Table I. ^{13}C Nuclear Magnetic Resonance Assignments[a]

position	1a[b]	1b[b]	2
C-1	159.1	155.8	159.6
C-2	123.7	123.2	129.2
C-3	156.1	123.2	153.5
C-4	119.4	155.8	126.2
C-5	39.1	38.2	62.9
$C(CH_3)_3$;	33.1 (1)	33.1 (1)	34.0 (5)
ring position	32.1 (3)		33.8 (1)
in parentheses			31.8 (3)
$C(CH_3)_3$;	29.7 (1)	30.9 (1)	32.0 (1)
ring position	30.9 (3)		30.3 (3)
in parentheses			29.6 (5)

[a] Assignments made by ^{13}C SAT (Varian), ^1H-^{13}C NOE difference, and DEPT techniques. [b] Analysis performed on a mixture of **1a** and **1b**. The relative intensities of peaks in each region of the spectrum were used to assign resonances to either **1a** or **1b**.

composition. Chromatography of the crude material over silica gel yielded di-*tert*-butylcyclopentadiene; overall calculated yield, 90% based on starting cyclopentadiene.

Although tri-*tert*-butylcyclopentadiene can be prepared directly by the reaction of cyclopentadiene and *tert*-butyl bromide, we have found it more convenient to prepare it by *tert*-butylation of di-*tert*-butylcyclopentadiene. The procedure is essentially the same as described above, but 55% aqueous KOH is used. The reaction is monitored by GC, and additional *tert*-butyl bromide and Adogen 464 are added as needed until about half of the mixture has been converted to **2**. After workup to remove KOH, Adogen 464, and amines, the di- and tri-*tert*-butylcyclopentadienes can be separated by distillation, yielding 50% recovered **1**, bp 100–105 °C at 30 Torr, and 30% **2**, bp 135–140 °C at 30 Torr.

Structure proofs relied primarily on ^{13}C NMR, although elemental analyses are consistent with the empirical formulas, $C_{13}H_{22}$ for di-*tert*-butylcyclopentadiene and $C_{17}H_{30}$ for tri-*tert*-butylcyclopentadiene. Chemical shifts and assignments are recorded in Table I. The ^{13}C NMR spectrum of **1a** has previously been reported.[19]

Di-*tert*-butylcyclopentadiene exists as a mixture, the two major isomers being **1a** and **1b** in a 3:1 ratio as determined by gas chromatography. The identity of the two isomers was easily assigned from the ^{13}C NMR spectra of mixtures by the relative intensities of the resonances and the symmetry of **1b**.[21]

Tri-*tert*-butylcyclopentadiene exists as a single isomer, 1,3,5-tris(1,1-dimethylethyl)cyclopentadiene. The downfield position of the ring C-5, 62.9 ppm, compared with that found in **1a** and **1b**, 39.2 ppm and 38.3 ppm, respectively, clearly signals that one of the *tert*-butyl groups is on C-5. The reported position of the C-5 carbon in tetra-*tert*-butylcyclopentadiene, 64.1 ppm,[20] in which one *tert*-butyl is also presumed to be on C-5, supports the assignment.

The predominance of the 1,3,5-isomer arises since it is the only arrangement that does not put *tert*-butyl groups on three adjacent carbons nor two *tert*-butyl groups on adjacent sp^2 carbons. For less sterically bulky substituents, *n*-alkyl groups, trialkyl derivatives are also predominantly single isomers, but they are the 1,2,4- rather than 1,3,5-isomers,[1] placing all three alkyl groups on sp^2 carbons.

The conditions under which these reactions are run, strong base in the presence of a phase-transfer catalyst, inevitably favor elimination reactions with tertiary substrates.[12-14] Consequently, the operation of previously recognized substitution mechanisms involving tertiary halides seems unlikely. The fact that alkylation competes so favorably with elimination argues for a unique reaction pathway involving cyclopentadiene prior to the rate-determining step. Although the delineation of the mechanism of this unique transformation would be interesting, we have no plans to do so at this time.

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(21) A small amount of a third isomer, probably 2,5-di-*tert*-butylcyclopentadiene (**1c**) is also apparently present. Our colleague Dr. J. S. McKennis observed that, on standing, a sample of **1** yielded a crystalline precipitate, **3**, mp 120–123 °C. Gas chromatography showed a single peak, neither **1a** nor **1b**, but at only a slightly longer retention time, suggesting an isomeric $C_{13}H_{22}$ compound. Dr. McKennis believes that all of this data is consistent with **3** being the self-Diels–Alder dimer of **1c**. The ^{13}C NMR spectrum of **3** showed at least 17 unique carbons of the 18 expected for the dimer. Note that **1c** has both a diene and an ene with no *tert*-butyl substituents on the reactive carbons. Work to confirm the structure of **3** is in progress.

