows that the equilibrium is shifted significantly toward the alkyl isomer **5b** compared to methylene chloride.

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Structural Consequences of Nickel versus Macrocycle Reductions in F430 Models: EXAFS Studies of a Ni(I) Anion and Ni(II) π Anion Radicals

Lars R. Furenlid,[1a] Mark W. Renner,[1a] Kevin M. Smith,[1b] and Jack Fajer*,[1a]

Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973
Department of Chemistry, University of California
Davis, California 95616
Received September 11, 1989

Factor 430 (F430) is a nickel tetrapyrrole (hydrocorphin) found in methyl coenzyme M reductase, the enzyme that catalyzes the final stages of the reduction of carbon dioxide to methane in methanogenic bacteria.[2] Detection of EPR signals attributable to Ni(I) in the catalytic cycle of *Methanobacterium thermoautotrophicum*[3] has led to intensive investigations of the reductive chemistry of F430 and of nickel porphyrins and hydroporphyrins.[4-8] Reduction of Ni(II) F430[4] and isobacteriochlorins[5,6] unambiguously results in Ni(I) species whereas porphyrins,[5-9] chlorins,[5,6] and hexahydro- and octahydroporphyrins[6] yield anions variously ascribed to Ni(I) or Ni(II) π radicals with some metal character.

The structural consequences associated with the reduction of Ni(II) to Ni(I) in porphyrin derivatives are unknown.[9] Changes as large as 0.2 Å in Ni–N distances have been suggested by Stolzenberg and Stershic for isobacteriochlorins.[5] They and Renner et al.[6] further suggested that, in addition to the relative ordering of the Ni(II) and π* orbitals, the ability of the macrocycle to accommodate the larger Ni(I) controlled the sites of reduction, i.e., Ni(I) versus π anion radical.

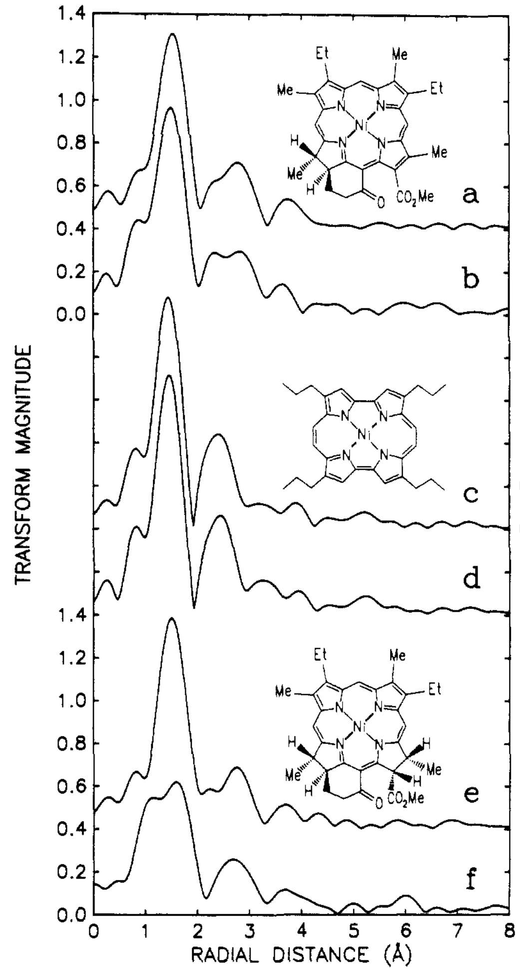

Figure 1. Chemical structures and Fourier transforms of k^2 weighted EXAFS oscillations for (a) Ni(II) chlorin, (b) Ni(II) chlorin π anion radical, (c) Ni(II) porphycene, (d) Ni(II) porphycene π anion radical, (e) Ni(II) iBC,and (f) Ni(I) iBC anion. Comparable spectra are offset for clarity (in THF; Bu_4N^+ is the counterion in all reduced species; T = 298 K).

We present here EXAFS results for the Ni(II) radical anions of a chlorin and a porphycene and for the Ni(I) anion of an isobacteriochlorin (iBC) that clearly demonstrate the structural consequences of metal versus macrocycle reductions.

Low-spin Ni(II) chlorin,[10] porphycene[11] and iBC[10] (see Figure 1 for structures) undergo reversible one-electron electrochemical reductions in tetrahydrofuran[6,11] ($E_{1/2}$ = −1.04, −0.80, and −1.33 V, respectively, in the presence of 0.1 M $(Bu)_4NClO_4$ vs SCE). Upon reduction, the chlorin and the porphycene exhibit optical spectra diagnostic of π anion radicals: loss of the visible bands and the appearance of weak broad bands stretching into the near infrared region.[6,11-13] In frozen THF, at 115 K, the reduced species display EPR spectra typical of free radicals[6,11,13] (the chlorin spectrum includes a shoulder on the high-field side,[6,13] also noted by Kadish et al.[8] for the π anion of a Ni porphyrin, sug-

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(13) Data are included in the supplementary material.

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