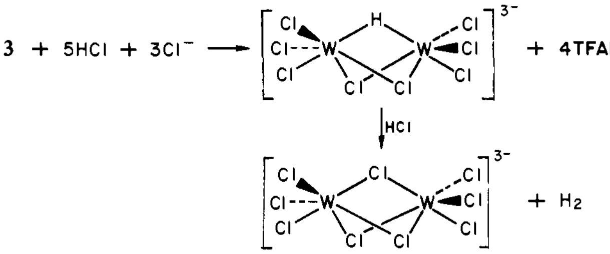
except for bands at 1538 and 1240 cm^{-1}. We tentatively assign these bands to the symmetric and antisymmetric W–H–W vibrations[22] of confacial bioctahedral $W_2Cl_8H^{3-}$. These bands are absent when the reaction is run in concentrated aqueous DCl and are replaced by new bands at 1120 and 896 cm^{-1}. Dissolution of the mixture in aqueous HCl produced hydrogen and clean conversion (by UV spectroscopy) to $W_2Cl_9^{3-}$ (eq 5).[25]



(5)

X-ray quality crystals of unsolvated **3** have not yet been isolated, but we have prepared and crystallized (by vacuum sublimation) a diglyme adduct of **3**. The structure of $W_2(O_2CCF_3)_4{\cdot}{}^2/_3(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ was determined from diffraction data collected at −160 °C.[27] A view of the structure, which emphasizes the "tridentate" nature[29] of the diglyme, is shown in Figure 1. Tungsten dimers A and B are crystallographically independent and are in the same unit cell as the polyether.[30] Tungsten dimer B′ is related to B by a unit translation. As anticipated, each $W_2(TFA)_4$ molecule has idealized D_{4h} symmetry with the tungsten atoms bridged by trifluoroacetate ligands. The W–W bond lengths are 2.211 (2) and 2.207 (2) Å for dimers A and B, respectively. The axial solvent oxygen contacts with the dimers vary from 2.48 (1) to 2.70 (1) Å (see Figure 1). Full details of the structure will be reported elsewhere.

The results presented here clearly demonstrate that quadruply bonded tungsten(II) carboxylate complexes are isolable and stable in the absence of potential oxidizing agents. We believe that they will serve as valuable synthetic intermediates in dimeric tungsten(II) chemistry. Further elaboration of the chemistry and physical properties of tungsten(II) carboxylates will be reported in the near future.

Acknowledgment. The Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for support of this work. We also thank the Marshall H. Wrubel Computing Center, Indiana University, for a generous gift of computing time. The Finnegan mass spectrometer used in this research was purchased, in part, by funds provided by the National Science Foundation.

Supplementary Material Available: The solid-state Raman spectra of $Mo_2(O_2CCF_3)_4$ and $W_2(O_2CCF_3)_4$ and tables of fractional coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(22) These vibrational assignments fit nicely with the data of Katovic and McCarley[23] on $Mo_2Cl_8H^{3-}$ and $MoWCl_8H^{3-}$. Essentially identical results are obtained with $W_2(mhp)_4$[4] dissolved in concentrated aqueous HCl and DCl.[24]

(23) Katovic, V.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1268–1270.

(24) Sattelberger, A. P.; McLaughlin, K. W., unpublished results.

(25) Metathetical primary products such as $W_2Cl_8^{4-}$ or $W_2Cl_7(H_2O)^{3-}$ are conceivable intermediates in this reaction, but we have no proof for their existence. For a discussion of binuclear oxidative addition to molybdenum–molybdenum quadruple bonds, see ref 26.

(26) Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1976**, *15* 522–524.

(27) $W_2(TFA)_4{\cdot}{}^2/_3(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 23.046$ (9), $b = 9.108$ (2), $c = 9.222$ (2) Å; $\alpha = 99.64$ (1), $\beta = 59.45$ (1), $\gamma = 103.55$ (1)°; $V = 1617.9$ Å^3; ρ (calcd) = 2.800 g cm^{-3} for M_r 909.2 and $Z = 3$. Diffraction data were collected at −160 °C by a θ–2θ scan technique with equipment described in detail elsewhere.[28] Data were corrected for absorption (μ 110.35 cm^{-1}) and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, excluding diglyme hydrogen atoms, have been located and their positional and thermal parameters (anisotropic for W, C, O, and F) refined. The current discrepancy indices are $R_f = 0.047$ and $R_{wf} = 0.046$ for those 3486 reflections with $F_o \geq 3.0\ \sigma(F_o)$. The limits of data collection were $6 \leq 2\theta \leq 45°$ (Mo Kα radiation).

