Iron(II) Vinylidenes and Chromium Carbene Complexes in β-Lactam Synthesis

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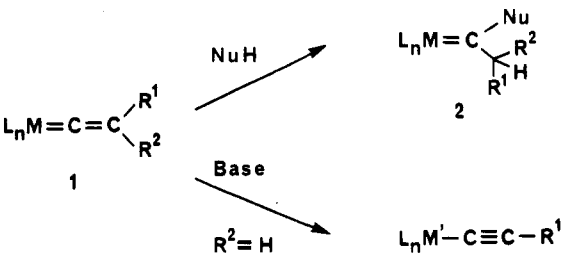
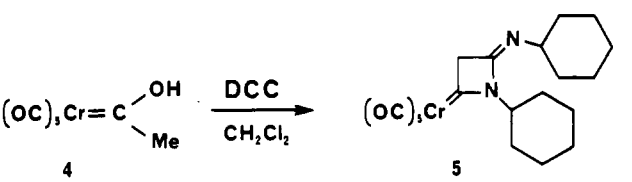
Reaction of the chromium carbene **7** with toluene-4-sulfonyl chloride and the imine **8a** gave **9a** (26%). Alternatively reactions of the cationic iron(II) vinylidene reagents **20a,b**, and **23a–d** with the imines **8a–d** and 2-thiazolines **28a–c** gave the corresponding azetidinylidene complexes **21a,b**, **24a–f**, and **29a–d** (11–82%). Subsequent oxidation of these complexes using iodosobenzene, pyridine *N*-oxide, bromine, air, or tetrabutylammonium nitrite gave the monocyclic or bicyclic β-lactams **10a–c**, **25a–d**, and **30a–c** (8–97%).

Mononuclear metal vinylidenes **1** are a group of transition-metal complexes that contain the formal carbon–carbon–metal cumulene bond system. A diverse array of these substances have been prepared from the dehydration of metal acyls, the reaction of acetylides with protic acids or methylating agents, or the rearrangement of η^2-acetylene complexes etc.[1,2] The reactivity of vinylidenes can be varied by changing the metal, ligands, or carbon substituents, and many examples have been isolated as crystalline solids.[1] Vinylidenes **1** are potent electrophiles, and their chemistry is dominated by nucleophilic addition to produce the carbene complexes **2** or deprotonation (R^2 = H) to provide the acetylides **3** (Scheme I). In 1974 Fischer reported that (1-hydroxyethylidene)pentacarbonylchromium (**4**) reacted with dicyclohexylcarbodiimide (DCC) in dichloromethane solution to produce the iminoazetidinylidene complex **5** (47%)[3] (Scheme II). We were intrigued by this reaction since, as Fischer speculated, it is possible that **5** was formed via a formal [2 + 2] cycloaddition between excess DCC and the parent chromium vinylidene **6**.[4] If such an assumption was correct, then the vinylidene **6** would be acting as ketene surrogate. Since the formal cycloaddition reaction of ketenes with imines is widely used in the synthesis of β-lactam antibacterials,[5] we set out to explore the use of metal vinylidenes[6] in β-lactam construction.[7] In principle, such an approach should be versatile in that the reactivity of the reagent **1** should be easily varied by changing M and/or L. Additionally it may be possible to control the absolute stereochemistry of the cycloaddition reaction via chiral elements present in the L_nM fragment.

Scheme I



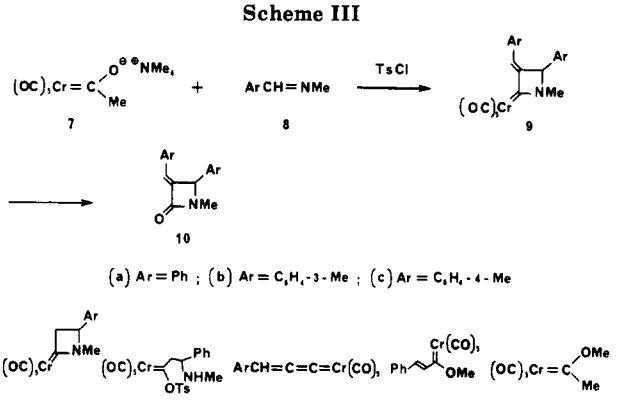
Scheme II



$H_2C=C=Cr(CO)_5$

6

Scheme III



Results and Discussion

Preparation of (Azetidinylidene)chromium Carbene Complexes. We sought to prepare the vinylidene **6** and use this reactive intermediate in the preparation of β-lactams. Thus **7**[8] was reacted with toluene-4-sulfonyl chloride in the presence of the imines **8a–c** (Scheme III). Much to our delight this provided the corresponding azetidinylidene complexes **9a–c**.[9] Subsequent oxidation gave

