temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on alumina eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.126 g (56%) of the desired product as a yellow oil: IR (Nujol) ν 2016.4 (vs), 1927.1 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.32, 6.26 (d, 1 H), 6.04, 5.98 (d, 1 H), 5.41-5.42 (t, 2 H), 5.25-5.27 (t, 2 H), 0.304 (t, 3 H, J_{W-H} = 1.8 Hz), 0.0962 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 229.04, 216.20, 134.14, 133.04, 110.99, 89.03, 88.85, -1.257, -28.61; HRMS exact mass for $C_{14}H_{18}O_3{}^{28}Si^{184}W$, calcd m/z 446.0536, found 446.0529. Anal. Calcd for $C_{14}H_{19}O_3SiW$: C, 37.68; H, 4.292. Found: C, 37.73; H, 4.07.

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Synthesis of 2-Ferrapyridine Complexes and Their Use as Precursors for Substituted Pyridinones and Pyrroles

Thomas E. Snead, Chad A. Mirkin,† Kuang-Lieh Lu, Heather L. Beckman, and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold and Brian S. Haggerty

Department of Chemistry, The University of Delaware, Newark, Delaware 19716

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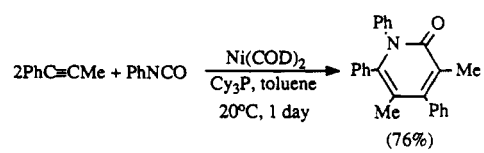
The 2-ferra-3-azetine complexes $Fe_2(\mu\text{-}CHCH{=}NR)(CO)_6$, which form from the reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines, have been found to react photochemically with a variety of alkynes ($R^1C{\equiv}CR^2$) by inserting the alkyne into the four-membered metallacycle to give the 2-ferrapyridine complexes $Fe_2(\mu\text{-}C(R^1)C(R^2)CHCH{=}NR)(CO)_6$. Two of the 2-ferrapyridine complexes have been crystallographically characterized and shown to consist of six-membered metallacycles having adjacent iron and nitrogen atoms with this metallacycle π-coordinated to the second iron atom by three carbon atoms and an Fe-Fe bond. Terminal alkynes (R^1 = Me, Ph, Bu^t, $SiMe_3$) undergo the insertion regioselectively to give only the 2-ferrapyridine isomer with the substituted carbon adjacent to the iron atom. Unsymmetrical internal alkynes insert to give generally a mixture of isomers which is influenced by the steric and electronic nature of the alkyne substituents. The 2-ferrapyridine complex $Fe_2(\mu\text{-}C(Ph)CHCHCH{=}NBu^t)(CO)_6$ was shown to undergo a ring contraction when heated at 160 °C under CO (500 psi) to give the new 2-ferra-3-azetine complex $Fe_2\{\mu\text{-}C[CH{=}C(Ph)(H)]CH{=}NR\}(CO)_6$, which has also been crystallographically characterized and has a vinyl substituent attached to the 3-carbon of the 2-ferra-3-azetine ring. When heated, the 2-ferrapyridine complexes released 2-pyridinones and pyrroles with the ratio of these products dependent upon the ring substituents and the conditions employed. For example, the 2-ferrapyridine complexes prepared from terminal alkynes gave 2-pyridinones as the major products. The reaction of 2-ferrapyridine complexes prepared from internal alkynes gave mixtures of 2-pyridinones and pyrroles. The presence of electron-donating substituents on the 2-ferrapyridine ring favored the formation of 2-pyridinones, as did the presence of halide ion and an atmosphere of CO in the thermolysis reactions.

Introduction

The pyridinone framework is an integral part of many biologically active molecules.[1,2] As a consequence, there has been a great deal of interest in the development of new synthetic procedures for this class of heterocycles.[1] There are many synthetic routes to substituted pyridinones which involve classical organic reactions,[1,2] but only a few organometallic methods for the preparation of these compounds have been described.[3] The latter routes generally involve the metal-assisted regiospecific coupling of an isocyanate unit with 2 equiv of an alkyne to yield either tri- or pentasubstituted 2-pyridinones. For example, Hoberg showed that unsymmetrical alkynes react with isocyanates in the presence of a nickel catalyst to produce 2-pyridinones with the larger substituent in the 4- and 6-positions as illustrated in eq 1.[3b] In a complementary



(76%) (1)

route, Hong and Diversi used a cobalt catalyst to produce trisubstituted 2-pyridinones from terminal alkynes and

† Present address: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.

(1) (a) Earl, R. A.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 4786 and references therein. (b) Tieckelmann, H. In *Pyridine and its Derivatives*; Abramovitch, R. A., Ed.; Interscience: New York, 1974; Vol. 14 Supplement, Part 3, Chapter 12, p 597, and references therein. (c) Smith, D. M. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1976; Vol. 4F, Chapter 24.

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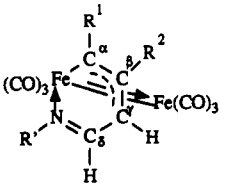
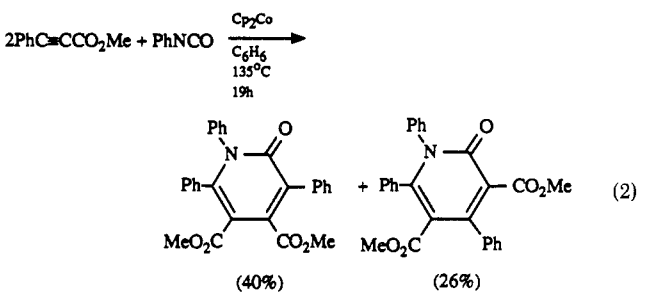
Table I. Yields and Selected NMR Data for Substituted 2-Ferrapyridine Complexes 2a–o Prepared by Reaction 4



reagents		products					^{1}H NMR[b]				^{13}C NMR[c]	
ferraazetine	alkyne		R′	R^1	R^2	yield, %	$C_\alpha R^1$	$C_\beta R^2$	$C_\gamma H$	$C_\delta H$	$C_\alpha C$	$C_\beta C$
1a	MeC≡CH	**2a**	Bu^t	Me	H	9	3.20	5.72	3.20	8.13	35.0	
1a	Bu^{t}C≡CH	**2b**	Bu^t	Bu^t	H	89	1.60	5.70	3.37	8.19	45.4	
1a	Me$_3$SiC≡CH	**2c**	Bu^t	SiMe$_3$	H	69	0.43	5.94	3.57	8.10		
1a	PhC≡CH	**2d**	Bu^t	Ph	H	77		5.90	3.34	8.26	153.8	
1a	MeC≡CMe	**2e**	Bu^t	Me	Me	85	3.11	2.22	3.22	8.05	32.5	23.4
1a	EtC≡CEt	**2f**	Bu^t	Et	Et	86			3.24	8.12	40.8	30.3
1a	PhC≡CPh	**2g**	Bu^t	Ph	Ph	78			3.59	8.44	151.8	141.3
1a	MeC≡CBu^t	**2h**	Bu^t	Me	Bu^t	47	3.37	1.35	3.59	8.06	35.7	36.7
1a	Me$_3$SiC≡CMe	**2i**	Bu^t	Me	SiMe$_3$	59[d]	3.34	0.30	3.3	8.11	35.8	
		2i′	Bu^t	SiMe$_3$	Me	28[d]	0.49	2.36	3.42	8.06		29.7
1a	PhC≡CMe	**2j**	Bu^t	Ph	Me	66[d]		1.93	3.34	8.24	152.3	24.6
		2j′	Bu^t	Me	Ph	20[d]	3.01		3.34	8.24	31.9	141.2
1a	PhC≡CSiMe$_3$	**2k**	Bu^t	Ph	SiMe$_3$	47[d]		−0.08	3.46	8.28	152.9	
		2k′	Bu^t	SiMe$_3$	Ph	25[d]	0.13		3.61	8.15		144.2
1a	MeO$_2$CC≡CMe	**2l**	Bu^t	CO$_2$Me	Me	40	3.93	2.30	3.17	8.08	164.6	24.8
		2l′	Bu^t	Me	CO$_2$Me	26	3.36	3.83	3.74	8.12	34.7	169.8
1a	MeO$_2$CC≡CSiMe$_3$	**2m**	Bu^t	CO$_2$Me	SiMe$_3$	45	3.91	0.23	3.37	8.09	177.2	
		2m′	Bu^t	SiMe$_3$	CO$_2$Me	22	0.43	3.80	3.86	8.03		172.9
1b	Bu^{t}C≡CH	**2n**	Ph	Bu^t	H	78		6.05	3.41	7.93	45.7	
1b	PhC≡CPh	**2o**	Ph	Ph	Ph	72			3.64	8.13	152.3	141.1

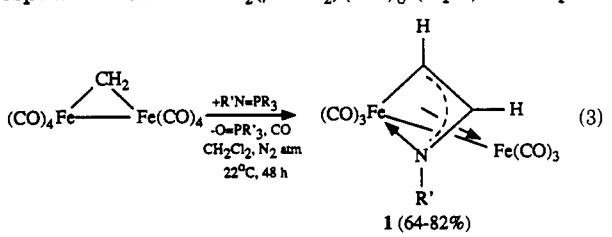
[a] $CDCl_3$ solutions; all values in δ. [b] Chemical shifts refer to either the proton or the substituent attached to the ring carbon atom. Chemical shifts for substituents which gave complex multiplets are omitted (see Experimental Section). [c] Chemical shifts refer to the carbon atom directly attached to the ring. [d] Yields of the isomers were calculated from ^{1}H NMR integrations.

pentasubstituted 2-pyridinones from internal alkynes (eq 2).[3c-e]



(2)

We recently reported the preparation of a series of binuclear 2-ferra-3-azetine complexes by the reaction of phosphinimines with $Fe_2(\mu\text{-}CH_2)(CO)_8$ (eq 3).[4] As previously communicated,[5] these complexes were found to readily insert alkynes into the 2-ferra-3-azetine ring to give



(3)

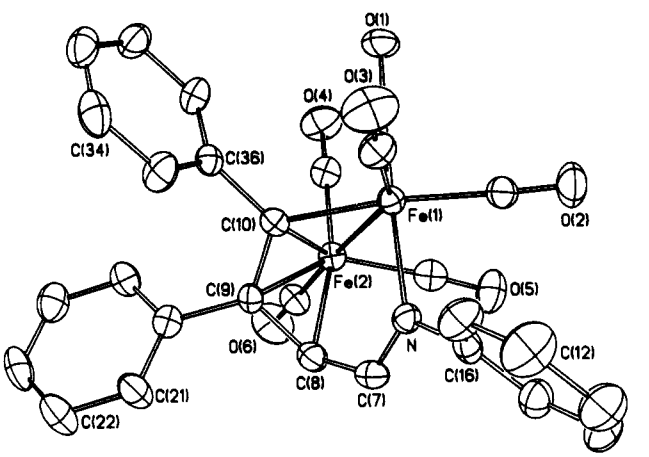


Figure 1. Molecular view and labeling scheme for $Fe_2(\mu\text{-}C\{Ph\}C\{Ph\}CHCHNPh)(CO)_6$ (**2o**). Hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 35% probability.

2-ferrapyridine complexes with generally good regioselectivity. Upon thermal decomposition these 2-ferrapyridine complexes were found to give 2-pyridinones and pyrroles, depending upon the conditions employed. Reported herein are full details of these reactions, including an analysis of the factors which influence the regioselectivity of alkyne insertion, the synthetic advantages and limitations of this approach, and crystal structures of two 2-ferrapyridine complexes along with the structure of a novel 2-ferra-3-azetine complex formed upon thermally induced ring contraction of one of the 2-ferrapyridine complexes.

Results

Photoinduced Reactions of Alkynes with Binuclear 2-Ferra-3-azetine Complexes To Form 2-Ferrapyridine Complexes. Under photochemical conditions, the 2-ferra-3-azetine complexes **1a** and **1b** readily

(3) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081 and references therein. (b) Hoberg, H.; Oster, B. W. *Synthesis* **1982**, 324. (c) Hong, P.; Yamazaki, H. *Tetrahedron Lett.* **1977**, 1333. (d) Hong, P.; Yamazaki, H. *Synthesis* **1977**, 50. (e) Diversi, P.; Ingrosso, G.; Lucherini, A.; Malquori, S. J. *J. Mol. Catal.* **1987**, *40*, 267.

(4) (a) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. *J. Am. Chem. Soc.* **1989**, *111*, 7279. (b) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800.

(5) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 2809.

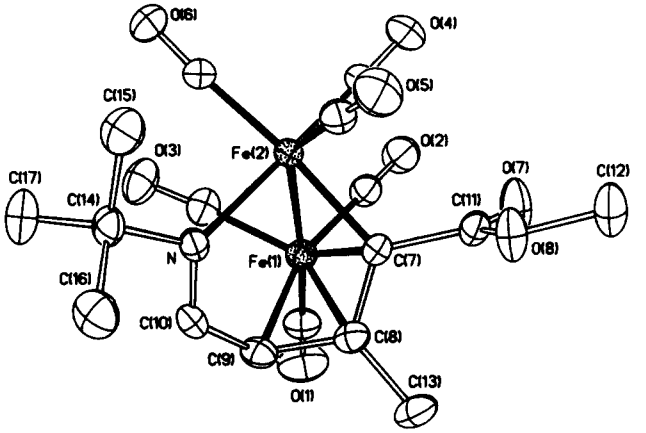
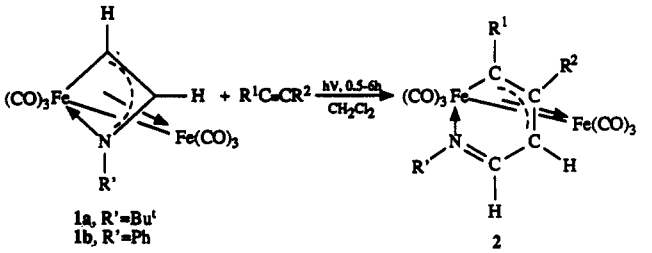


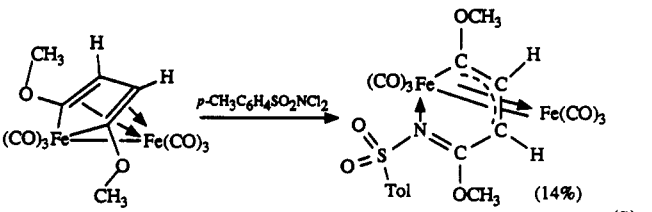
Figure 2. Molecular view and labeling scheme for $Fe_2(\mu$-C{CO_2Me}C{Me}CHCHNBu^t)$(CO)_6$ (**2l**). Hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 35% probability.

insert a variety of alkynes into the Fe–carbon bond to give a series of 2-ferrapyridine complexes (**2**; eq 4). Table I



(4)

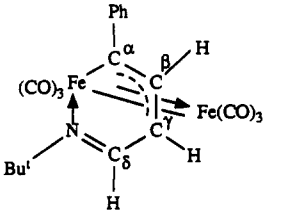
lists the alkynes employed and the yields obtained. These 2-ferrapyridine complexes were isolated as oils or microcrystalline solids and have been spectroscopically characterized. Complexes **2l** and **2o** have been fully defined by X-ray diffraction studies, and ORTEP drawings are shown in Figures 1 and 2. Hubel and co-workers have reported a low-yield route to a complex similar to **2** by the reaction shown in eq 5,[6] and analogues to **2** in which the



(5)

nitrogen atom is replaced by oxygen, sulfur, and tellurium atoms are also known.[7] The 2-ferrapyridine complexes **2d** and **2g** were generated under thermal, rather than photochemical, conditions by reacting the 2-ferra-3-azetine complex **1a** with the appropriate alkyne in refluxing toluene, but the yields were substantially lower than from the photochemical route (see Experimental Section).