(28) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

(29) (a) The crystal structure[29b] of $Mo_2(O_2CPh)_4{\cdot}2(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ reveals two dilgyme molecules bound axially to the molybdenum(II) carboxylate in a monodentate fashion, i.e., one methoxy oxygen from each solvent molecule binds to the dimer. The Mo⋯O distance in this example is 2.633 (6) Å. (b) Collins, D. M.; Cotton, F. A.; Murillo, C. A. *Inorg. Chem.* **1976**, *15*, 2950–2951.

(30) The symmetry related partner of tungsten dimer B has not been included in the drawing.

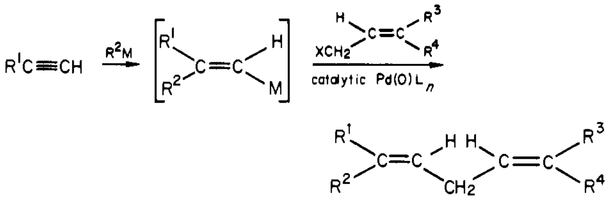
Palladium-Catalyzed Stereo- and Regiospecific Coupling of Allylic Derivatives with Alkenyl- and Arylmetals.[1] A Highly Selective Synthesis of 1,4-Dienes

Hajime Matsushita† and Ei-ichi Negishi*

Department of Chemistry, Purdue University
Lafayette, Indiana 47907

Received December 22, 1980

We wish to describe a remarkably facile and highly selective Pd-catalyzed cross-coupling reaction[2] of alkenylmetals containing Al or Zr with allylic halides or acetates, which not only proceeds with essentially complete retention of the stereo- and regiochemistry of both alkenyl and allyl groups but is free from the formation of the homocoupled products. When used in conjunction with hydroalumination,[3] hydrozirconation,[4] or carboalumination[5] of acetylenes, the reaction provides a uniquely expeditious route to 1,4-dienes[6,7] (eq 1). We further report that the corresponding



(1)

R^1 = carbon group; R^2 = H or alkyl; R^3 and R^4 = two hydrogens or two alkyl groups; M = Al or Zr

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† On leave from the Japan Tobacco & Salt Public Corp.

(1) Selective Carbon–Carbon Bond Formation via Transition-Metal Catalysis. 18. Part 17: Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276.

(2) (a) For a review, see: Negishi, E. In "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum: New York, 1978; p 285. (b) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (c) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. (d) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821. (e) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1977**, 683. (f) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (g) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (h) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254. (i) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358. (j) Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298. (k) Kobayashi, M.; Negishi, E. *J. Org. Chem.* **1980**, *45*, 5223.

(3) Wilke, G.; Müller, H. *Liebigs Ann. Chem.* **1960**, *629*, 222.

(4) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. See also: Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(5) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252.

(6) The reactions of allylmetal derivatives with alkenyl halides are generally nonstereoselective. For a review on the reaction of π-allylnickel complexes with organic halide, see: Semmelhack, M. F. *Org. React.* **1972**, *19*, 117.

(7) Stereo- and regiodefined alkenylmetals containing Al, B, and Cu have been shown to cross couple with allylic halides. The scope of the selective alkenyl–allyl coupling involving Al and B is practically limited to γ-unsubstituted allylic halides. Although the reactions of alkenylcoppers with allylic electrophiles are highly promising, examples of the reactions of stereodefined alkenylcoppers with stereodefined allylic electrophiles appear to be essentially unknown. Al: (a) Lynd, R. A.; Zweifel, G. *Synthesis* **1974**, 658. (b) Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927. (c) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. (d) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215. B: Yamamoto, Y.; Yatagai, H.; Sonoda, A.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1976**, 452. Cu: (a) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* **1971**, 2583. (b) Corey, E. J.; Cane, D.; Libit, L. *J. Am. Chem. Soc.* **1971**, *93*, 7016. (c) Raynolds, P. W.; Manning, M. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1977**, 499. (d) Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, 826.