Table I. Preparation of Carbene Complexes 9 and β-Lactams 10

entry	imine	carbene (%)	β-lactam (%)
1	**8a**	**9a** (26)	**10a** (97)[a] (96)[b]
2	**8b**	**9b** (8)	**10b** (85)[b]
3	**8c**	**9c** (8)	**10c** (81)[b]

[a] PhIO oxidation. [b] Pyridine *N*-oxide oxidation.

(1) For an excellent review on metal vinylidene complexes, see: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
(2) For a recent example of the use of vinylidene intermediates in synthesis see: Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025.
(3) Weiss, K.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1974**, *107*, 3548.
(4) For examples of isolated chromium vinylidenes see: Berke, H.; Härter, P.; Huttner, G.; v. Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317. Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 929.
(5) Ketenes are widely applied in β-lactam synthesis. For diverse examples, see: Mukerjee, A. K.; Singh, A. K. *Tetrahedron* **1978**, *34*, 1731.
(6) Barrett, A. G. M.; Sturgess, M. A. *Tetrahedron Lett.* **1986**, *27*, 3811. Barrett, A. G. M.; Sturgess, M. A. *J. Org. Chem.* **1987**, *52*, 3940.
(7) For reviews on β-lactam antibiotics see: Cooper, R. D. G. In *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Ellis Horwood Ltd.: Chichester, 1980; Vol. 3, pp 43–199. *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Ellis Horwood Ltd.: Chichester, **1980**; Vol. 4, pp 9–278.
(8) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.
(9) The X-ray crystal data of carbene **9a** is available as supplementary material on our previous communication. See: Barrett, A. G. M.; Brock, C. P.; Sturgess, M. A. *Organometallics* **1985**, *4*, 1903.

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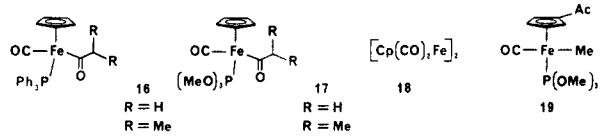
the corresponding β-lactams **10a–c** (Table I). It is possible that complexes **9** were formed via **6** and **11** and subsequent aldol condensation with more imine. This expectation is reasonable in the light of the known high acidity of C–H protons flanking a C=Cr(CO)$_5$ substituent.[10] There are, however, the alternatives that **9a** was produced via **12**, subsequent aldol chemistry and late N1–C2 formation or even via the cumulene carbene **13**. We briefly examined several experiments to attempt to clarify the mechanism. Thus reaction of **7**, toluene-4-sulfonyl chloride, and **8a** was carried out in the presence of *tert*-butyl alcohol or methanol. With *tert*-butyl alcohol **9a** was formed in comparable yield (24%) although at a faster rate. Reaction in methanol, however, gave **9a** (9%) and the known α,β-unsaturated carbene **14**[11] (9%). Additionally the carbene **14** (12%) was prepared by sequential reaction of **15** with *n*-butyllithium to produce the enolate, imine **8a**, and hydrogen chloride. All these results are consistent with the carbene **9a** being formed via a stepwise process. While this evidence is not conclusive, it is likely that **9a** and **14** were formed via the common intermediate **12**. Attempts to extend the method for the preparation of 2-azetidinylidene complexes from more heavily substituted imines or carbenes were unsuccessful. Thus, although simple β-lactams[12] could be prepared from imines and the carbene **7**, the process was clearly neither general nor efficient.