Spectroscopic data for complexes **2a–o** are fully consistent with their proposed structures and with the structures crystallographically determined for **2l** and **2o**. Selected ^{1}H and ^{13}C NMR data for the new complexes are summarized in Table I. The ^{1}H NMR spectrum of each complex shows a doublet in the δ 8.5–7.9 region with J_{HH} = 5.0–6.1 Hz assigned to the proton on the δ-carbon adjacent to the nitrogen atom (see labeling scheme illustrated for **2d**).



2d

This resonance compares to the α-proton resonance of pyridine at δ 8.51.[8] The proton attached to the next carbon (C_γ) is observed in the δ 3.6–3.1 range with a coupling pattern consistent with the presence of one or two adjacent hydrogens, as appropriate for the substituents present. For example, complex **2d**, which was prepared from PhC≡CH, shows a doublet of doublets at δ 3.34 (J_{HH} = 5.5, 5.6 Hz) with the coupling arising from the presence of a single hydrogen on each of the two adjacent carbon atoms. Complex **2d** also showed a second doublet at δ 5.90 (J_{HH} = 5.5 Hz) due to the proton on C_β. This resonance was absent when **2d'** was formed from PhC≡CD. The ^{13}C NMR spectra also support the assigned structures, as illustrated by complex **2d**, which shows resonances at δ 186.2 (C_α), 178.3 (ddd, $^1J_{CH}$ = 161.7 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 3.1 Hz, C_δ), 91.0 (dd, $^1J_{CH}$ = 169.8 Hz, $^2J_{CH}$ = 3.1 Hz, C_β), and 49.8 (ddd, $^1J_{CH}$ = 158.7 Hz, $^2J_{CH}$ = 12.2 Hz, $^2J_{CH}$ = 10.7 Hz, C_γ). When **2d** was prepared from PhC≡CD, the δ 91.0 resonance appeared as a triplet due to C–D coupling (J_{CD} = 25.0 Hz), consistent with its assignment to C_β. A C–H correlation NMR experiment on **2d** confirmed the ^{1}H and ^{13}C resonance assignments. A similar analysis of the ^{1}H NMR data showed that all the terminal alkynes examined underwent insertion to give a single regioisomer having the alkyne substituent attached to the α-carbon (see the labeling scheme for **2d**).

The regiochemistry of the 2-ferrapyridines formed from methyl-substituted internal alkynes, $CH_3C{\equiv}CR$, has been assigned on the basis of the following NMR correlation, which indicates that a methyl group attached to C_α shows a ^{1}H NMR resonance near δ 3.0 whereas a methyl group on the β-carbon resonantes near δ 2.0. This conclusion is derived from the ^{1}H NMR data, which unambiguously show that the methyl group of **2a**, formed from MeC≡CH, is attached to C_α and its resonance is at δ 3.20. Complex **2e**, prepared from MeC≡CMe, shows two methyl resonances at δ 2.97 and 1.98. The data for **2a** lead to the assignment of the downfield resonance of **2e** to the methyl group attached to C_α and the upfield resonance to the methyl group on C_β.

A single regioisomer of 2-ferrapyridine **2h** was formed from the reaction of **1a** with MeC≡CBu^t. It showed a ^{1}H NMR methyl resonance at δ 3.37, and the above correlation implies this methyl group is attached to C_α. The reaction of **1a** with MeC≡CSiMe$_3$ gave two regioisomers, **2i** and **2i'**, in a 2:1 ratio with an overall yield of 87%. Similar analysis of the ^{1}H NMR data (Table I) implies that the major isomer **2i** has the methyl group attached to the

(6) (a) Braye, E. H.; Hübel, W. *J. Organomet. Chem.* **1967**, *9*, 370. (b) Rodrique, P. L.; van Meerssche, M.; Piret, P. *Acta Crystallogr.* **1969**, *B25*, 519.

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(8) *Aldrich Catalog of ^{1}H NMR Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, 1983; Vol. 2, spectrum 611A.

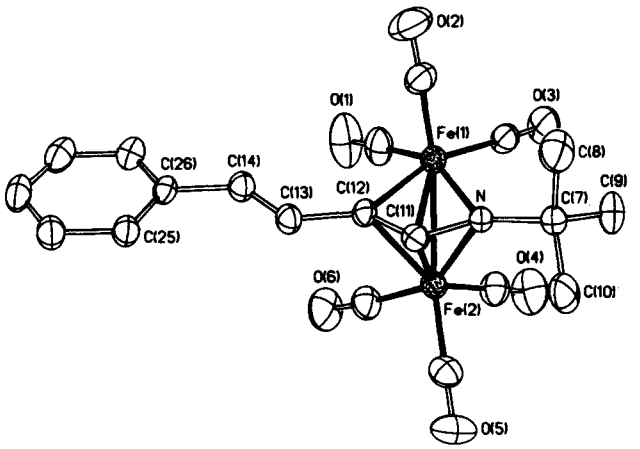


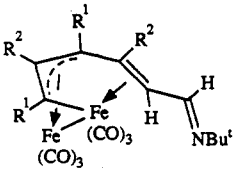
Figure 3. Molecular view and labeling scheme for $Fe_2(\mu$-C{CH=CPh}=CHNBu^t)(CO)$_6$ (**1c**). Hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 35% probability.

α-carbon. The reaction of PhC≡CMe with **1a** gave a 3:1 mixture of regioisomers **2j** and **2j′** with the former in greater yield, having the methyl group attached to the β-carbon. Irradiation of **1a** in the presence of $MeO_2CC{\equiv}CMe$ gave a 1.5:1 mixture of regioisomers **2l** and **2l′**. These isomers were separated by silica gel chromatography, and pure samples of each were obtained. The ^{1}H NMR spectrum of the major isomer **2l** showed a ring methyl resonance at δ 2.30, implying its location on the β-carbon. This assignment was then confirmed by an X-ray diffraction study, the results of which are shown in Figure 1. Irradiation of CH_2Cl_2 solutions of each of the pure isomers gave no isomerization in either case, indicating that the photochemical insertion reaction is irreversible and that the observed product ratio is the result of a kinetic distribution of isomers.

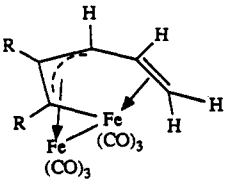
Reaction of **1a** with PhC≡CSiMe$_3$ gave a 2:1 mixture of regioisomers **2k** and **2k′**. The regiochemistry of the major isomer **2k** was assigned by comparison of its ^{13}C NMR data to those of **2d** and **2g**. The ^{13}C NMR spectrum of **2d**, prepared from PhC≡CH, showed a resonance at δ 153.8 due to the phenyl ipso carbon attached to the α-carbon of the 2-ferrapyridine ring. The ^{13}C NMR spectrum of **2g**, prepared from PhC≡CPh, showed a similar resonance at δ 153.8, analogously assigned to its C_α phenyl ipso carbon, and an additional resonance at δ 141.3 attributed to the C_β phenyl ipso carbon. The remaining phenyl carbon resonances are well separated, appearing in the δ 132.5–123.9 range. The above results imply that a phenyl group attached to C_α shows its ipso carbon resonance near δ 154 whereas a phenyl group on C_β has an ipso carbon resonance near δ 141. The downfield position of the phenyl ipso carbon resonance of **2k** at δ 152.9 thus implies that the phenyl group of this species is on the α-carbon of the 2-ferrapyridine ring.

A 2:1 mixture of regioisomers **2m** and **2m′** was formed upon irradiation of **1a** in the presence of $MeO_2CC{\equiv}CSiMe_3$. These compounds were separated by silica gel chromatography and independently characterized (see Table I). The resonance for the SiMe$_3$ group appeared at δ 0.23 and 0.43 for the major isomer **2m** and the minor isomer **2m′**, respectively. By comparison to the chemical shift for the SiMe$_3$ group of **2i** (δ 0.49) and **2i′** (δ 0.30), the isomer **2m** is assigned the structure with the SiMe$_3$ group on the β-carbon.

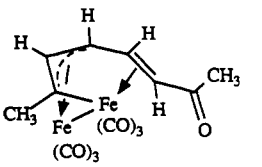
A second type of product was isolated from the reaction of the 2-ferra-3-azetine complex **1a** with $CH_3C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$. These complexes, **3a** (39%) and **3e** (<5%), result from the insertion of 2 equiv of alkyne into the Fe–carbon bond of **1a** and are related to the complexes **4a** and **4b** prepared by Pettit[9] and by Aumann[10] by quite different reactions. Spectroscopic data for **3a** and **3e** are



3a R^1=CH$_3$, R^2=H
3e R^1, R^2=CH$_3$



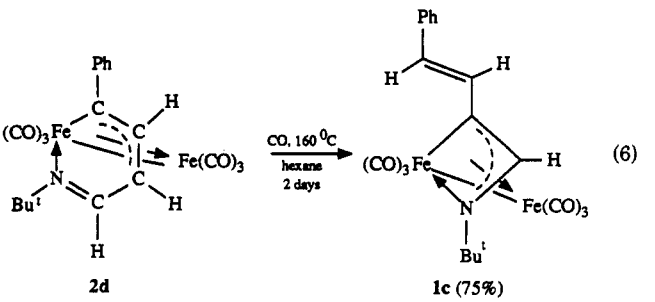
4a (R=H,CH$_3$)



4b

consistent with the proposed structures and are similar to data reported for **4a** and **4b**. For example, complex **3a** shows an IR band at 1625 cm^{-1} assigned to the uncomplexed imine group. This is in the 1690–1590-cm^{-1} range characteristic of free imines.[11] The ^{1}H NMR spectrum shows a doublet at δ 7.00 (J_{HH} = 8.7 Hz) assigned to the imine proton, and resonances at δ 4.67 (dd, J_{HH} = 8.2, 1.4 Hz, C*H*=CHCH=NBu^t), δ 2.99 (dd, J_{HH} = 8.7, 8.2 Hz, CH=C*H*CH=NBu^t), and δ 4.18 (d, J_{HH} = 1.4 Hz, Fe–C(Me)–C*H*) are assigned to the protons attached to the chain carbons. Additional singlets were observed at δ 2.44 and 2.12 for the methyl groups attached to the chain carbons and at δ 1.14 for the *tert*-butyl group.

Ring Contraction of the 2-Ferrapyridine Complex 2d. In an attempt to eliminate a free heterocycle from the 2-ferrapyridine complex **2d**, this species was heated at 160 °C under 500 psi of CO in hexane. A free heterocycle was not formed, but instead complex **2d** rearranged to give the 2-ferraazetine complex **1c** shown in eq 6. This complex



2d **1c** (75%) (6)

results from a 1,3-shift of the hydrogen atom initially attached to the γ-carbon and extrusion of the vinyl group from the metallacycle. Complex **1c** has been fully characterized by an X-ray diffraction study, the results of which are shown in Figure 3, and its spectroscopic data (see Experimental Section) are fully consistent with the determined structure.

Formation of Substituted Pyridinones and Pyrroles from the 2-Ferrapyridine Complexes. Various reaction conditions were explored for releasing free heterocycles from the 2-ferrapyridine complexes. First, it was found

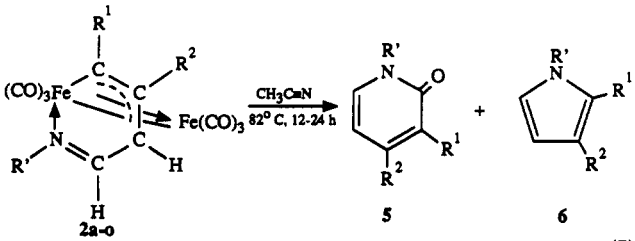
(9) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.
(10) Aumann, R.; Averbeck, H.; Krüger, C. *Chem. Ber.* **1975**, *108*, 3336.
(11) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978; Chapter 7.

Table II. Formation of 2-Pyridinones and Pyrroles from the 2-Ferrapyridine Complexes by Reaction 7

2-ferrapyridine				pyridinone		pyrrole	
	R′	R¹	R²		yield, %		yield, %
2a	Bu^t	Me	H	**5a**	65	**6a**	–
2b	Bu^t	Bu^t	H	**5b**	86	**6b**	–
2c	Bu^t	$SiMe_3$	H	**5c**	74	**6c**	–
2d	Bu^t	Ph	H	**5d**	61	**6d**	25
2e	Bu^t	Me	Me	**5e**	31	**6e**	2
2f	Bu^t	Et	Et	**5f**	48	**6f**	39
2g	Bu^t	Ph	Ph	**5g**	–	**6g**	82
2h	Bu^t	Me	Bu^t	**5h**	47	**6h**	26
2i	Bu^t	Me	$SiMe_3$	**5i**	18	**6i**	–
2i′	Bu^t	$SiMe_3$	Me	**5i′**		**6i′**	
2j	Bu^t	Ph	Me	**5j**	40	**6j**	30
2j′	Bu^t	Me	Ph	**5j′**		**6j′**	
2k	Bu^t	Ph	$SiMe_3$	**5k**	30	**6k**	22[a]
2k′	Bu^t	$SiMe_3$	Ph	**5k′**		**6k′**	
2l	Bu^t	CO_2Me	Me	**5l**	44	**6l**	16
2l′	Bu^t	Me	CO_2Me	**5l′**	4	**6l′**	55
2m	Bu^t	CO_2Me	$SiMe_3$	**5m**	3	**6m**	38
2m′	Bu^t	$SiMe_3$	CO_2Me	**5m′**	38	**6m′**	16
2n	Ph	Bu^t	H	**5n**	89	**6n**	–
2o	Ph	Ph	Ph	**5o**	–	**6o**	92

[a] Some desilylation resulted under the reaction conditions, resulting in the formation of 1-*tert*-butyl-2-phenylpyrrole (10%) and 1-*tert*-butyl-3-phenylpyrrole (5%).

that free pyridinones **5a–o** and pyrroles **6a–o** were formed when complexes **2a–o** were refluxed in acetonitrile solution *in air* (eq 7). The product distributions for these reactions

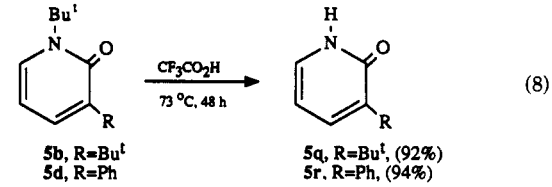


(7)

are given in Table II. IR monitoring of the reactions showed the gradual disappearance of all ν_{CO} bands as the complexes decomposed, and no tractable organometallics were formed. The heterocycles were isolated by preparative thin-layer chromatography and were spectroscopically characterized. Each gave a characteristic high-resolution mass spectrum and consistent ^1H NMR and IR data (see Experimental Section). Decomposition of the 2-ferrapyridines **2a–c** and **2n** gave the pyridinones **5a–c** and **5n** as the only products in high yield. In contrast, decomposition of **2g** and **2o** gave only the pyrroles **6g** and **6o**, again in high yields. The other 2-ferrapyridine complexes gave mixtures of pyridinones and pyrroles. The reactions were substantially faster when the reactions were conducted at 160 °C in an autoclave reactor with no measures taken to exclude air, but the product distributions were essentially the same in the few cases examined (see Experimental Section). The pyrroles **6g** and **6o** could also be obtained from **2g** and **2o** by oxidation with excess $AgBF_4$. This latter reaction occurred quickly and gave the pyrroles in excellent yields (**6g**, 89%; **6o**, 83%) with no evidence for pyridinone formation.