Synthesis of Substituted Pyridinones from the Combination of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with Phosphinimines and Alkynes

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The pyridinone ring is an integral unit of many important molecules. 2-Pyridinones in particular have therapeutic value[1a,2] and are versatile synthetic intermediates for many alkaloids.[2] A continuing need exists for improved synthetic routes to pyridinones that tolerate a wide variety of substituents with a high degree of regiospecificity in ring substitution. Previous organometallic routes to 2-pyridinones have generally involved regiospecific coupling of two alkynes with an isocyanate, yielding tri- or pentasubstituted products.[3] Reported herein is a complementary but mechanistically different metal-assisted route to mono-, di-, and trisubstituted 2-pyridinones involving reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines and alkynes.

We earlier reported the high-yield reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines to form the binuclear complexes **1** shown in Scheme I.[4] These complexes have since been found to readily insert alkynes into the Fe–carbon bond under photochemical conditions[5] to give the ferrapyridine complexes **2a–g**. These latter species were isolated in 72–87% yields as microcrystalline solids and have been spectroscopically characterized,[6] with complex **2e** (R^1, R^2, R^3 = Ph) fully defined by an X-ray diffraction study, Figure 1,[7] Terminal alkynes insert regiospecifically into the

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(5) Photolyses were conducted in Pyrex Schlenk vessels by using an unfiltered Hanovia 450-W medium-pressure Hg discharge lamp (Ace Glass, Inc.; catalog no. 7825-35) in a Pyrex water-cooled immersion well by placing the Schlenk vessel with a CH_2Cl_2 solution of alkyne and complex **2** adjacent to the lamp at the midpoint of the lamp's arc.

(6) **2e**: Anal. C, H. IR (CH_2Cl_2): ν_{CO} = 2061 (m), 2013 (vs), 1988 (s), 1956 (w) cm^{-1}. MS: m/z = 575 (M^+). ^1H NMR (CD_2Cl_2): δ 8.13 (d, 1 H, J = 5.1 Hz, C*H*), 7.59–6.92 (m, 10 H, 3Ph), 3.64 (d, 1 H, J = 5.1 Hz, C*H*). ^{13}C NMR (C_6D_6): δ 211.0, 208.7, 208.0 (CO), 181.0 (dd, N=*C*H, $^1J_{CH}$ = 167.7 Hz, $^2J_{CH}$ = 2.6 Hz), 179.0 (m, *C*Ph), 154.9–121.8 (Ph), 109.0 (d, *C*Ph, $^2J_{CH}$ = 4.0 Hz), 54.1 (dd, *C*H, $^1J_{CH}$ = 158.9 Hz, $^2J_{CH}$ = 12.0 Hz).

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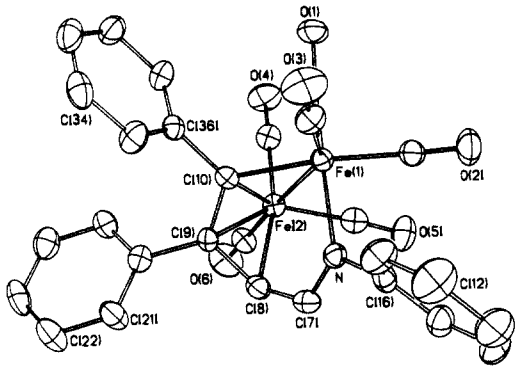
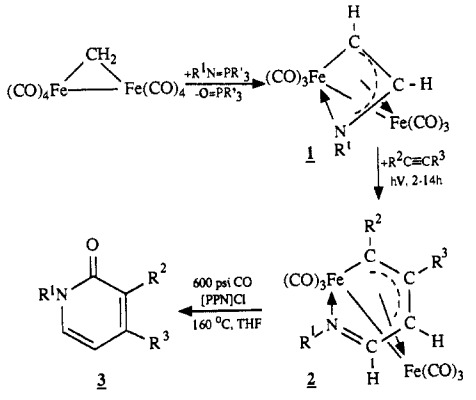


Figure 1. Molecular structure and labeling scheme for **2e** (40% thermal ellipsoids). Fe(1)-Fe(2), 2.632 (1) Å; Fe(1)-N, 2.028 (5) Å; Fe(1)-C(10), 2.028 (5) Å; Fe(2)-C(8), 2.102 (5) Å; Fe(2)-C(9), 2.085 (5) Å; Fe(2)-C(10), 2.111 (5) Å; N-C(7), 1.283 (7) Å; C(7)-C(8), 1.451 (8) Å; C(8)-C(9), 1.455 (8) Å; C(9)-C(10), 1.404 (7) Å.

Scheme I



Fe-carbon bond of **1** to give only the isomer with the substituted carbon adjacent to the iron center. For example, the ferrapyridine complex formed from reaction of **1** (R^1 = Ph) with PhC≡CH shows three ^{1}H NMR resonances for the ring hydrogens at δ 8.26 (d, J = 5.5 Hz), 5.6 (d, J = 6.1 Hz), and 3.34 (dd), with the coupling pattern implying adjacent hydrogen atoms.