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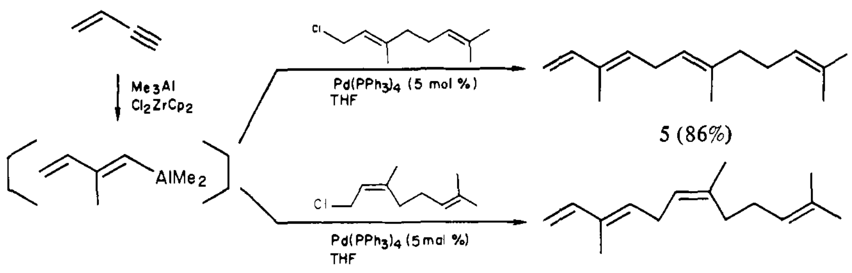

5 (86%)

6 (77%)

(2)

reaction of arylmetals, such as those containing Zn, can also be markedly promoted by Pd catalysts, although that of simple alkylmetals, such as those containing Al or Zn, does not seem to be catalyzed by them. Consequently, the results herein reported significantly broaden the scope of the Pd-catalyzed allylation involving allylic electrophiles[8,9] which has been essentially limited to the allylation of a few limited types of enolates[8] and organometals containing highly electronegative metals.[10]

Specifically, (*E*)-(2-methyl-1-octenyl)dimethylalane (**1**), prepared by the Zr-catalyzed carboalumination[5] of 1-octyne with Me$_3$Al, reacts with 1 equiv of allyl bromide or isoprenyl chloride in THF under the influence of 5 mol % of Pd(PPh$_3$)$_4$ to produce the expected cross-coupled products **2** and **3** in 90 and 98% yields, respectively. Significantly, each of these reaction mixtures displays essentially one GLC peak in the product region. In the absence of the Pd catalyst the yields of the cross-coupled products, after 1 h, are negligible (<1-2%). Therefore, these reactions are indeed markedly catalyzed by the Pd complex. Using isoprenyl chloride as a model allylic halide the scope of the reaction has then been briefly explored. Under mild catalytic conditions comparable to those used above, simple alkylmetals, such as *n*-butyllithium (28%), *n*-butylzinc chloride (≤trace), and trimethylalane (≤trace), give the expected cross-coupled products only in very low yields, the yield for each reaction being indicated in parentheses. On the other hand, (*E*)-1-octenylchlorobis(η^5-cyclopentadienyl)zirconium[4] (97%), and phenylzinc chloride[11] (97%) readily give within 1 h at room temperature the expected isoprenylated derivatives in the yields indicated in parentheses. In the absence of Pd(PPh$_3$)$_4$ no cross-coupled product is formed from the alkenylzirconium derivative in 1 h. Phenylzinc chloride does give isoprenylbenzene in 57% yield after 24 h along with biphenyl (10% based on phenylzinc chloride) and 1,1-dimethyl-2-propenylbenzene (7%). The product yield after 1 h, however, was only 3%. Clearly, both of these reactions are catalyzed by Pd(PPh$_3$)$_4$. Solely on the basis of these factual observations, one may tentatively conclude that alkenyl- and arylmetals containing Al, Zr, or Zn readily undergo the Pd-catalyzed cross coupling with allylic halides, while alkylmetals do not. We have also found that allyl acetate reacts with **1** to give **2** in 84% yield in the presence of 5 mol % of Pd(PPh$_3$)$_4$ in 1 h at room temperature, whereas no reaction occurs in the absence of the catalyst.

1,4-Dienes are ubiquitous in nature. Although a number of methods are available for their synthesis via cross coupling,[6,7] few are highly stereo- and regiospecific. It is therefore gratifying to find that the reaction of geranyl chloride[12] with (*E*)-(2-methyl-1-hexenyl)dimethylalane[5] in the presence of 5 mol % of Ph(PPh$_3$)$_4$ produces the expected cross-coupled product **4** in 92% isolated yield with ≥98% retention of the stereo- and regiochemistry of both of the participating carbon groups. This procedure was then directly applied to the one-step synthesis of α-farnesene[13] (**5**) from geranyl chloride and butenyne[14] in 86% isolated yield (98% GLC yield), as shown in eq 2. Furthermore, the use of neryl chloride[12] cleanly gives the *Z*-isomer **6** in 77% isolated yield in an analogous manner. The stereochemical assignments are based on the comparison of the ^{1}H and ^{13}C NMR chemical shifts for the allylic methyl groups[15] in **5** and **6**. On the basis of GLC examination as well as ^{1}H and ^{13}C NMR spectra, we estimate that the overall stereoselectivity and regioselectivity are ≥98% in each case.