Other conditions were explored in an attempt to optimize the yield of pyridinone products and minimize the formation of pyrroles. As described in the Experimental Section, improved yields of pyridinones were obtained from the 2-ferrapyridines **2d**, **2f**, **2g**, **2j**, **2j′**, and **2o** with robust aryl and alkyl substituents by combining the complex with 1 equiv of [PPN]Cl in THF and heating the mixture in an autoclave at 180 °C under a CO atmosphere (500 psi) for 48 h. For example, 2-ferrapyridine complex **2f** gave the 2-pyridinone **5f** in 71% yield as compared to the 48% yield obtained under the conditions given in Table II. The role of [PPN]Cl is not known, although other workers have shown halides to be excellent promoters for carbonylation reactions.[12]

Transformation of *N*-*tert*-Butylpyridinones into *N*-Hydridopyridinones by Refluxing in CF_3CO_2H. It is well-known that thermolysis of *tert*-butylamides in strong acid media often results in loss of isobutylene and formation of the corresponding N–H compounds.[13] A similar reaction has been found to occur with the pyridinones **5b** and **5d** (eq 8). This simple reaction gives entry



(8)

into N–H pyridinones, which are an important class of biologically active molecules. For example, complex **5r** is patented as a potent anti-inflammatory agent.[2e] N–H-substituted pyridinones also give a much wider substituent variability at this position through well-demonstrated organic methods for replacing a hydrogen atom with alkyl and aryl groups.[1b,c]

Molecular Structures of the 2-Ferrapyridine Complexes 2l and 2o. ORTEP drawings of **2l** and **2o** are shown in Figures 1 and 2, respectively, and pertinent crystallographic details are given in Tables III–VII. In **2o** the 2-ferrapyridine ring is defined by C(7), C(8), C(9), C(10), Fe(1), and the nitrogen atom, and it is bound to Fe(2) via a π-type coordination of C(8), C(9), and C(10) and through an Fe–Fe single bond (2.632 (1) Å).[14] The short C(7)–N distance of 1.283 Å is in the range typical of organic imines (1.30 Å)[15] and indicates a localized double bond between these atoms. The similar C(8)–C(7) and C(8)–C(9) distances of 1.451 (8) and 1.455 (8) Å are midway between C–C single-bond (1.54 Å) and double-bond (1.34 Å) values and are similar to the C–C distances typically found in allyl complexes.[14] The 2-ferrapyridine ring is not planar, having a maximum deviation of 0.408 Å associated with C(8).

The structure of **2l** is similar to that of **2o**. In **2l**, the 2-ferrapyridine ring is defined by C(7), C(8), C(9), C(10), Fe(2), and the nitrogen atom, and it is bound to Fe(1) via a π-type coordination of C(7), C(8), and C(9) and through an Fe–Fe single bond (2.628 (1) Å).[14] The short C(10)–N distance of 1.279 (5) Å is similar to that found in **2o**, as are the C(8)–C(7) and C(8)–C(9) bond distances of 1.402 (5) and 1.428 (6) Å. The 2-ferrapyridine ring for **2l** is also not planar, having a maximum deviation of 0.293 Å associated with Fe(2).

The structures of **2o** and **2l** are similar to the structure determined for their oxygen analogue **7**.[7a] However, the structures of **2o**, **2l**, and **7** differ in two important aspects

(12) (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. (b) Lavigne, G.; Lugan, N.; Bonnet, J. *Inorg. Chem.* **1987**, *26*, 2345. (c) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Knozinger, H., Gates, B. C., Guczi, L., Eds.; Elsevier: Amsterdam, 1986; pp 68–69.

(13) (a) Haslam, E. In *Protective Groups in Organic Chemistry*; McOmie, J. F. W., Ed.; Plenum Press: New York, 1973. (b) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981.

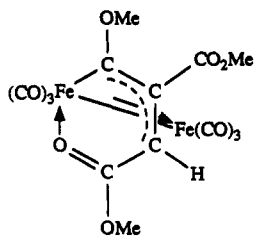
(14) Wells, A. F. *Structural Inorganic Chemistry*, 5th Ed.; Oxford University Press: London, 1984.

(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

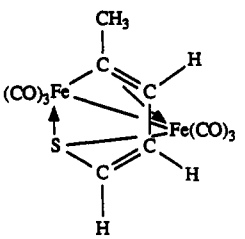
Table III. Crystal, Data Collection, and Refinement Parameters for $Fe_2(\mu\text{-}C\{Ph\}C\{Ph\}CHCHNBu^t)(CO)_6$ (2o), $Fe_2(\mu\text{-}C\{CO_2Me\}C\{Me\}CHCHNBu^t)(CO)_6$ (2l), and $Fe_2(\mu\text{-}C\{CHCHPh\}C{=}CHNBu^t)(CO)_6$ (1c)

	2o	2l	1c
	(a) Crystal Parameters		
formula	$C_{28}H_{17}Fe_2NO_6$	$C_{17}H_{17}Fe_2NO_8$	$C_{20}H_{17}Fe_2NO_6$
fw	575.14	475.02	479.08
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	10.797 (3)	9.523 (3)	8.5087 (13)
b, Å	19.580 (4)	15.349 (3)	20.0278 (28)
c, Å	12.454 (2)	13.588 (3)	12.6838 (18)
β, deg	103.61 (2)	94.61 (2)	96.231 (12)
V, Å^3	2559.1 (10)	1979.8 (9)	2148.7 (5)
Z	4	4	4
size, mm	0.06 × 0.13 × 0.26	0.31 × 0.31 × 0.46	0.32 × 0.40 × 0.45
color	orange	orange-red	orange
D_{calc}, g cm^{-3}	1.493	1.593	1.481
μ(Mo Kα), cm^{-1}	11.74	15.06	13.83
temp, K	298	298	298
T(max)/T(min)	1.079	1.162	1.136
	(b) Data Collection		
diffractometer		Nicolet R3m	
monochromator		graphite	
radiation		Mo Kα	
wavelength, Å		0.710 73	
2θ scan range, deg	4–42	4–52	4–50
data collected (hkl)	±11,+20,+13	±12,+19,+17	±11,+24,+16
no. of rflns collected	3028	4226	4087
no. of indpt rflns	2760	3894	3777
no. of indpt obsd rflns, $F_o \geq n\sigma(F_o)$	1915 (n = 5)	2554 (n = 5)	2227 (n = 5)
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
var in stds	~2%	<1	<1
	(c) Refinement		
$R(F)$, %	3.61	4.35	4.40
R(wF), %	3.82	4.81	4.33
$\Delta(\rho)$, e Å^{-3}	0.269	0.776	0.280
Δ/σ_{max}	0.039	0.035	0.021
N_o/N_v	6.30	10.1	7.00
GOF	0.998	1.021	1.156

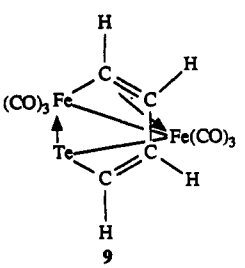
from the structure of their crystallographically characterized sulfur and tellurium analogues **8** and **9**.[7] The



7



8



9

chalcogenide atoms in these last two compounds are coordinated to both Fe atoms, whereas the nitrogen atoms of **2o** and **2l** and the oxygen atom of **7** are bonded only to Fe(2). The structural results for **8** and **9** also indicate localized double bonds between the carbon atoms of the metallacycles with only one of the double bonds π-coordinated to the second Fe atom, in contrast to the delocalized structures of **2l**, **2o**, and **7**.

Molecular Structure of the 2-Ferraazetine Complex 1c. An ORTEP drawing of **1c** is shown in Figure 3, and pertinent crystallographic details are given in Tables III, VIII, and IX. The molecule is similar in bonding and structural parameters to the previously characterized **1a**.[4] In **1c**, the 2-ferra-3-azetine ring is defined by C(11), C(12), Fe(1), and the nitrogen atom, and this ring is bound to Fe(2) via an Fe–Fe single bond (2.632 (1) Å)[14] and a π-type coordination of C(11), C(12), and the nitrogen atom. The four-membered ring is nearly planar with a maximum deviation of 0.082 Å associated with C(11). The C(13)–C(14) distance of 1.303 (7) Å in the vinyl group is in the normal range for C–C double bonds.[15]

Discussion

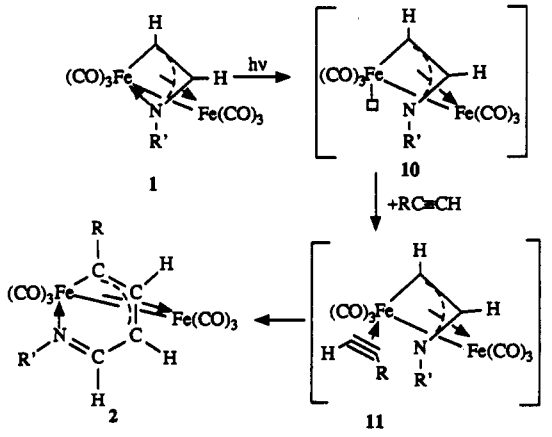
The results reported herein demonstrate that alkynes readily insert into the Fe–carbon bond of the 2-ferraazetine complexes **1a,b** to give 2-ferrapyridine complexes, generally with high regiospecificity, and that 2-pyridinones and pyrroles having specific substitution patterns can be released from these metallacycles. The alkyne insertion step proceeds in highest yield when photochemical conditions are used, and reasonable mechanisms for this reaction include photoinduced CO loss or rearrangement of the 2-ferraazetine complex to a more reactive form that incorporates the alkyne. The CO-loss pathway seems unlikely on the basis of the observation that photolysis of **1a** in the presence of PEt_3 does not lead to photosubstitution of PEt_3 for CO but gives mainly unreacted **1a**, along with some decomposition and a trace amount of the 3-ferra-4-pyrrolin-2-one complex, which is known to result from CO insertion into the 2-ferra-3-azetine ring.[4] Furthermore, a separately described[16] low-temperature matrix isolation

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Fe_2(\mu$-C{Ph}C{Ph}CHCHNBu^t)(CO)$_6$ (2o)

	x	y	z	U[a]
Fe(1)	2934.6 (7)	5786.9 (4)	1231.9 (6)	31.9 (3)
Fe(2)	1291.5 (7)	6470.9 (4)	−283.8 (6)	33.5 (3)
N	2490 (4)	6407 (2)	2390 (4)	35 (2)
O(1)	3330 (4)	4852 (2)	−492 (3)	57 (2)
O(2)	1725 (4)	4636 (2)	2154 (4)	68 (2)
O(3)	5584 (4)	5476 (3)	2372 (4)	76 (2)
O(4)	1261 (4)	5638 (2)	−2263 (3)	67 (2)
O(5)	−492 (4)	5675 (2)	679 (4)	67 (2)
O(6)	−527 (4)	7340 (2)	−1811 (4)	79 (2)
C(1)	3173 (5)	5228 (3)	166 (4)	38 (2)
C(2)	2174 (6)	5089 (3)	1802 (5)	42 (2)
C(3)	4567 (5)	5627 (3)	1968 (4)	48 (2)
C(4)	1313 (5)	5953 (3)	−1466 (4)	42 (2)
C(5)	251 (5)	5963 (3)	323 (4)	44 (2)
C(6)	172 (5)	7009 (3)	−1211 (5)	47 (2)
C(7)	1821 (5)	6944 (3)	2082 (5)	40 (2)
C(8)	1581 (5)	7215 (3)	967 (4)	40 (2)
C(9)	2607 (5)	7225 (3)	391 (4)	30 (2)
C(10)	3267 (5)	6611 (3)	353 (4)	31 (2)
C(11)	3965 (3)	6137 (2)	4169 (3)	58 (3)
C(12)	4175	5963	5284	79 (3)
C(13)	3144	5879	5769	74 (3)
C(14)	1904	5968	5139	68 (3)
C(15)	1694	6142	4024	50 (3)
C(16)	2724	6227	3539	42 (2)
C(21)	3062 (4)	8473 (2)	501 (3)	54 (3)
C(22)	3289	9097	40	69 (3)
C(23)	3309	9134	−1074	62 (3)
C(24)	3101	8547	−1728	59 (3)
C(25)	2874	7924	−1268	46 (2)
C(26)	2854	7887	−153	38 (2)
C(31)	4481 (3)	6315 (2)	−1126 (3)	48 (3)
C(32)	5596	6349	−1506	55 (3)
C(33)	6661	6691	−888	63 (3)
C(34)	6611	6999	111	60 (3)
C(35)	5496	6965	491	50 (2)
C(36)	4431	6624	−127	34 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I



study of **1a** and **1c** has shown that the initial step in the reaction is photoinduced cleavage of one of the iron–nitrogen bonds to form the coordinatively unsaturated complex **10** shown in Scheme I. The low-temperature study also showed that a critical step in the mechanism involves coordination of the alkyne to **10** to yield intermediate **11**. It was also observed that warmup of **11** to

(16) Mirkin, C. A.; Oyer, T. J.; Wrighton, M. S.; Snead, T. E.; Geoffroy, G. L. *J. Am. Chem. Soc.*, in press.

Table V. Selected Bond Distances and Angles for $Fe_2(\mu$-C{Ph}C{Ph}CHCHNBu^t)(CO)$_6$ (2σ)

(a) Bond Distances (Å)

Fe(1)–Fe(2)	2.632 (1)	Fe(1)–N	2.028 (5)
Fe(1)–C(1)	1.785 (6)	Fe(1)–C(2)	1.822 (6)
Fe(1)–C(3)	1.812 (5)	Fe(1)–C(10)	2.028 (5)
Fe(2)–C(4)	1.793 (6)	Fe(2)–C(5)	1.795 (6)
Fe(2)–C(6)	1.802 (5)	Fe(2)–C(8)	2.102 (5)
Fe(2)–C(9)	2.085 (5)	Fe(2)–C(10)	2.111 (5)
N–C(7)	1.283 (7)	N–C(16)	1.437 (6)
O(1)–C(1)	1.144 (7)	O(2)–C(2)	1.146 (8)
O(3)–C(3)	1.134 (7)	O(4)–C(4)	1.157 (7)
O(5)–C(5)	1.150 (8)	O(6)–C(6)	1.132 (7)
C(7)–C(8)	1.451 (8)	C(8)–C(9)	1.455 (8)
C(9)–C(10)	1.404 (7)	C(9)–C(26)	1.514 (6)
C(10)–C(36)	1.515 (7)		

(b) Bond Angles (deg)