As illustrated in Scheme I, free 2-pyridinones are readily released from the ferrapyridine complexes by heating THF solutions under 600 psi of CO in the presence of 1 equiv of [PPN]Cl or by refluxing acetonitrile solutions in air overnight. The 2-pyridinones **3a-g** shown in Table I were isolated in moderate to high yield by silica gel chromatography and were spectroscopically characterized.[8] Due to the regiospecificity of the alkyne insertion step, monosubstituted alkynes gave 2-pyridinones substituted only in the 3-position. As illustrated by the entries for **3h** and **3i** in Table I, the NBu^t pyridinones can be converted in high yield into NH pyridinones by refluxing in neat CF_3CO_2H followed by aqueous K_2CO_3 workup. The NH pyridinones constitute an important class of biologically active molecules, with **3i** being a patented antiinflammatory agent.[2d] Furthermore, NH pyridinones give potentially wide substituent variability at the nitrogen atom by employing known methods for alkyl, acyl, and aryl substitution at this position.[1b,2b,c] The use of HC≡CSiMe$_3$ to prepare **3g** is significant since the SiMe$_3$ functionality allows for further manipulation at the 3-position by known organic methods.[9]

Table I

compd	R^1	R^2	R^3	yield,[a] %	yield,[b] %
3a	Ph	Bu^t	H	87	57
3b	Bu^t	Bu^t	H	86	66
3c	Bu^t	Ph	H	79	57
3d	Bu^t	Ph	D	79	57
3e	Ph	Ph	Ph	34	16
3f	Bu^t	Et	Et	76	61
3g	Bu^t	SiMe$_3$	H	79	73
3h[c]	H	Bu^t	H	81	62
3i[c]	H	Ph	H	68	54

[a] Isolated yields based on conversion from **2**. [b] Isolated yields based on conversion from $Fe_2(\mu\text{-}CH_2)(CO)_8$. [c] **3h** and **3i** were synthesized by using the same methodology to produce **3b** and **3c** followed by a 48-h reflux in neat CF_3CO_2H.

The reactions of Scheme I offer a convenient synthesis of substituted 2-pyridinones from alkynes, phosphinimines, and the readily available $Fe_2(\mu\text{-}CH_2)(CO)_8$.[10] The method appears to have considerable substituent variability at the 1- and 3-positions, and the yields of the sequential reactions are high. If desired, the entire reaction can be conducted without isolation of any of the intermediates, giving the overall yields from $Fe_2(\mu\text{-}CH_2)(CO)_8$ shown in Table I. Finally, the starting complex $Fe_2(\mu\text{-}CH_2)(CO)_8$ and the intermediate metallacycles are not particularly air sensitive, and the reactions can be readily conducted under tank N_2. Its present limitation is that only mono-, di-, and trisubstituted pyridinones can be formed as the substituents in the 5- and 6-positions are restricted to hydrogen atoms.[4]

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Supplementary Material Available: Tables of atomic positional parameters for **2e**, analytical data for **2a-c,e,f**, and spectroscopic data for **2a-f** and **3a-i** (4 pages). Ordering information is given on any current masthead page.

(7) **2e**: $P2_1/n$, a = 10.797 (3) Å, b = 19.580 (4) Å, c = 12.454 (2) Å, β = 103.61 (2)°, V = 2559.1 (10) Å^3, Z = 4, R_F = 4.78%, R_{wF} = 4.80% for 1915 reflections ($F_o \geq 5\sigma(F_o)$).

(8) **3a**: Anal. C, H. MS (EI): m/z for M$^+$ 227.1310 (calcd), 227.1309 (found). ^{1}H NMR ($CDCl_3$): δ 7.39, 7.36 (m, 5 H, Ph), 7.33 (dd, 1 H, ^3J = 7.0 Hz, ^4J = 2.1 Hz, C*H*), 7.26 (dd, 1 H, ^3J = 6.7 Hz, ^4J = 1.9 Hz, C*H*), 6.18 (dd, 1 H, ^3J = 7.0, 6.7 Hz, C*H*), 1.38 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} = 1653 cm^{-1}.

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Synthetic and Structural Studies of Sapphyrin, a 22-π-Electron Pentapyrrolic "Expanded Porphyrin"

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Sapphyrin, **1**, first discovered serendipitously by Woodward,[1] is one of the more intriguing products to emerge from initial studies directed toward the synthesis of vitamin B_{12}.[1-3] It is a 22-π-electron pentapyrrolic macrocycle that forms a dark blue solid (hence the name sapphyrin) which exhibits an intense Soret-like band at ca. 450 nm ($CHCl_3$) along with weaker Q-type transitions

(1) (a) First reported by R. B. Woodward at the Aromaticity Conference, Sheffield, U.K., 1966 (see ref 1b). (b) Bauer, V. J.; Clive, D. R.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429-6436. To date only tetracoordinated metal complexes have been prepared from these potentially pentadentate ligand systems.

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