The following procedure for the synthesis of α-farnesene is representative. To a solution of trimethylalane (*pyrophoric!*) (2.88 g, 3.84 mL, 40 mmol) and dichlorobis(η^5-cyclopentadienyl)zirconium (2.24 g, 8 mmol) in 1,2-dichloroethane (30 mL) is added at room temperature under nitrogen 1-buten-3-yne (1.04 g, 20 mmol) in xylene.[14] After stirring the reaction mixture for 12 h at room temperature, geranyl chloride (3.45 g, 20 mmol), tetrakis(triphenylphosphine)palladium (1.15 g, 1 mmol), and THF (40 mL) are added at 0 °C. The reaction mixture is stirred for 3 h at room temperature, treated with water (30 mL), and extracted with pentane. The extract is washed with aqueous NaHCO$_3$ and dried over MgSO$_4$. After filtration and evaporation, simple distillation yields 3.50 g (86%) of α-farnesene: bp 30-32 °C (0.15 mmHg); $n^{23}{}_{\mathrm{D}}$ 1.4977; IR (neat) 3080 (w), 2960 (s), 2900 (s), 1664 (w), 1635 (m), 1601 (m), 981 (m), 883 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.59 (s, 3 H), 1.63 (s, 3 H), 1.66 (s, 3 H), 1.74 (s, 3 H), 2.03 (m, 4 H), 2.82 (t, J = 6 Hz, 2 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 11.62, 16.07, 17.63, 25.69, 26.89, 27.35, 39.88, 110.37, 122.36, 124.50, 131.10, 131.74, 133.79, 135.55, 141.69; high-resolution MS. Anal. Calcd. for C$_{15}$H$_{24}$: 204.188. Found: 204.191.

It is worth noting that the observed stereochemistry is in sharp contrast with that of the reaction of π-allylnickel derivatives with organic halides which is reported to involve extensive stereochemical scrambling.[6] In this regard, however, it would be of interest to examine the reaction of π-allylnickel derivatives with organometallic reagents.

Although we have been preoccupied with the synthetic aspects, the following observations shed some light on the mechanism. Treatment of the dimer of π-allylpalladium bromide[16] (**7**) with 4 equiv of PPh$_3$ (P/Pd = 2:1) has been reported to give σ-allylbromobis(triphenylphosphine)palladium[17] (**8**). The reaction of **8** with **1** in a 1:1 molar ratio gives **2** in 90% yield at a rate at least comparable to the corresponding catalytic reaction.[18] It

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[8] (a) For a recent review, see: Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2591.

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[11] Prepared in situ by treating phenylmagnesium bromide with 1 equiv of anhydrous ZnCl$_2$.

[12] Calzada, J. G.; Hooz, J. *Org. Synth.* **1974**, *54*, 63.

[13] Murray, K. E. *Aust. J. Chem.* **1969**, *22*, 197.

[14] Purchased from Chem. Samples Co., Columbus, OH, as a 50% solution in xylene. A detailed study of the Zr-catalyzed carbometallation of functionalized acetylenes is in progress with C. L. Rand.

[15] In terpenoids, such as **5** and **6**, the allylic methyl groups of the *E* isomers exhibit ^{1}H and ^{13}C NMR signals in the ranges 1.60 ± 0.04 and 15 ± 4 ppm, respectively, whereas the corresponding signals for the *Z* isomers appear at 1.70 ± 0.04 and ≥20 ppm, respectively. For pertinent papers, see ref 10b and references therein.

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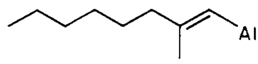

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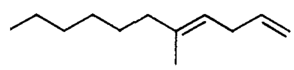

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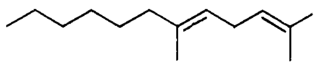

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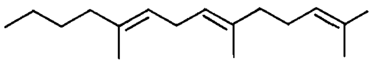

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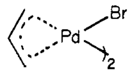

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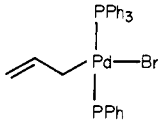

8

is therefore entirely possible that, unlike Trost's reaction of π-allylpalladium derivatives with "soft" carbanions which has been shown to involve the backside attack of π-allylpalladium cations by the carbanionic species,[8] our reaction might involve attack of σ-allylpalladium derivatives by organometals via transmetalation which is followed by reductive elimination, as we have suggested for various other Pd-catalyzed cross-coupling reactions.[2]

Acknowledgment. We thank the National Institutes of Health and the Japan Tobacco & Salt Public Corp. for support of this research.