Fe(2)–Fe(1)–N	88.5 (1)	Fe(2)–Fe(1)–C(1)	88.3 (2)
N–Fe(1)–C(1)	174.8 (2)	Fe(2)–Fe(1)–C(2)	111.8 (2)
N–Fe(1)–C(2)	88.2 (2)	C(1)–Fe(1)–C(2)	89.3 (3)
Fe(2)–Fe(1)–C(3)	149.5 (2)	N–Fe(1)–C(3)	96.2 (2)
C(1)–Fe(1)–C(3)	88.7 (3)	C(2)–Fe(1)–C(3)	98.5 (3)
Fe(2)–Fe(1)–C(10)	51.9 (1)	N–Fe(1)–C(10)	90.5 (2)
C(1)–Fe(1)–C(10)	90.7 (2)	C(2)–Fe(1)–C(10)	163.7 (2)
C(3)–Fe(1)–C(10)	97.8 (2)	Fe(1)–Fe(2)–C(4)	99.4 (2)
Fe(1)–Fe(2)–C(5)	78.4 (2)	C(4)–Fe(2)–C(5)	99.4 (3)
Fe(1)–Fe(2)–C(6)	173.9 (2)	C(4)–Fe(2)–C(6)	86.6 (3)
C(5)–Fe(2)–C(6)	101.7 (3)	Fe(1)–Fe(2)–C(8)	82.1 (1)
C(4)–Fe(2)–C(8)	166.5 (3)	C(5)–Fe(2)–C(8)	94.1 (2)
C(6)–Fe(2)–C(8)	91.7 (2)	Fe(1)–Fe(2)–C(9)	77.9 (1)
C(4)–Fe(2)–C(9)	126.3 (2)	C(5)–Fe(2)–C(9)	131.1 (2)
C(6)–Fe(2)–C(9)	97.7 (2)	C(8)–Fe(2)–C(9)	40.7 (2)
Fe(1)–Fe(2)–C(10)	49.1 (1)	C(4)–Fe(2)–C(10)	100.1 (2)
C(5)–Fe(2)–C(10)	126.2 (2)	C(6)–Fe(2)–C(10)	129.1 (2)
C(8)–Fe(2)–C(10)	70.8 (2)	C(9)–Fe(2)–C(10)	39.1 (2)
Fe(1)–N–C(7)	119.3 (4)	Fe(1)–N–C(16)	123.1 (3)
C(7)–N–C(16)	117.0 (5)	Fe(1)–C(1)–O(1)	177.7 (5)
Fe(1)–C(2)–O(2)	177.7 (6)	Fe(1)–C(3)–O(3)	173.8 (5)
Fe(2)–C(4)–O(4)	175.8 (5)	Fe(2)–C(5)–O(5)	174.4 (5)
Fe(2)–C(6)–O(6)	178.6 (6)	N–C(7)–C(8)	123.2 (5)
Fe(2)–C(8)–C(7)	114.7 (4)	Fe(2)–C(8)–C(9)	69.0 (3)
C(7)–C(8)–C(9)	119.5 (5)	Fe(2)–C(9)–C(8)	70.3 (3)
Fe(2)–C(9)–C(10)	71.5 (3)	C(8)–C(9)–C(10)	117.1 (5)
Fe(2)–C(9)–C(26)	126.9 (3)	C(8)–C(9)–C(26)	117.9 (4)
C(10)–C(9)–C(26)	125.0 (5)	Fe(1)–C(10)–Fe(2)	78.9 (2)
Fe(1)–C(10)–C(9)	120.5 (4)	Fe(2)–C(10)–C(9)	69.4 (3)
Fe(1)–C(10)–C(36)	119.7 (3)	Fe(2)–C(10)–C(36)	135.5 (3)
C(9)–C(10)–C(36)	118.3 (4)	N–C(16)–C(11)	120.8 (2)
N–C(16)–C(15)	119.2 (2)	C(9)–C(26)–C(21)	117.6 (2)
C(9)–C(26)–C(25)	122.4 (2)	C(10)–C(36)–C(31)	123.7 (2)
C(10)–C(36)–C(35)	116.3 (2)		

room temperature gave insertion of the alkyne into the Fe–carbon bond to yield the 2-ferrapyridine product **2**. It is significant that the ferrapyridine products formed are generally those that have substituents on the α-carbon that are known to stabilize carbene ligands, implying carbene-like character in the transition state between **11** and **2**. For example, terminal alkynes give the 2-ferrapyridine product having the alkyl or aryl substituent on the α-carbon of **2**, consistent with the general observation that carbene complexes having alkyl or aryl substituents are more stable than those having a hydrogen substituent.[17a] The results obtained with disubstituted alkynes also imply carbene character on the α-carbon in the transition state. For example, the major isomers of the 2-ferrapyridine complexes formed from the alkynes PhC≡CMe, PhC≡CSiMe$_3$, MeO$_2$CC≡CMe, and MeO$_2$CC≡CSiMe$_3$ are those having the carbene stabilizing phenyl or ester groups[18] on

(17) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3, and references therein. (b) *Ibid.*, Chapter 6, and references therein.
(18) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

Table VI. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Fe_2(\mu\text{-}C\{CO_2Me\}C\{Me\}CHCHNBu^t)(CO)_6$ (21)

	x	y	z	U[a]
Fe(1)	2552.6 (6)	8832.1 (4)	3094.1 (4)	39.4 (2)
Fe(2)	5237.5 (5)	8775.7 (3)	2771.4 (4)	35.2 (2)
N	4829 (3)	7615 (2)	2053 (2)	37 (1)
O(1)	−465 (4)	8724 (3)	3323 (3)	88 (2)
O(2)	2564 (4)	10363 (2)	4366 (3)	73 (1)
O(3)	3499 (4)	7496 (2)	4538 (3)	76 (1)
O(4)	5750 (4)	10370 (2)	3904 (3)	70 (1)
O(5)	7378 (4)	9357 (3)	1474 (3)	71 (1)
O(6)	6797 (4)	7898 (2)	4457 (3)	71 (1)
O(7)	3372 (5)	10901 (2)	2181 (3)	83 (2)
O(8)	4504 (4)	10389 (2)	985 (3)	64 (1)
C(1)	781 (5)	8760 (3)	3222 (4)	54 (2)
C(2)	2606 (5)	9786 (3)	3853 (3)	49 (2)
C(3)	3198 (5)	8028 (3)	3968 (3)	53 (2)
C(4)	5520 (4)	9746 (3)	3461 (3)	48 (1)
C(5)	6582 (5)	9105 (3)	1975 (3)	47 (1)
C(6)	6198 (4)	8204 (3)	3792 (3)	46 (1)
C(7)	3640 (4)	9358 (3)	1993 (3)	36 (1)
C(8)	2464 (4)	8906 (3)	1567 (3)	43 (1)
C(9)	2356 (4)	8015 (3)	1854 (3)	45 (1)
C(10)	3534 (4)	7425 (3)	1834 (3)	42 (1)
C(11)	3784 (4)	10300 (3)	1745 (3)	44 (1)
C(12)	4823 (7)	11255 (3)	647 (4)	75 (2)
C(13)	1322 (5)	9317 (4)	881 (4)	63 (2)
C(14)	5867 (4)	6874 (3)	1903 (3)	46 (1)
C(15)	7388 (5)	7196 (4)	2013 (4)	67 (2)
C(16)	5600 (5)	6523 (3)	859 (4)	64 (2)
C(17)	5639 (6)	6175 (3)	2659 (4)	75 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Selected Bond Distances and Angles for $Fe_2(\mu\text{-}C\{CO_2Me\}C\{Me\}CHCHNBu^t)(CO)_6$ (21)

(a) Bond Distances (Å)

Fe(1)–Fe(2)	2.628 (1)	Fe(1)–C(7)	2.051 (4)
Fe(1)–C(8)	2.072 (4)	Fe(1)–C(9)	2.096 (4)
Fe(2)–N	2.053 (3)	Fe(2)–C(7)	1.993 (4)
N–C(10)	1.279 (5)	N–C(14)	1.531 (5)
C(7)–C(8)	1.402 (5)	C(8)–C(9)	1.428 (6)
C(9)–C(10)	1.443 (6)	C(7)–C(11)	1.493 (6)
C(8)–C(13)	1.513 (6)		

(b) Bond Angles (deg)

Fe(2)–Fe(1)–C(7)	48.5 (1)	Fe(2)–Fe(1)–C(8)	78.3 (1)
Fe(2)–Fe(1)–C(9)	82.7 (1)	C(7)–Fe(1)–C(8)	39.8 (2)
C(7)–Fe(1)–C(9)	70.6 (2)	C(8)–Fe(1)–C(9)	40.1 (2)
Fe(1)–Fe(2)–N	87.6 (1)	N–Fe(2)–C(7)	91.7 (1)
Fe(1)–Fe(2)–C(7)	50.4 (1)	Fe(2)–N–C(10)	116.8 (3)
Fe(2)–N–C(14)	127.5 (2)	C(10)–N–C(14)	114.9 (3)
Fe(1)–C(7)–Fe(2)	81.0 (1)	Fe(1)–C(7)–C(8)	70.9 (2)
Fe(2)–C(7)–C(8)	123.1 (3)	Fe(1)–C(7)–C(11)	127.3 (3)
Fe(2)–C(7)–C(11)	118.3 (3)	C(8)–C(7)–C(11)	118.1 (3)
Fe(1)–C(8)–C(9)	70.9 (2)	Fe(1)–C(8)–C(7)	69.3 (2)
C(7)–C(8)–C(9)	115.7 (3)	Fe(1)–C(8)–C(13)	127.6 (3)
C(7)–C(8)–C(13)	124.0 (4)	C(9)–C(8)–C(13)	120.2 (4)
Fe(1)–C(9)–C(8)	69.1 (2)	Fe(1)–C(9)–C(10)	111.7 (3)
C(8)–C(9)–C(10)	121.5 (4)	N–C(10)–C(9)	126.1 (4)

the α-carbon. The regioselectivity for the insertion of unsymmetrical disubstituted alkynes that do not have carbene stabilizing substituents appears to be determined mainly by steric factors, as illustrated by the observation that the major or only isomer of the 2-ferrapyridine complexes formed from $CH_3C{\equiv}CSi(CH_3)_3$ and $CH_3C{\equiv}CBu^t$ are those that possess the less sterically demanding substituent on the α-carbon of the 2-ferrapyridine ring.

Also noteworthy is the reaction of $CH_3C{\equiv}CH$ with the 2-ferraazetine complex **1a** to give the mono-insertion product **2a** and the di-insertion product **3a** in low yields. Apparently, the photochemical insertion of $CH_3C{\equiv}CH$ into the iron–carbon bond of **2a** is more efficient than the insertion into **1a** under the reaction conditions employed. Even at low conversion a substantial amount of **3a** is formed before all of **1a** has been consumed. This situation did not exist for any other alkynes used in this study, which gave clean conversion to the mono-insertion products. Presumably the second insertion step is more sensitive to the size of the alkyne than is the first insertion. The reaction of bridging alkylidene complexes of ditungsten and other diiron complexes have been implicated in alkyne polymerizations, and similar mono- and di-insertion products have been isolated from some of these

Table VIII. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Fe_2(\mu\text{-}C\{CHCHPh\}C{=}CHNBu^t)(CO)_6$ (1c)

	x	y	z	U[a]
Fe(1)	2696.9 (8)	8162.6 (4)	784.7 (5)	48.1 (2)
Fe(2)	794.3 (8)	8531.3 (3)	1930.6 (6)	47.6 (2)
O(1)	3749 (7)	9414 (2)	−116 (4)	132 (2)
O(2)	5752 (5)	7428 (3)	693 (4)	107 (2)
O(3)	1085 (5)	7811 (2)	−1294 (3)	97 (2)
O(4)	−1695 (6)	8560 (3)	157 (4)	112 (2)
O(5)	−1224 (5)	8461 (2)	3676 (4)	95 (2)
O(6)	1300 (5)	9967 (2)	1893 (4)	112 (2)
N	1686 (4)	7624 (2)	1800 (3)	40 (1)
C(1)	3393 (7)	8921 (3)	224 (4)	80 (2)
C(2)	4592 (7)	7706 (3)	722 (4)	66 (2)
C(3)	1719 (6)	7919 (3)	−476 (4)	63 (2)
C(4)	−734 (7)	8542 (3)	842 (5)	70 (2)
C(5)	−441 (6)	8489 (3)	2992 (4)	65 (2)
C(6)	1059 (6)	9412 (3)	1936 (5)	73 (2)
C(7)	1002 (5)	6940 (2)	1840 (4)	50 (2)
C(8)	2377 (9)	6446 (4)	1849 (8)	87 (3)
C(9)	−111 (7)	6826 (3)	851 (5)	75 (2)
C(10)	148 (9)	6859 (4)	2821 (4)	91 (3)
C(11)	2521 (5)	7919 (2)	2671 (4)	43 (2)
C(12)	3293 (5)	8453 (2)	2271 (4)	43 (2)
C(13)	4352 (5)	8897 (3)	2910 (4)	51 (2)
C(14)	5355 (6)	9320 (3)	2582 (4)	54 (2)
C(21)	7400 (4)	10190 (2)	2661 (2)	65 (2)
C(22)	8476	10620	3223	77 (3)
C(23)	8627	10623	4329	74 (2)
C(24)	7701	10196	4873	66 (2)
C(25)	6625	9766	4311	55 (2)
C(26)	6474	9763	3205	46 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IX. Selected Bond Distances and Angles for $Fe_2(\mu\text{-}C\{CHCHPh\}C{=}CHNBu^t)(CO)_6$ (1c)

(a) Bond Distances (Å)

Fe(1)–Fe(2)	2.470 (1)	Fe(1)–N	1.995 (4)
Fe(1)–C(11)	2.487 (5)	Fe(1)–C(12)	1.974 (4)
Fe(2)–N	1.983 (4)	Fe(2)–C(11)	2.061 (5)
Fe(2)–C(12)	2.129 (4)	N–C(7)	1.492 (6)
N–C(11)	1.380 (6)	C(11)–C(12)	1.381 (7)
C(12)–C(13)	1.450 (6)	C(13)–C(14)	1.303 (7)
C(14)–C(26)	1.468 (6)		

(b) Bond Angles (deg)

Fe(2)–Fe(1)–N	51.4 (1)	Fe(2)–Fe(1)–C(11)	49.2 (1)
N–Fe(1)–C(11)	33.8 (1)	Fe(2)–Fe(1)–C(12)	55.9 (1)
N–Fe(1)–C(12)	67.1 (2)	C(11)–Fe(1)–C(12)	33.8 (2)
Fe(1)–Fe(2)–N	51.8 (1)	Fe(1)–Fe(2)–C(11)	65.6 (1)
N–Fe(2)–C(11)	39.9 (2)	Fe(1)–Fe(2)–C(12)	50.2 (1)
N–Fe(1)–C(12)	64.3 (2)	C(11)–Fe(2)–C(12)	38.4 (2)
Fe(1)–N–Fe(2)	76.8 (1)	Fe(1)–N–C(7)	137.1 (3)
Fe(2)–N–C(7)	133.2 (3)	Fe(1)–N–C(11)	92.7 (3)
Fe(2)–N–C(11)	73.1 (2)	C(7)–N–C(11)	122.3 (4)
Fe(1)–C(11)–Fe(2)	65.2 (1)	Fe(1)–C(11)–N	53.5 (2)
Fe(2)–C(11)–N	67.0 (2)	Fe(1)–C(11)–C(12)	52.7 (3)
Fe(2)–C(11)–C(12)	73.5 (3)	N–C(11)–C(12)	105.1 (4)
Fe(1)–C(12)–Fe(2)	73.9 (1)	Fe(1)–C(12)–C(11)	93.6 (3)
Fe(2)–C(12)–C(11)	68.1 (3)	Fe(1)–C(12)–C(13)	140.4 (4)
Fe(2)–C(12)–C(13)	127.9 (3)	C(11)–C(12)–C(13)	124.1 (4)
C(12)–C(13)–C(14)	127.5 (4)	C(13)–C(14)–C(26)	129.1 (4)

polymerization reactions.[19]

As noted above, the 2-ferrapyridines release free pyridinones and pyrroles when allowed to decompose in acetonitrile solution, but no intermediates were observed in these reactions.[20] The pyrroles would appear to result from the extrusion of iron from the metallacycle of the 2-ferrapyridine ring, whereas the pyridinones must incorporate CO into the ring prior to the extrusion step. The results given in Table II show that the product distribution is not affected by the substituent attached to the nitrogen atom of the 2-ferrapyridine ring (see examples **2b** and **2n**) but is markedly affected by the substituents on the α-carbon of the metallacycle. When an electron-donating group (Bu^t, $SiMe_3$, Et) is bound to the α-carbon of a monosubstituted 2-ferrapyridine ring, decomposition always results in pyridinone formation. However, when an electron-withdrawing phenyl or methoxycarbonyl group is attached to the α-carbon of a monosubstituted 2-ferrapyridine ring, decomposition of the metallacycle yields a pyrrole. These results are consistent with the well-known observation that alkyl migration to a CO ligand is facilitated by electron-donating groups on the migrating carbon whereas electron-withdrawing groups retard or prevent migration.[17b]

Experimental Section

The compounds $Fe_2(\mu\text{-}CH{=}CHNR)(CO)_6$ (R = Bu^t, Ph),[4] $Me_3Si{\equiv}CCO_2CH_3$,[21a] and $Me_3SiC{\equiv}CPh$[21b] were prepared by literature methods. $CH_3C{\equiv}CH$ was purchased from Matheson Gas Products, Inc., $EtC{\equiv}CEt$ from Wiley Organics, Inc., and $CH_3C{\equiv}CBu^t$ from Farchan Laboratories, Inc. All other alkynes used were purchased from Aldrich Chemical Co. Solvents were dried by stirring over Na/benzophenone (THF, ether) or CaH_2 (CH_2Cl_2, pentane, hexane) and were freshly distilled prior to use. Spectroscopic grade acetonitrile was purchased from Aldrich Chemical Co. and used as received. The silica gel chromatography support (Baker 3405, 60–200 mesh) was purchased from Thomas Scientific, and neutral alumina (Brockmann I, ~150 mesh) was purchased from Aldrich Chemical Co. and adjusted to Brockmann II by addition of 3% H_2O prior to use. All manipulations were performed using standard Schlenk techniques unless otherwise specified. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorption mode, NMR spectra were obtained on a Bruker AM 300 FT NMR spectrometer, and mass spectra were recorded on an AEI-MS9 mass spectrometer (EI) or a Kratos MS-25 magnetic mass spectrometer using isobutane as the ionizing gas (CI). Photolyses were conducted in Pyrex Schlenk vessels 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 next to the lamp at the midpoint of the arc. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

Photoinduced Reaction of 1a and 1b with Alkynes To Form 2-Ferrapyridine Complexes 2a–o. The appropriate complex **1a** or **1b** (0.13 mmol) was placed in a 100-mL Schlenk flask, to which was added CH_2Cl_2 (60 mL) and 1.1 equiv of the appropriate alkyne. The resulting orange solution was then irradiated for 3–12 h using the above-described lamp with constant stirring. The color changed to dark red, and the solvent was removed by rotary evaporation. Complexes **2b–d, 2f–h, 2i,i′, 2j,j′, 2k,k′, 2n**, and **2o** were purified by column chromatography on silica gel, which gave in each case a single orange band of complex **2**. For **2l,l′** and **2m,m′**, the isomers were chromatographically separated by elution of the minor isomer (**2l′**, **2m′**) first with a relatively nonpolar solvent mixture followed by elution of the major isomer with a more polar eluent (see below for details). Complexes **2a** and **2e** were purified by column chromatography on neutral alumina (grade II). After elution of the 2-ferrapyridine complexes, the eluent was changed to a more polar mixture (see below) and complexes **3a** and **3e** were eluted as red-brown bands which gave dark red oils upon solvent evaporation. These oils did not crystallize despite repeated attempts. Also observed in the reaction of **1a** with $CH_3C{\equiv}CH$ was the deposition of an insoluble brown powder which showed a KBr IR pattern (ν 3021–2848 (s), 2049 (w), 2015 (m), 1970 (m), 1620 (s), 1420 (s) cm^{-1}) indicative of the presence of an $Fe_2(CO)_6$ unit as in the other compounds described herein. This material was not further investigated, but its insolubility suggests that it may be a hexacarbonyl-capped propyne oligomer or polymer formed by multiple alkyne insertion into **3a**.

2a: photolysis time 0.5 h; chromatography eluent pentane; yield 9%. Anal. Calcd for $C_{20}H_{17}Fe_2NO_6$: C, 43.21; H, 3.63. Found: C, 43.05; H, 3.63. IR (pentane): ν_{CO} 2060 (m), 2012 (vs), 1987 (s), 1977 (S), 1961 (m), 1948 (w) cm^{-1}. MS: m/z 361 ($M^+ - 2CO$) and fragment ions corresponding to the loss of four carbonyls. ^1H NMR ($CDCl_3$): δ 7.27 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 5.26 (d, 1 H, J = 5.5 Hz, $C_\beta H$), 3.05 (s, 3 H, CH_3), 2.61 (dd, 1 H, J = 5.5, 5.5 Hz, $C_\gamma H$), 0.71 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 212.8, 210.5, 209.4 (CO), 183.9 (m, $C_\alpha Bu^t$), 177.8 (ddd, $C_\delta H$, $^1J_{CH}$ = 159.9 Hz, $^2J_{CH}$, $^3J_{CH}$ = 2.6 Hz), 88.2 (dm, $C_\beta H$, $^1J_{CH}$ = 166.3 Hz), 62.2 (CMe_3), 50.9 (ddd, $C_\gamma H$, $^1J_{CH}$ = 157.5 Hz, $^2J_{CH}$ = 11.0 Hz, $^3J_{CH}$ = 4.9 Hz), 35.0 (m, $C_\alpha CH_3$), 31.7 ($C(CH_3)_3$).

2b: photolysis time 5 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield 89%. Anal. Calcd for $C_{18}H_{21}Fe_2NO_6$: C, 47.06; H, 4.58. Found: C, 46.73; H, 4.31. IR (CH_2Cl_2): ν_{CO} 2053 (m), 2006 (vs), 1976 (s), 1948 (m) cm^{-1}. MS: m/z 459 (M^+). ^1H NMR (CD_2Cl_2): δ 8.19 (d, 1 H, J = 5.4 Hz, $C_\delta H$), 5.70 (d, 1 H, J = 5.5 Hz, $C_\beta H$), 3.37 (m, 1 H, $C_\gamma H$), 1.60 (s, 9 H, Bu^t), 1.19 (s, 9 H, Bu^t). ^{13}C NMR (C_6D_6): δ 214.4, 212.6, 211.5, 210.2 (CO), 203.9 ($C_\alpha Bu^t$), 177.9 ($C_\delta H$), 84.2 ($C_\beta H$), 62.2 ($NC(Me)_3$), 51.0 ($C_\gamma H$), 45.4 ($CC(CH_3)_3$), 35.1 ($NC(CH_3)_3$), 31.1 ($CC(CH_3)_3$).

2c: photolysis time 3 h; chromatography eluent pentane; yield 67%. Anal. Calcd for $C_{17}H_{21}Fe_2NO_6Si$: C, 42.97; H, 4.45. Found: C, 42.88; H, 4.84. IR (CH_2Cl_2): ν_{CO} 2055 (m), 2006 (vs), 1987 (s), 1977 (S), 1952 (w) cm^{-1}. MS: m/z 419 ($M^+ - 2CO$) and fragment ions corresponding to the loss of four carbonyls. ^1H NMR ($CDCl_3$): δ 8.10 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 5.94 (d, 1 H, J = 5.5 Hz, $C_\beta H$), 3.57 (dd, 1 H, J = 5.5, 5.5 Hz, $C_\gamma H$), 1.16 (s, 9 H, $C(CH_3)_3$), 0.43 (s, 9 H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 212.7, 210.3, 209.1 (CO), 176.4 ($C_\delta H$), 174.3 ($C_\alpha SiMe_3$), 94.8 ($C_\beta H$), 62.5 (CMe_3), 55.4 ($C_\gamma H$), 31.6 ($C_\alpha CH_3$), 1.80 ($Si(CH_3)_3$).

2d: photolysis time 5 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield 77%. Anal. Calcd for $C_{20}H_{17}Fe_2NO_6$: C, 50.14; H, 3.55. Found: C, 50.08; H, 3.67. IR (CH_2Cl_2): ν_{CO} 2058 (m), 2010 (vs), 1985 (s), 1976 (s), 1955 (m) cm^{-1}. MS: m/z 479 (M^+) and fragment ions corresponding to the loss of six carbonyls. ^1H NMR (CD_2Cl_2): δ 8.26 (d, 1 H, J = 5.6 Hz, $C_\delta H$), 7.72–7.31 (m, 5 H, Ph), 5.90 (d, 1 H, J = 6.1 Hz, $C_\beta H$), 3.34 (t, 1 H, $C_\gamma H$), 1.27 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 214.0, 210.8, 210.0 (CO), 186.2 (ddd, $C_\alpha Ph$, $^2J_{CH}$, $^3J_{CH}$, $^4J_{CH}$ = 4.6 Hz), 178.3 (ddd, $C_\delta H$, $^1J_{CH}$ = 161.7 Hz, $^2J_{CH}$, $^3J_{CH}$ = 3.1 Hz), 153.8, 128.5, 128.3, 127.0 (Ph), 91.0 (dd, $C_\beta H$, $^1J_{CH}$ = 169.4 Hz, $^2J_{CH}$ = 3.1 Hz), 63.5 (m, CMe_3), 49.8 (ddd, $C_\gamma H$, $^1J_{CH}$ = 158.7 Hz, $^2J_{CH}$ = 12.2, 10.7 Hz), 31.9 (m, $C(CH_3)_3$).

2d′: prepared from $PhC{\equiv}CD$; photolysis time 5 h; chromatography eluent 3:1 pentane/CH_2Cl_2; yield 77%. ^1H NMR (CD_2Cl_2): δ 8.26 (d, 1 H, J = 5.6 Hz, $C_\delta H$), 7.71–7.37 (m, 5 H, Ph), 3.34 (d, 1 H, J = 5.5 Hz, $C_\gamma H$), 1.27 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 214.0, 210.8, 210.0 (CO), 186.2 ($C_\alpha Ph$), 178.3 ($C_\delta H$), 153.8, 128.5, 128.3, 127.0 (Ph), 91.0 (t, $C_\beta H$, $^1J_{CD}$ = 25.0 Hz), 63.5 (CMe_3), 49.8 ($C_\gamma H$), 31.9 ($C(CH_3)_3$).

2e: photolysis time 4 h; chromatography eluent pentane; yield 43%. Anal. Calcd for $C_{16}H_{17}Fe_2NO_6$: C, 44.59; H, 4.00. Found: C, 44.84; H, 4.03. IR (CH_2Cl_2): ν_{CO} 2054 (m), 2005 (vs), 1974 (s),

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1948 (w) cm^{-1}. MS: m/z 403 (M^+ – 1CO) and fragment ions corresponding to the loss of five carbonyls. ^1H NMR ($CDCl_3$): δ 8.05 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 3.22 (d, 1 H, J = 5.5 Hz, $C_\gamma H$), 3.11 (s, 3 H, $C_\alpha CH_3$), 2.22 (s, 3 H, $C_\beta CH$), 1.16 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 213.4, 210.6, 209.9 (*C*O), 177.4 (C_δH), 176.8 (C_αMe), 99.3 (C_βMe), 62.0 (CMe_3), 56.7 (C_γH), 32.5 ($C_\alpha CH_3$), 31.6 ($C(CH_3)_3$), 23.4 ($C_\beta CH_3$).

2f: photolysis time 6 h; chromatography eluent pentane; yield 86%. Anal. Calcd for $C_{18}H_{21}Fe_2NO_6$: C, 47.06; H, 4.58. Found: C, 47.00; H, 4.72. IR (CH_2Cl_2): ν_{CO} 2055 (m), 2008 (vs), 1983 (s), 1971 (s), 1959 (m) cm^{-1}. MS: m/z 459 (M^+). ^1H NMR (CD_2Cl_2): δ 8.12 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 3.24 (d, 1 H, J = 5.5 Hz, $C_\gamma H$), 3.60 (m, 1 H, CH_2CH_3), 3.18 (m, 1 H, CH_2CH_3), 3.07 (m, 1 H, CH_2CH_3), 1.86 (m, 1 H, CH_2CH_3), 1.60 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.17 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.20 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 214.3, 211.4, 211.2 (*C*O), 185.6 (m, C_αEt), 178.0 (dd, C_δH, $^1J_{CH}$ = 159.9 Hz, $^2J_{CH}$ = 2.4 Hz), 105.9 (m, C_βEt), 62.7 (CMe_3), 53.7 (d, C_γH, $^1J_{CH}$ = 150.9 Hz), 40.8 (CH_2CH_3), 31.8 ($C(CH_3)_3$), 30.3 (CH_2CH_3), 18.4 (CH_2CH_3), 17.3 (CH_2CH_3).

2g: photolysis time 5 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield 78%. Anal. Calcd for $C_{26}H_{21}Fe_2NO_6$: C, 56.19; H, 3.81. Found: C, 55.47; H, 3.69. IR (CH_2Cl_2): ν_{CO} 2057 (m), 2009 (vs), 1978 (s), 1953 (m) cm^{-1}. MS: m/z 555 (M^+). ^1H NMR (CD_2Cl_2): δ 8.44 (d, 1 H, J = 5.3 Hz, $C_\delta H$), 7.34–7.05 (m, 10 H, Ph), 3.59 (d, 1 H, J = 5.3 Hz, $C_\gamma H$), 1.31 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 213.8, 209.6, 209.4 (*C*O), 179.5 (m, C_αPh), 178.3 (dd, C_δH, $^1J_{CH}$ = 161.7 Hz, $^2J_{CH}$ = 3.1 Hz), 151.8, 141.3, 131.6, 128.5, 127, 127.5, 125.3 (Ph), 107.3 (m, C_βPh), 63.3 (CMe_3), 53.7 (dd, C_γH, $^1J_{CH}$ = 157.2 Hz, $^2J_{CH}$ = 12.2 Hz), 32.0 ($C(CH_3)_3$).

2h: photolysis time 5 h; chromatography eluent pentane; yield 47%. Anal. Calcd for $C_{19}H_{23}Fe_2NO_6$: C, 48.24; H, 4.90. Found: C, 47.67; H, 5.02. HRMS: m/z (EI) calcd for $C_{19}H_{23}Fe_2NO_6$ 473.0223, found 473.0210. IR (CH_2Cl_2): ν_{CO} 2068 (m), 2023 (vs), 1988 (s), 1949 (m) cm^{-1}. MS: m/z 473 (M^+) and fragment ions corresponding to the loss of six carbonyls. ^1H NMR (CD_2Cl_2): δ 8.06 (d, 1 H, J = 5.8 Hz, $C_\delta H$), 3.59 (d, 1 H, J = 5.8 Hz, $C_\gamma H$), 3.37 (s, 3 H, Me), 1.35 (s, 9 H, Bu^t), 1.18 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 214.7, 211.3, 210.9 (*C*O), 178.6 (C_δH), 178.2 (C_αMe), 113.6 ($C_\beta Bu^t$), 62.4 ($NC(CH_3)_3$), 52.3 (C_γH), 36.7 ($CCMe_3$), 35.7 ($C_\alpha CH_3$), 31.7 ($NC(CH_3)_3$), 31.4 ($CC(CH_3)_3$).

2i, 2i′ (inseparable mixture): photolysis time 5 h; chromatography eluent pentane; yield 87%. HRMS: m/z (EI) calcd for $C_{18}H_{23}Fe_2NO_6Si$ 488.9993, found 488.9997. IR (CH_2Cl_2): ν_{CO} 2054 (m), 2004 (vs), 1978 (s), 1946 (w) cm^{-1}. MS: m/z 489 (M^+) and fragment ions corresponding to the loss of six carbonyls. ^1H NMR (CD_2Cl_2): **2i**, δ 8.11 (d, 1 H, J = 5.8 Hz, $C_\delta H$), 3.37 (d, 1 H, J = 5.8 Hz, $C_\gamma H$), 3.34 (s, 3 H, $C_\alpha CH_3$), 1.18 (s, 9 H, Bu^t), 0.30 (s, 9 H, $SiMe_3$); **2i′**, δ 8.03 (d, 1 H, J = 5.8 Hz, $C_\delta CH$), 3.43 (d, 1 H, J = 5.8 Hz, $C_\gamma CH$), 2.36 (s, 3 H, $C_\beta CH_3$), 1.17 (s, 9 H, Bu^t), 0.49 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): **2i**, δ 213–209 (*C*O), 193.5 (C_αMe), 176.9 (C_δH), 93.5 ($C_\beta SiMe_3$), 62.0 (CMe_3), 55.0 (C_γH), 35.8 ($C_\alpha CH_3$), 31.7 ($C(CH_3)_3$), 0.38 ($Si(CH_3)_3$); **2i′**, δ 213–209 (*C*O), 176.4 (d, C_δH), 167.5 ($C_\alpha SiMe_3$), 107.6 (C_βMe), 62.4 (CMe_3), 60.0 (C_γH), 31.7 ($C(CH_3)_3$), 29.7 ($C_\beta CH_3$), 3.47 ($Si(CH_3)_3$).