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(18) The reaction of **7** with the same alkenylalane also produces **2** in 42% yield. The reaction, however, is accompanied by competitive isomerization of **2** into a conjugated diene which is complete in 10 h as well as by formation of 2-methyl-1-octene (~40%). Addition of a small aliquot (~5 mol %) of the above reaction mixture to pure **2** does include the same isomerization but that of **7** to **2** does not.

High-Valent Iron–Porphyrin Complexes Related to Peroxidase and Cytochrome P-450

John. T. Groves,* Robert C. Haushalter, Mikio Nakamura, Thomas E. Nemo, and B. J. Evans

Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109

Received December 8, 1980

The higher valent iron porphyrin intermediates which play an important role in the mechanisms of hemoproteins such as the peroxidases[1] and cytochromes P-450[2] are poorly understood. The enigmatic spectral characteristics of the oxidized states of the peroxidases and the lack of simple model compounds of similar structure and oxidation state have elicited much conjecture regarding the structure of such species. For example, the properties of compounds I of horseradish peroxidase[3] (HRP) and chloroperoxidase[4] are consistent with an iron(IV)–porphyrin π-cation radical formulation,[5] whereas the two-electron oxidized intermediate of cytochrome c peroxidase appears to have unpaired electron density on a protein functional group.[6] No reactive iron–oxygen species has ever been observed for cytochrome P-450. This fact has been used to support recent suggestions[2a] that a protein-derived radical may be responsible for the C–H bond cleavage of cytochrome P-450 mediated aliphatic hydroxylation reactions. We report here the preparation and characterization of a new high-valent iron-porphyrin complex with spectral properties similar to those reported for horseradish peroxidase compound I and reactivity toward olefins indicative of cytochrome P-450 activity.

The oxidation of chloro-5,10,15,20-tetramesitylporphinatoiron(III)[7] [TMPFeCl] with 1.5 equiv of *m*-chloroperoxybenzoic acid in methylene chloride–methanol (4:1) at −78 °C produced a green intermediate A. This change was detected by the disappearance of the β-pyrrole hydrogen resonance at δ 120 in the ^{1}H NMR spectrum of TMPFeCl and the appearance of a new resonance of equivalent intensity at δ −27. Similarly, the EPR signals of high-spin TMPFe(III)Cl were absent in toluene solutions of A.

The ^{1}H NMR spectrum of A at −77 °C in methylene chloride–methanol showed absorbances at δ 68 (*m* H), 26 and 24 (*o*-methyl), 11.1 (*p*-methyl) and −27 (β-pyrrole H).[8] These chemical shifts were highly temperature dependent and obeyed the Curie law between −26 and −89 °C. The magnetic susceptibility of A was determined by the Evans method[9] to be 4.2 μ_B, slightly larger than expected for an $S = {}^3/_2$ system. The visible spectrum of A showed a broad Soret band at 406 nm and another broad band centered at 645 nm. The Mössbauer spectrum of A derived from ^{57}Fe-enriched TMPFeCl showed a quadrupole doublet centered at 0.05 mm/s (ΔE_q = 1.49 mm/s).[10] A showed no strong EPR absorbances above 20 K.[11]

The distinctive visible spectrum suggests that A is a porphyrin π-cation radical.[5] The large downfield shifts of the proton resonances of the pendant mesityl groups indicate that significant spin density resides on the porphyrin meso carbons as would be expected for the loss of an electron from the a_{2u} porphyrin π orbital.[12] The small isomer shift in the Mössbauer spectrum of A is similar to that reported for HRP I (δ = 0.08 mm/s, ΔE_Q = 1.25 mm/s) and is in the range expected for iron(IV).[13] The very high-field position of the β-pyrrole hydrogen resonances in the ^{1}H NMR spectrum of A contrasts sharply with the low-field position of those protons in the spectrum reported[14,20] for a [TPP(cation radical)Fe^{III}]$^{2+}$ or [TPPFe^{IV}]$^{2+}$ and the δ 5.0 position reported by Balch and LaMar for an oxo-TPPFe(IV) complex.[15] High-field proton NMR resonances have been reported for the pyrrole hydrogens of HRP-I[16] and a vinylidene carbene porphinatoiron(III) complex[17] which is, formally, at the same oxidation state.

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