2j, 2j′ (inseparable mixture): photolysis time 6 h; chromatography eluent pentane; yield 86%. Anal. Calcd for $C_{23}H_{25}Fe_2NO_6Si$: C, 51.12; H, 4.09. Found: C, 50.99; H, 3.91. IR (CH_2Cl_2): ν_{CO} 2056 (m), 2008 (vs), 1981 (s), 1950 (m) cm^{-1}. MS: m/z 437 (M^+ – 2CO) and fragment ions corresponding to the loss of four carbonyls. ^1H NMR (CD_2Cl_2): δ 8.24 (m, $C_\delta H$, **2j** and **2j′**), 7.51–7.22 (m, Ph, **2j** and **2j′**), 3.34 (m, $C_\gamma H$, **2j** and **2j′**), 3.01 (s, Me, **2j′**), 1.93 (s, Me, **2j**), 1.25 (s, Bu^t, **2j** and **2j′**). ^{13}C NMR (CD_2Cl_2): **2j** (major), δ 214.3, 210.6, 210.0 (*C*O), 180.6 (C_αPh), 178.3 (C_δH), 152.3 (Ph ipso), 133.0–125.5 (Ph), 101.5 (C_βMe), 63.2 ($NCMe_3$), 54.3 (C_γH), 31.9 ($C(CH_3)$), 24.6 (CH_3); **2j′** (minor), δ 214.1, 213.7, 211.6 (*C*O), 178.9 ($C_\alpha CH_3$), 178.3 (C_δH), 141.2 (Ph ipso), 133.0–125.5 (Ph), 107.9 (C_βPh), 62.8 ($NCMe_3$), 55.6 (C_γH), 32.7 ($C(CH_3)_3$), 31.9 (CH_3).

2k, 2k′ (inseparable mixture): photolysis time 5 h; chromatography eluent pentane; yield 87%. Anal. Calcd for $C_{23}H_{25}Fe_2NO_6Si$: C, 50.12; H, 4.57. Found: C, 50.34; H, 4.71. IR (CH_2Cl_2): ν_{CO} 2056 (m), 2006 (vs), 1983 (s), 1948 (w) cm^{-1}. MS: m/z 552 (M^+ – 2CO) and fragment ions corresponding to the loss of four carbonyls. ^1H NMR (CD_2Cl_2): **2k**, δ 8.28 (d, 1 H, J = 5.2 Hz, $C_\delta H$), 7.58–7.19 (m, 5 H, Ph), 3.61 (d, 1 H, J = 5.2 Hz, $C_\gamma H$), 1.24 (s, 9 H, Bu^t), –0.08 (s, 9 H, $SiMe_3$); **2k′**, δ 8.15 (d, 1 H, J = 5.2 Hz, C*H*), 7.58–7.19 (m, 5 H, Ph), 3.46 (d, 1 H, J = 5.2 Hz, C*H*), 1.24 (s, 9 H, Bu^t), 0.13 (s, 9 H, $SiMe_3$). ^{13}C NMR (CD_2Cl_2): **2k**, δ 215.6, 213.4, 209.8, 209.4 (*C*O), 195.4 (C_αPh), 178.0 (C_δH), 152.9 (Ph ipso), 132.5–123.9 (Ph), 105.7 ($C_\beta SiMe_3$), 63.2 (CMe_3), 53.4 (C_γH), 32.2 ($C(CH_3)_3$), 0.6 ($Si(CH_3)_3$); **2k′**, δ 214.0, 212.1, 208.8 (*C*O), 177.4 (C_δH), 173.2 ($C_\alpha SiMe_3$), 144.2 (Ph ipso), 132.5–123.9 (Ph), 94.6 (C_βPh), 61.0 (CMe_3), 53.1 (C_γH), 32.1 ($C(CH_3)_3$), 4.4 ($Si(CH_3)_3$).

2l: photolysis time 2 h; chromatography eluent CH_2Cl_2/pentane (75/25); yield 40%. Anal. Calcd for $C_{17}H_{17}Fe_2NO_8$: C, 42.99; H, 3.61. Found: C, 42.97; H, 3.67. IR (CH_2Cl_2): ν_{CO} 2062 (m), 2016 (vs), 1983 (s), 1703 (w) cm^{-1}. MS: m/z 419 (M^+ – 2CO). ^1H NMR ($CDCl_3$): δ 8.04 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 3.94 (s, 3 H, OCH_3), 3.09 (d, 1 H, J = 5.5 Hz, $C_\gamma H$), 2.30 (s, 3 H, $C_\beta CH_3$), 1.19 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 214.4, 208.7, 208.2 (*C*O), 178.4 (dd, ^1J = 162.4 Hz, ^2J = 2.4 Hz, C_δH), 177.4 (m, $C_\alpha CO_2Me$), 164.6 (s, CO_2Me), 101.0 (dd, $^2J_{CH}$, $^3J_{CH}$ = 3.7 Hz, C_βMe), 63.2 (m, CMe_3), 53.8 (dm, $^1J_{CH}$ = 157.2 Hz, C_γH), 52.4 (q, $^1J_{CH}$ = 146.7 Hz, OCH_3), 31.9 ($C(CH_3)_3$), 24.8 (m, $C_\beta CH_3$).

2l′: photolysis time 1 h; chromatography eluent CH_2Cl_2/pentane (25/75); yield 26%. Anal. Calcd for $C_{17}H_{17}Fe_2NO_8$: C, 42.99; H, 3.61. Found: C, 43.39; H, 3.68. IR (CH_2Cl_2): ν_{CO} 2062 (m), 2016 (vs), 1983 (s), 1710 (w) cm^{-1}. MS: m/z 445 (M^+ – CO). ^1H NMR ($CDCl_3$): δ 8.07 (d, 1 H, J = 5.6 Hz, $C_\delta H$), 3.83 (s, 3 H, OCH_3), 3.68 (d, 1 H, J = 5.6 Hz, $C_\gamma H$), 3.36 (s, 3 H, $C_\alpha CH_3$), 1.18 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 212.0, 209.3 (*C*O), 185.3 (C_αMe), 177.7 (C_δH), 169.8 (CO_2Me), 92.1 ($C_\beta CO_2Me$), 62.6 (CMe_3), 52.3 (OCH_3), 51.3 (C_γH), 34.7 ($C_\alpha CH_3$), 31.7 ($C(CH_3)_3$).

2m: photolysis time 3 h; chromatography eluent CH_2Cl_2/pentane (30/70); yield 45%. IR (CH_2Cl_2): ν_{CO} 2064 (m), 2016 (vs), 1987 (s), 1964 (m), 1726 (w) cm^{-1}. HRMS: m/z calcd for $C_{19}H_{23}Fe_2NO_8Si$ 533.9891, found 533.9852. ^1H NMR ($CDCl_3$): δ 8.09 (d, 1 H, J = 5.6 Hz, $C_\delta H$), 3.91 (s, 3 H, OCH_3), 3.37 (d, 1 H, J = 5.6 Hz, $C_\gamma H$), 1.18 (s, 9 H, $C(CH_3)_3$), 0.23 (s, 9 H, $C_\beta Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 212.5, 207.8, 206.8 (*C*O), 177.5 ($C_\alpha CO_2Me$), 177.2 (CO_2Me), 177.0 (C_δH), 95.3 ($C_\beta SiMe_3$), 62.6 (CMe_3), 52.0 (C_γH), 51.9 (OCH_3), 31.7 ($C(CH_3)_3$), –0.8 ($Si(CH_3)_3$).

2m′: photolysis time 2 h; chromatography eluent CH_2Cl_2/pentane (15/85); yield 26%. IR (CH_2Cl_2): ν_{CO} 2059 (m), 2014 (vs), 1979 (s), 1721 (w) cm^{-1}. HRMS: m/z calcd for $C_{19}H_{23}Fe_2NO_8Si$ 533.9891, found 533.9858. ^1H NMR ($CDCl_3$): δ 8.03 (d, 1 H, J = 5.5 Hz, $C_\delta H$), 3.86 (d, 1 H, J = 5.5 Hz, $C_\gamma H$), 3.80 (s, 3 H, CO_2CH_3), 1.16 (s, 9 H, $C(CH_3)_3$), 0.43 (s, 3 H, $C_\alpha Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 212.4, 211.0, 207.7 (*C*O), 176.1 (C_δH), 172.9 ($C_\alpha SiMe_3$), 172.1 (CO_2Me), 103.2 ($C_\beta CO_2Me$), 62.9 (CMe_3), 56.5 (OCH_3), 52.7 (C_γH), 31.6 ($NC(CH_3)_3$), 2.8 ($Si(CH_3)_3$).

2n: photolysis time 6 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield 81%. Anal. Calcd for $C_{20}H_{17}Fe_2NO_6$: C, 50.14; H, 3.55. Found: C, 50.11; H, 3.38. IR (CH_2Cl_2): ν_{CO} 2055 (m), 2008 (vs), 1981 (s), 1951 (w) cm^{-1}. MS: m/z 479 (M^+) and fragment ions corresponding to loss of six carbonyls. ^1H NMR (CD_2Cl_2): δ 7.93 (d, 1 H, J = 5.0 Hz, $C_\delta H$), 7.33–6.74 (m, 5 H, Ph), 6.05 (d, 1 H, J = 6.3 Hz, $C_\beta H$), 3.41 (dd, 1 H, $C_\gamma H$), 1.69 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 211.8, 209.9 (*C*O), 203.1 (m, $C_\alpha Bu^t$), 181.6 (dd, C_δH, $^1J_{CH}$ = 163.3 Hz, $^2J_{CH}$ = 3.1 Hz), 154.8, 129.5, 127.1, 122.1 (Ph), 86.8 (dd, C_βH, $^1J_{CH}$ = 166.3 Hz, $^2J_{CH}$ = 2.7 Hz), 52.3 (ddd, C_γH, $^1J_{CH}$ = 158.6 Hz, $^2J_{CH}$ = 10.6, 3.6 Hz), 45.7 (CMe_3), 35.5 ($C(CH_3)_3$).

2o: photolysis time 5 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield 72%. Anal. Calcd for $C_{28}H_{17}Fe_2NO_6$: C, 58.47; H, 2.96. Found: C, 58.69; H, 2.96. 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, $C_\delta H$), 7.59–6.92 (m, 10 H, 3 Ph), 3.64 (d, 1 H, J = 5.1 Hz, $C_\gamma H$). ^{13}C NMR (C_6D_6): δ 211.0, 208.7, 208.0 (CO), 181.0 (dd, C_δH, $^1J_{CH}$ = 167.7 Hz, $^2J_{CH}$ = 2.6 Hz), 179.0 (m, C_αPh), 154.9, 152.3, 141.1, 131.4, 129.4, 128.9, 128.8, 127.1, 126.5, 126.2, 125.7, 121.8 (Ph), 109.0 (d, C_βPh, $^2J_{CH}$ = 4.0 Hz), 54.1 (dd, C_γH, $^1J_{CH}$ = 158.9 Hz, $^2J_{CH}$ = 12.0 Hz).

3a: photolysis time 0.5 h; chromatography eluent 3:1 pentane/CH_2Cl_2; yield 39% (as an oil). IR (CH_2Cl_2): ν_{CO} 2062 (m), 2024 (vs), 1992 (s), 1971 (m), 1625 (w) cm^{-1}. CI/MS: m/z (M^+ – 2CO) and fragment ions corresponding to the loss of four carbonyls. ^1H NMR ($CDCl_3$): δ 7.00 (d, 1 H, J = 8.7 Hz, C*H*NBu^t), 4.67 (dd, 1 H, J = 8.2, 1.4 Hz, C*H*), 4.18 (d, 1 H, J = 1.4 Hz, C*H*), 2.99 (dd, 1 H, J = 8.7, 8.2 Hz, C*H*), 2.44 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 1.14 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 210.3 (*C*O),

167.5 (s, CCH_3), 158.0 (d, $^1J_{CH}$ = 161.2 Hz, *C*H), 90.2 (d, J = 157.9 Hz, *C*H), 85.4 (d, *C*H, $^1J_{CH}$ = 163.9 Hz), 69.3 (CMe_3), 57.5 (s, CCH_3), 56.1 (d, J = 170.9 Hz, *C*H), 31.3 (m, CCH_3), 29.6 ($C(CH_3)_3$), 23.8 (m, CCH_3).

3e: photolysis time 4 h; chromatography eluent 3:1 pentane-/CH_2Cl_2; yield <5% (as an oil). IR (CH_2Cl_2): ν_{CO} 2054 (m), 2017 (vs), 1985 (s), 1963 (m), 1627 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.79 (d, 1 H, J = 8.5 Hz, *CH*NBu^t), 3.07 (d, 1 H, J = 8.5 Hz, *CH*), 2.46 (s, 3 H, CH_3), 2.20 (d, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.14 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (CD_2Cl_2): δ 212.0, 211.1 (*C*O), 162.9 (s, CCH_3), 159.0 (dd, $^1J_{CH}$ = 161.2, 11.0 Hz, *C*H), 104.6 (s, CCH_3), 100.1 (s, CCH_3), 75.6 (d, J = 13.4 Hz, CMe_3), 62.7 (dd, J = 153.8, 15.8 Hz, *C*H), 57.6 (s, CCH_3), 30.0 (m, CCH_3), 29.8 ($C(CH_3)_3$), 28.4 (m, CCH_3), 22.4 (m, CCH_3), 15.0 (m, CCH_3).

Thermal Reactions of $Fe_2(\mu$-CH=CHNBu^t)(CO)$_6$ (1a) with PhC≡CH and $Fe_2(\mu$-CH=CHNPh)(CO)$_6$ (1b) with PhC≡CPh. Complex **1a** (50 mg, 0.13 mmol) was placed in a 100-mL Schlenk flask and dissolved in 50 mL of toluene, and PhC≡CH (14.2 mg, 0.14 mmol) was added. The resulting orange solution was then refluxed for 8 h with constant stirring as the color changed to dark red. The solvent was evaporated, and the residue was separated by column chromatography on silica gel with pentane as eluent to give a band of unreacted **1a**. The eluent was then changed to 30% CH_2Cl_2/70% pentane, which led to the elution of an orange band of complex **2d** (31.7 mg, 0.064 mmol, 49%). A similar reaction of complex **1b** (50 mg, 0.13 mmol) and PhC≡CPh gave complex **2o** in 49% yield (37 mg, 0.064 mmol).

Ring Contraction of the 2-Ferrapyridine Complex 2d. Complex **2d** (202.0 mg, 0.42 mmol) was dissolved in hexane (30 mL) and the solution transferred to a 300-mL stainless steel Parr reactor under a N_2 atmosphere. The reactor was sealed, pressurized with 500 psi of CO, and heated to 160 °C for 48 h. After depressurization, the solvent was removed by rotary evaporation and the resulting residue purified by column chromatography on silica gel with pentane eluent to give complex **1c** as a red oil.

1c: yield 75%. Anal. Calcd for $C_{20}H_{17}Fe_2NO_6$: C, 50.14; H, 3.55. Found: C, 50.72; H, 3.89. IR (pentane): ν_{CO} 2071 (m), 2027 (vs), 1997 (s), 1985 (s), 1972 (w) cm^{-1}. MS: m/z 479 (M$^+$) and fragment ions corresponding to the loss of six carbonyls. ^{1}H NMR ($CDCl_3$): δ 7.42–7.39 (m, 2 H, Ph), 7.34–7.25 (m, 3 H, Ph), 6.83 (d, 1 H, J = 15.6 Hz, *CH*), 6.72 (d, 1 H, J = 15.6 Hz, *CH*), 6.54 (s, 1 H, *CH*), 1.06 (s, 9 H, Bu^t). ^{13}C NMR ($CDCl_3$): δ 210.9 (*C*O), 136.6 (s, Ph ipso), 134.6 (d, $^1J_{CH}$ = 157.7 Hz, *C*H), 128.7 (d, $^1J_{CH}$ = 150.9 Hz, *C*H), 128.6, 128.1, 126.6 (Ph), 105.7 (dd, $^1J_{CH}$ = 174.3 Hz, $^2J_{CH}$ = 6.8 Hz, *C*HNBu^t), 57.7 (m, CMe_3), 30.3 (m, $C(CH_3)_3$).

Formation of 2-Pyridinones and Pyrroles from the 2-Ferrapyridine Complexes 2a–o. The appropriate complex **2a–o** (0.18 mmol) was placed in a 50-mL Schlenk flask and dissolved in 30 mL of acetonitrile. The solution was heated at reflux for 12–24 h until IR analysis indicated complete reaction by loss of all metal carbonyl bands. The resulting solution was filtered through a 1-in. pad of silica gel, and the solvent was evaporated to leave a white crystalline solid or a light yellow oil. If further purification was needed, the product was chromatographed on silica gel with 20:1 pentane/CH_2Cl_2 eluent. When both were formed, the pyrrole product eluted before the pyridinone product in each case. Pyrroles **6e**, **6h**, and **6i** were extracted from the acetonitrile solution with pentane before isolating the 2-pyridinones. Yields and spectroscopic data are given below.

5a: yield 65%. HRMS: m/z (EI) M$^+$ 165.1154 (calcd), 165.1149 (found). ^{1}H NMR ($CDCl_3$): δ 7.39 (dd, 1 H, ^3J = 7.6 Hz, *CH*), 7.13 (dd, 1 H, ^3J = 6.4 Hz, *CH*), 6.00 (dd, 1 H, ^3J = 7.6, 6.4 Hz, *CH*), 2.10 (s, 3 H, CH_3), 1.67 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1646 cm^{-1}.

5b: yield 86%. HRMS: m/z (EI) M$^+$ 207.1623 (calcd), 207.1621 (found). ^{1}H NMR ($CDCl_3$): δ 7.43 (dd, 1 H, ^3J = 7.0 Hz, ^4J = 1.7 Hz, *CH*), 7.18 (dd, 1 H, ^3J = 7.0 Hz, ^4J = 1.7 Hz, *CH*), 6.00 (t, 1 H, ^3J = 7.0 Hz, *CH*), 1.67 (s, 9 H, Bu^t), 1.34 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1646 cm^{-1}.

5c: yield 74%. HRMS: m/z (EI) M$^+$ 223.1392 (calcd), 223.1398 (found). ^{1}H NMR ($CDCl_3$): δ 7.49 (dd, 1 H, ^3J = 7.3 Hz, ^4J = 2.1 Hz, *CH*), 7.34 (dd, 1 H, ^3J = 6.1 Hz, ^4J = 2.1 Hz, *CH*), 6.05 (dd, 1 H, ^3J = 7.3, 6.1 Hz, *CH*), 1.64 (s, 9 H, Bu^t), 1.64 (s, 9 H, $SiMe_3$). IR (CH_2Cl_2): ν_{CO} 1636 cm^{-1}.

5d: yield 61%. HRMS: m/z (EI) M$^+$ 227.1310 (calcd), 227.1319 (found). ^{1}H NMR ($CDCl_3$): δ 7.61, 7.37 (m, 5 H, Ph), 7.53 (d, 1 H, ^3J = 7.3 Hz, *CH*), 7.29 (d, 1 H, ^3J = 7.3 Hz, *CH*), 6.16 (t, 1 H, ^3J = 7.3 Hz, *CH*), 1.71 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1646 cm^{-1}.

6d: yield 25%. HRMS: m/z (EI) M$^+$ 199.1361 (calcd), 199.1357 (found). ^{1}H NMR ($CDCl_3$): δ 7.40–7.32 (m, 5 H, Ph), 6.91 (dd, 1 H, ^3J = 3.1 Hz, ^4J = 2.0 Hz, *CH*), 6.14 (dd, 1 H, ^3J = 3.1, 3.1 Hz, *CH*), 6.02 (dd, 1 H, ^3J = 3.1 Hz, ^4J = 2.0 Hz, *CH*), 1.43 (s, 9 H, Bu^t).

5d′: HRMS: m/z (EI) M$^+$ 228.1373 (calcd), 228.1372 (found). ^{1}H NMR ($CDCl_3$): δ 7.61, 7.37 (m, 5 H, Ph), 7.54 (d, 1 H, ^3J = 7.3 Hz, *CH*), 6.17 (d, 1 H, ^3J = 7.3 Hz, *CH*), 1.71 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1646 cm^{-1}.

6d′: HRMS: m/z (EI) M$^+$ 200.1424 (calcd), 200.1419 (found). ^{1}H NMR ($CDCl_3$): δ 7.40, 7.32 (m, 5 H, Ph), 6.92 (d, 1 H, ^3J = 3.1 Hz, *CH*), 6.14 (d, 1 H, ^3J = 3.1 Hz, *CH*), 1.43 (s, 9 H, Bu^t).

5e: yield 31%. HRMS: m/z (EI) M$^+$ 179.1310 (calcd), 179.1305 (found). ^{1}H NMR ($CDCl_3$): δ 7.26 (d, 1 H, ^3J = 7.3 Hz, *CH*), 5.90 (d, 1 H, ^3J = 7.3 Hz, *CH*), 2.09 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.71 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1646 cm^{-1}.

6e: yield 2%. HRMS: m/z (EI) M$^+$ 151.1361 (calcd), 151.1353 (found). ^{1}H NMR ($CDCl_3$): δ 6.68 (d, 1 H, ^3J = 3.0 Hz, *CH*), 5.87 (d, 1 H, ^3J = 3.0 Hz, *CH*), 2.31 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 1.56 (s, 9 H, Bu^t).

5f: yield 48%. HRMS: m/z (EI) M$^+$ 207.1623 (calcd), 207.1608 (found). ^{1}H NMR ($CDCl_3$): δ 7.32 (d, 1 H, ^3J = 7.3 Hz, *CH*), 5.93 (d, 1 H, ^3J = 7.3 Hz, *CH*), 2.57 (q, 2 H, ^3J = 7.4 Hz, CH_2CH_3), 2.47 (q, 2 H, ^3J = 7.6 Hz, CH_2CH_3), 1.67 (s, 9 H, Bu^t), 1.16 (t, 3 H, ^3J = 7.4 Hz, CH_2CH_3), 1.10 (t, 3 H, ^3J = 7.6 Hz, CH_2CH_3). IR (CH_2Cl_2): ν_{CO} 1643 cm^{-1}.

6f: yield 39%. HRMS: m/z (EI) M$^+$ 179.1674 (calcd), 179.1669 (found). ^{1}H NMR ($CDCl_3$): δ 6.68 (d, 1 H, ^3J = 3.1 Hz, *CH*), 5.97 (d, 1 H, ^3J = 3.1 Hz, *CH*), 2.81 (q, 2 H, ^3J = 7.3 hz, CH_2CH_3), 2.43 (q, 2 H, ^3J = 7.3 Hz, CH_2CH_3), 1.21 (t, 3 H, ^3J = 7.3 Hz, CH_2CH_3), 1.17 (t, 3 H, ^3J = 7.3 Hz, CH_2CH_3), 1.60 (s, 9 H, Bu^t).

6g: yield 82%. HRMS: m/z (EI) M$^+$ 275.1674 (calcd), 275.1670 (found). ^{1}H NMR ($CDCl_3$): δ 7.39, 7.12 (m, 10 H, Ph), 6.98 (d, 1 H, J = 3.1 Hz, *CH*), 6.39 (d, 1 H, J = 3.1 Hz, *CH*), 1.45 (s, 9 H, Bu^t).

5h: yield 47%. HRMS: m/z (EI) M$^+$ 221.1780 (calcd), 221.1788 (found). ^{1}H NMR ($CDCl_3$): δ 7.29 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 6.14 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 2.24 (s, 3 H, CH_3), 1.64 (s, 9 H, $NC(CH_3)_3$), 1.32 (s, 9 H, $CC(CH_3)_3$). IR (CH_2Cl_2): ν_{CO} 1636 cm^{-1}.

6h: yield 26%. ^{1}H NMR ($CDCl_3$): δ 7.09 (d, 1 H, $^3J_{HH}$ = 3.0 Hz, *CH*), 6.77 (d, 1 H, $^3J_{HH}$ = 3.0 Hz, *CH*), 2.51 (s, 3 H, CH_3), 1.54 (s, 9 H, $NC(CH_3)_3$), 1.24 (s, 9 H, $CC(CH_3)_3$).

5i: yield 12%. HRMS: m/z (EI) M$^+$ 237.1549 (calcd), 237.1572 (found). ^{1}H NMR ($CDCl_3$): δ 7.33 (d, 1 H, $^3J_{HH}$ = 7.2 Hz, *CH*), 6.06 (d, 1 H, $^3J_{HH}$ = 7.2 Hz, *CH*), 2.18 (s, 3 H, CH_3), 1.64 (s, 9 H, $NC(CH_3)_3$), 0.26 (s, 9 H, $CSi(CH_3)_3$). IR (CH_2Cl_2): ν_{CO} 1632 cm^{-1}.

5i′: yield 6%. HRMS: m/z (EI) M$^+$ 237.1549 (calcd), 237.1558 (found). ^{1}H NMR ($CDCl_3$): δ 7.34 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, *CH*), 5.84 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, *CH*), 2.20 (s, 3 H, CH_3), 1.61 (s, 9 H, $NC(CH_3)_3$), 0.29 (s, 9 H, $CSi(CH_3)_3$). IR (CH_2Cl_2): ν_{CO} 1631 cm^{-1}.

6i, 6i′: yield 2%. HRMS: m/z (EI) M$^+$ 209.1600 (calcd), 209.1594 (found). ^{1}H NMR ($CDCl_3$): δ 6.83 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 6.04 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 2.46 (s, 3 H, CH_3), 1.58 (s, 9 H, $NC(CH_3)_3$), 0.19 (s, 9 H, $CSi(CH_3)_3$).

5j, j′ (inseparable mixture): yield 40%. HRMS: m/z (EI) M$^+$ 241.1467 (calcd), 241.1476 (found). ^{1}H NMR ($CDCl_3$): major, δ 7.40 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 7.39–7.34 (m, 2 H, Ph), 7.29–7.20 (m, 3 H, Ph), 6.02 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 1.97 (s, 3 H, CH_3), 1.66 (s, 9 H, $C(CH_3)_3$); minor, δ 7.39 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 7.39–7.34 (m, 2 H, Ph), 7.29–7.20 (m, 3 H, Ph), 6.04 (d, 1 H, $^3J_{HH}$ = 7.6 Hz, *CH*), 2.05 (s, 3 H, CH_3), 1.71 (s, 9 H, $C(CH_3)_3$). IR (CH_2Cl_2): ν_{CO} 1643 cm^{-1}.

6j,j′ (inseparable mixture): yield 30%. HRMS: m/z (EI) M$^+$ 213.1517 (calcd), 213.1521 (found). ^{1}H NMR ($CDCl_3$): major, δ 7.36–7.29 (m, 5 H, Ph), 6.81 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 6.01 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 1.75 (s, 3 H, CH_3), 1.37 (s, 9 H, $C(CH_3)_3$); minor, δ 7.36–7.29 (m, 5 H, Ph), 6.84 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 6.17 (d, 1 H, $^3J_{HH}$ = 3.1 Hz, *CH*), 2.50 (s, 3 H, CH_3), 1.64 (s, 9 H, $C(CH_3)_3$). IR (CH_2Cl_2): ν_{CO} 1603 cm^{-1}.

5k: yield 14%. HRMS: m/z (EI) M$^+$ 299.1705 (calcd), 299.1696 (found). ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, *CH*), 7.40–7.34 (m, 3 H, Ph), 7.27–7.20 (m, 2 H, Ph), 5.99 (d,

1 H, $^3J_{HH}$ = 7.3 Hz, C*H*), 1.71 (s, 9 H, C(CH_3)$_3$), −0.04 (s, 9 H, Si(CH_3)$_3$). IR ($CDCl_3$): ν_{CO} 1629 cm^{-1}.

5k′: yield 8%. HRMS: *m/z* (EI) M$^+$ 299.1705 (calcd), 299.1688 (found). ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, C*H*), 7.40–7.30 (m, 3 H, Ph), 7.21–7.17 (m, 2 H, Ph), 5.21 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, C*H*), 1.67 (s, 9 H, C(CH_3)$_3$), −0.10 (s, 9 H, Si(CH_3)$_3$). IR ($CDCl_3$): ν_{CO} 1628 cm^{-1}.

6k, 6k′ (inseparable mixture): yield 30%. HRMS: *m/z* (EI) M$^+$ 271.1756 (calcd), 271.1765 (found). ^{1}H NMR ($CDCl_3$): major, δ 7.40–7.27 (m, 5 H, Ph), 6.96 (d, 1 H, ^3J = 2.9 Hz, C*H*), 6.21 (d, 1 H, ^3J = 2.9 Hz, C*H*), 1.39 (s, 9 H, Bu^t), −0.14 (s, 9 H, Si(CH_3)$_3$); minor, δ 7.40–7.27 (m, 5 H, Ph), 7.01 (d, 1 H, ^3J = 3.1 Hz, C*H*), 6.27 (d, 1 H, ^3J = 3.1 Hz, C*H*), 1.59 (s, 9 H, Bu^t), −0.05 (s, 9 H, Si(CH_3)$_3$).

5l: yield 44%. HRMS: *m/z* (EI) M$^+$ 223.1208 (calcd), 223.1201 (found). ^{1}H NMR ($CDCl_3$): δ 7.42 (d, 1 H, ^3J = 7.5 Hz, C*H*NBu^t), 5.95 (d, 1 H, ^3J = 7.5 Hz, C*H*), 3.89 (s, 3 H, CO_2CH_3), 2.14 (s, 3 H, $C_\beta CH_3$), 1.38 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{max} 1725 (C=O), 1653 (C=O), 1599 (C=C) cm^{-1}.

6l: yield 16%. HRMS: *m/z* (EI) M$^+$ 195.1259 (calcd), 195.1255 (found). ^{1}H NMR ($CDCl_3$): δ 6.69 (d, 1 H, ^3J = 3.4 Hz, C*H*), 6.44 (d, 1 H, ^3J = 3.4 Hz, C*H*), 3.75 (s, 3 H, CO_2CH_3), 2.74 (s, 3 H, CH_3), 1.60 (s, 9 H, Bu^t). IR ($CDCl_3$): ν_{max} 1697 (C=O), 1545 (C=C) cm^{-1}.

5l′: yield 4%. HRMS: *m/z* (EI) M$^+$ 223.1208 (calcd), 223.1213 (found). ^{1}H NMR ($CDCl_3$): δ 7.41 (d, 1 H, ^3J = 7.6 Hz, C*H*NBu^t), 6.32 (d, 1 H, ^3J = 7.6 Hz, C*H*), 3.87 (s, 3 H, CO_2CH_3), 2.30 (s, 3 H, $C_\alpha CH_3$), 1.65 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{max} 1730 (C=O), 1647 (C=O), 1603 (C=C) cm^{-1}.

6l′: yield 55%. HRMS: *m/z* (EI) M$^+$ 195.1259 (calcd), 195.1255 (found). ^{1}H NMR ($CDCl_3$): δ 6.69 (d, 1 H, ^3J = 3.4 Hz, C*H*NBu^t), 6.44 (d, 1 H, ^3J = 3.4 Hz, C*H*), 3.75 (s, 3 H, CO_2CH_3), 2.74 (s, 3 H, $C_\alpha CH_3$), 1.60 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{max} 1697 (C=O), 1545 (C=C) cm^{-1}.

5m: yield 3%. HRMS: *m/z* (EI) M$^+$ 281.1447 (calcd), 281.1454 (found). ^{1}H NMR ($CDCl_3$): δ 7.48 (d, 1 H, ^3J = 7.3 Hz, C*H*NBu^t), 6.45 (d, 1 H, ^3J = 7.3 Hz, C*H*), 3.86 (s, 3 H, CO_2CH_3), 1.65 (s, 9 H, Bu^t), 0.22 (s, 3 H, C_βSi(CH_3)$_3$). IR (CH_2Cl_2): ν_{max} 1728 (C=O), 1633 (C=O), 1582 (C=C) cm^{-1}.

6m: yield 38%. HRMS: *m/z* (EI) M$^+$ 253.1498 (calcd), 281.1499 (found). ^{1}H NMR ($CDCl_3$): δ 7.12 (d, 1 H, ^3J = 2.7 Hz, C*H*NBu^t), 6.17 (d, 1 H, ^3J = 2.7 Hz, C*H*), 3.77 (s, 3 H, CO_2CH_3), 1.68 (s, 9 H, Bu^t), 0.19 (s, 3 H, C_βSi(CH_3)$_3$). IR (CH_2Cl_2): ν_{CO} 1705 (C=O) cm^{-1}.

5m′: yield 38%. HRMS: *m/z* (EI) M$^+$ = 281.1447 (calcd), 281.1443 (found). ^{1}H NMR ($CDCl_3$): δ 7.51 (d, 1 H, ^3J = 7.3 Hz, C*H*NBu^t), 6.06 (d, 1 H, ^3J = 7.3 Hz, C*H*), 3.82 (s, 3 H, CO_2CH_3), 1.63 (s, 9 H, Bu^t), 0.23 (s, 3 H, C_αSi(CH_3)$_3$). IR (CH_2Cl_2): ν_{max} 1730 (C=O), 1633 (C=O), 1593 (C=C) cm^{-1}.

6m′: yield 16%. HRMS: *m/z* (EI) M$^+$ 253.1498 (calcd), 253.1519 (found). ^{1}H NMR ($CDCl_3$): δ 6.98 (d, 1 H, ^3J = 3.1 Hz, C*H*NBu^t), 6.51 (d, 1 H, ^3J = 3.1 Hz, C*H*), 3.76 (s, 3 H, CO_2CH_3), 1.61 (s, 9 H, Bu^t), 0.44 (s, 3 H, C_αSi(CH_3)$_3$). IR (CH_2Cl_2): ν_{CO} 1705 cm^{-1}.

5n: yield 89%. HRMS: *m/z* (EI) 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}.

6o: yield 92%. HRMS: *m/z* (EI) 295.1361 (calcd), 295.1362 (found). ^{1}H NMR ($CDCl_3$): δ 7.22, 7.15 (m, 10 H, Ph), 6.97 (d, 1 H, ^3J = 3.1 Hz, C*H*), 6.53 (d, 1 H, ^3J = 3.1 Hz, C*H*).

Thermal Decomposition of the 2-Ferrapyridine Complexes in Tetrahydrofuran under 500 psi of CO in the Presence of [PPN]Cl. The appropriate complex **2d**, **2g**, **2j**, **2j′**, or **2o** was dissolved in THF and the solution transferred to a 300-mL stainless steel Parr reactor. One equivalent of [PPN]Cl (0.13 mmol) was added; the autoclave was sealed, pressurized with 600 psi of CO, and heated to 160 °C for 48 h. After depressurization, the IR spectrum of the resulting yellow solution showed bands at 2021 and 1995 cm^{-1} due to $Fe(CO)_5$. The solvent was removed by rotary evaporation, and the resulting residue was chromatographed on silica gel using 20:1 pentane/CH_2Cl_2 as eluent. The pyrrole product eluted before the pyridinone product in each case. Yields are as follows: from **2d**, **5d** (74%), **6d** (10%); from **2f**, **5f** (71%), **6f** (10%); from **2g**, **5g** (19%), **6g** (43%); from **2j,j′**, **5j,j′** (40%), **6j,j′** (29%); from **2o**, **5o** (29%), **6o** (44%).

5g: HRMS: *m/z* (EI) M$^+$ 303.1623 (calcd), 303.1628 (found). ^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1 H, ^3J = 7.6 Hz, C*H*), 7.30–7.12 (m, 10 H, Ph), 6.20 (d, 1 H, ^3J = 7.6 Hz, C*H*), 1.73 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1638 cm^{-1}.

5o: HRMS: *m/z* (EI) M$^+$ 323.1310 (calcd), 323.1284 (found). ^{1}H NMR ($CDCl_3$): δ 7.50, 7.29 (m, 15 H, Ph), 7.43 (d, 1 H, ^1J = 7.3 Hz, C*H*), 6.40 (d, 1 H, ^1J = 7.3 Hz, C*H*). IR (CH_2Cl_2): ν_{CO} 1645 cm^{-1}.

Transformation of the *N*-*tert*-Butylpyridinones 5b,d into the *N*-Hydridopyridinones 5q,r. Complex **5b** or **5d** (0.10 mmol) was placed in a 50-mL Schlenk flask, to which was added CF_3CO_2H (30 mL). The resulting solution was then refluxed at 73 °C for 48 h. The solution was filtered, and the CF_3CO_2H was removed from the supernatant by rotary evaporation. The resulting solid residue was washed with pentane to leave the product as a white crystalline compound (**5q**, yield 92%, 14 mg, 0.092 mmol; **5r**, yield 94%, 16 mg, 0.094 mmol).

5q: HRMS: *m/z* (EI) M$^+$ 151.0997 (calcd), 151.0991 (found). ^{1}H NMR ($CDCl_3$): δ 7.77 (d, 1 H, ^3J = 7.3 Hz, C*H*), 7.52 (d, 1 H, ^3J = 7.3 Hz, C*H*), 6.77 (m, 1 H, C*H*), 1.39 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} 1643 cm^{-1}.

5r: HRMS: *m/z* (EI) M$^+$ 171.0684 (calcd), 171.0687 (found). ^{1}H NMR ($CDCl_3$): δ 7.68–7.33 (m, 5 H, Ph), 7.57 (dd, 1 H, ^3J = 6.7 Hz, ^4J = 1.8 Hz, C*H*), 7.33 (dd, 1 H, ^3J = 6.7 Hz, ^4J = 1.8 Hz, C*H*), 6.35 (t, 1 H, ^3J = 6.7 Hz, C*H*). IR (CH_2Cl_2): ν_{CO} 1645 cm^{-1}.

Crystallographic Characterization of Fe_2(μ-C{CH=CH-(Ph)}=CHNBu^t)$(CO)_6$ (1c), Fe_2(μ-C{CO_2CH_3}C{CH_3}CHCH=NBu^t)$(CO)_6$ (2l), and Fe_2(μ-C{Ph}C{Ph}CHCH=NPh)$(CO)_6$ (2o). Crystal, data collection, and refinement parameters are collected in Table III. All samples were mounted on fine glass fibers with epoxy cement. The unit-cell parameters for **1c**, **2l**, and **2o** were each obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed 2/*m* Laue symmetry for each complex, and systematic absences in the diffraction data uniquely established the space groups as $P2_1/n$ for each complex. An empirical absorption correction was applied to each data set (T_{max}/T_{min} = 1.136, 1.162, and 1.079 for **1c**, **2l**, and **2o**, respectively).

The structures were solved by direct methods, which located the Fe atoms. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl rings in **1c** and **2o** were constrained to rigid, planar hexagons (*d*(CC) = 1.395 Å). The hydrogens of **2l** and **2o** were included as idealed isotropic contributions (*d*(CH) = 0.960 Å, *U* = 1.2 times the *U* value for attached C). The hydrogens of **1c** were all found and refined isotropically.

All computations used SHELXTL software (version 5.1; G. Sheldrick, Nicolet XRD, Madison, WI).

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Registry No. **1a**, 122539-46-2; **1b**, 122539-47-3; **1c**, 138053-61-9; **2a**, 138353-31-8; **2b**, 125641-62-5; **2c**, 125664-85-9; **2d**, 125641-63-6; **2d′**, 125641-64-7; **2e**, 138353-32-9; **2f**, 125641-65-8; **2g**, 138353-33-0; **2h**, 138353-34-1; **2i**, 138353-35-2; **2i′**, 138353-36-3; **2j**, 138353-37-4; **2j′**, 138353-38-5; **2k**, 138353-39-6; **2k′**, 138353-40-9; **2l**, 138353-41-0; **2l′**, 138353-42-1; **2m**, 138353-43-2; **2m′**, 138353-44-3; **2n**, 125664-83-7; **2o**, 125664-84-8; **3a**, 138353-45-4; **3e**, 138353-46-5; **5a**, 138336-65-9; **5b**, 125641-54-5; **5c**, 125641-59-0; **5d**, 125641-55-6; **5d′**, 125641-56-7; **5e**, 138336-66-0; **5f**, 125641-58-9; **5g**, 90331-05-8; **5h**, 138336-67-1; **5i**, 138336-68-2; **5i′**, 138336-69-3; **5j**, 138336-70-6; **5j′**, 138336-71-7; **5k**, 138336-72-8; **5k′**, 138336-73-9; **5l**, 138336-74-0; **5l′**, 138336-75-1; **5m**, 138336-76-2; **5m′**, 138336-77-3; **5n**, 125641-53-4; **5o**, 125641-57-8; **5q**, 125641-60-3; **5r**, 24228-13-5; **6d**, 138336-78-4; **6d′**, 138336-79-5; **6e**, 138336-80-8; **6f**, 138336-81-9; **6g**, 15811-41-3; **6h**, 138336-82-0; **6i**, 138336-83-1; **6i′**, 138336-84-2; **6j**, 138336-85-3; **6j′**, 138336-86-4; **6k**, 138336-87-5; **6k′**, 138336-88-6; **6l**, 138336-89-7; **6l′**, 138336-90-0; **6m**, 138336-91-1; **6m′**, 138336-92-2; **6o**, 53646-86-9; MeC≡CH, 74-99-7; Bu^{t}C≡CH, 917-92-0; $Me_3SiC{\equiv}CH$, 1066-54-2; PhC≡CH, 536-74-3; MeC≡CMe, 503-

17-3; EtC≡CEt, 928-49-4; PhC≡CPh, 501-65-5; MeC≡CBu^t, 999-78-0; Me_3SiC≡CMe, 6224-91-5; PhC≡CMe, 673-32-5; PhC≡$CSiMe_3$, 2170-06-1; MeO_2CC≡CMe, 23326-27-4; MeO_2CC≡$CSiMe_3$, 42201-71-8; 1-*tert*-butyl-3-phenylpyrrole, 20946-89-8.

Supplementary Material Available: For **1c**, **2l**, and **2o** tables of anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions (12 pages); tables of structure factors (21 pages). Ordering information is given on any current masthead page.

New C–C Bond Formation Reactions Using Bis(acylmethyl)- and Bis[(alkoxycarbonyl)methyl]tellurium Dichlorides

Rui Tamura,*,† Hiroshi Shimizu,‡ Noboru Ono,‡ Nagao Azuma,† and Hitomi Suzuki§

Departments of Chemistry, Faculty of General Education, Ehime University, Matsuyama 790, Japan, Faculty of Science, Ehime University, Matsuyama 790, Japan, and Faculty of Science, Kyoto University, Kyoto 606, Japan

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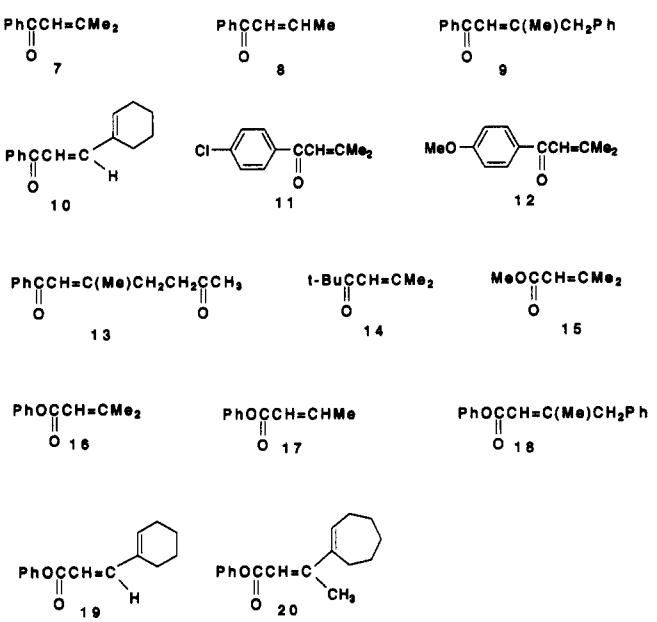
The reaction of organotellurium chlorides with nucleophilic stabilized carbanions has been surveyed. A combination of the bis(organo)tellurium dichlorides [$(R^1COCH_2)_2TeCl_2$] and lithium nitronates [LiC(NO_2)R^2R^3] led to the coupling products (R^1COCH=CR^2R^3) in high to modest yields. This reaction did not involve an S_N2 process nor a radical one with respect to C–C bond formation but was likely to proceed by a polar mechanism that was initiated by coordination of the nitronate oxygen atom to the tellurium followed by intramolecular C–C bond formation and subsequent elimination of nitro and tellurium moieties. To know the exact structure of the starting tellurium compounds, an X-ray analysis of $(PhOCOCH_2)_2TeCl_2$ was performed, and an intramolecular interaction between the carbonyl oxygen of a $PhOCOCH_2$ group and the tellurium was not observed.

Introduction

$TeCl_4$ serves as the Lewis acid[1] and exhibits moderate oxo- and thiophilicity to undergo coordination of the heteroatoms to the tellurium.[2] By using this property, several useful chemical transformations have been devised.[2] Bis(organo)tellurium dichlorides and organotellurium trichlorides are also considered to possess Lewis acidity, due to the inductive effect of the chlorine atoms linked to the tellurium and the general ability of a tellurium atom to take hypervalent bond state.[3] Further, this inductive effect of the chlorine atoms forced the carbon atom of the C–Te bond to positively polarize, in spite of the lower electronegativity of tellurium (2.1) compared with that of carbon (2.55). Thus, we envisioned that this Lewis acidity or oxophilicity and highly polarized nature of organotellurium chlorides must permit them to serve as appropriate electrophiles for nucleophilic substitution reaction, especially for the selective C-alkylation of ambident nucleophiles having O- and C-alkylation sites by blocking O-alkylation owing to an interaction between the oxygen and tellurium atoms. In this context, C-phenylation of phenols, 1,3-dicarbonyl compounds, and other stabilized anions with pentavalent triphenyl- or tetraphenylbismuthonium reagents has been accomplished by Barton and co-workers.[4] To the best of our knowledge, however, there has been no report that organotellurium chlorides, which are now readily available,[3,5,6] could be used as the electrophile for new C–C bond forming reaction.

We have been exploring new bond forming reactions using aliphatic nitro compounds as both the nucleophile and the electrophile.[7] Selective S_N2 type C-alkylation of ambident anions of nitroalkanes is still a remaining problem to be solved.[8] As specific cases, it was found that primary and secondary alkyl cobaloximes[9] and alkylmercury halides[10] and perfluoroiodides[11] underwent C-

Chart I



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† Faculty of General Education, Ehime University.
‡ Faculty of Science, Ehime University.
§ Kyoto University.

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