Preparation of Monocyclic β-Lactams from Cationic Iron(II) Vinylidenes. Hughes and co-workers have prepared a series of cationic iron(II) vinylidene complexes by the dehydration of iron acyls using trifluoromethanesulfonic anhydride.[13] Since such vinylidenes are isolable, stable crystalline solids they were easy to assay in our projected [2 + 2] cycloaddition route to β-lactams. Variation in one of the iron ligands should dramatically vary the electrophilicity of the vinylidene substituent and thus reactivity toward imines. The precursor acyls **16a**,[14] **16b**,[15] **17a**, and **17b** were easily prepared via reductive[16] alkylation of the commercial dimer **18**. Although **16b** was most conveniently prepared by the double methylation[17] of **16a**, this strategy failed for **17b**. Thus sequential reaction of **17a** with lithium diisopropylamide and iodomethane gave a material tentatively assigned as the acetylcyclopentadienyl complex **19**. Presumably **19** was formed via



16 R = H, R = Me **17** R = H, R = Me **18** **19**

Scheme IV

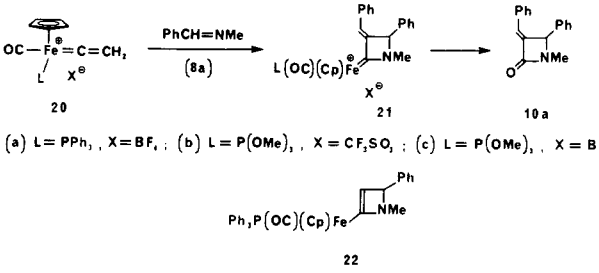


Table II. Preparation of Cationic Iron(II) Carbenes 21 and 24 and Derived β-Lactams

entry	vinylidene	imine	carbene (%, ds[a])	β-lactam (%)
1	**20a**	**8a** (R = Ph)	**21a** (46)[a]	**10a** (77)[b]
2	**20b**	**8a** (R = Ph)	**21b** (11,[f] 2:1)	**10a** (47)[b]
3	**23a**	**8a** (R = Ph)	**24a** (52, 3:1)	**25a** (19)[c]
4	**23b**	**8a** (R = Ph)	**24b** (58, 3:1)	
5	**23a**	**8b** (R = C_6H_4-3-Me)	**24c** (31, 4:3)	**25b** (8)[c]
6	**23a**	**8c** (R = C_6H_4-4-Me)	**24d** (38, 4:3)	**25c** (14)[b]
7	**23a**	**8d** (R = (*E*)-PhCH=CH)	**24e** (33, 4:1)	**25d** (29)[d]
8	**23c**	**8a** (R = Ph)	**24f** (74, 8:5)	**25a** (72)[e]

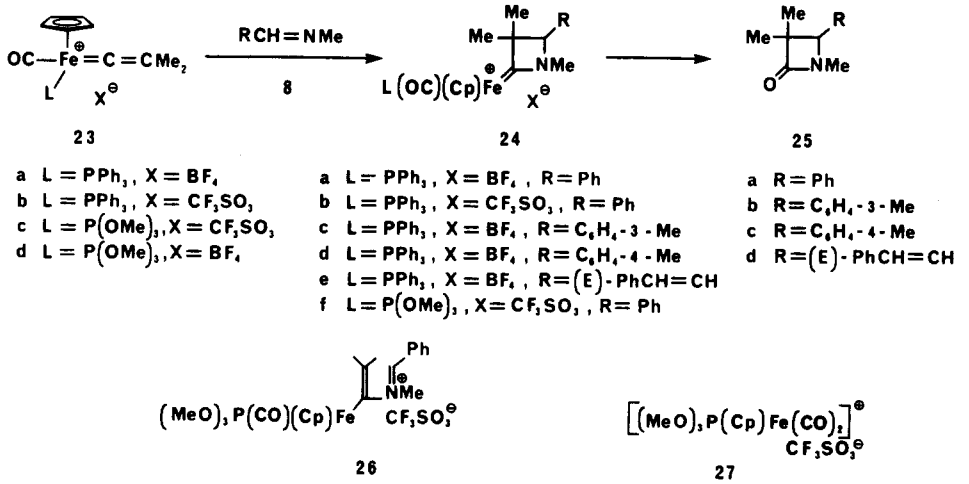
[a] Ratio of diastereoisomers (not determined in entry 1). [b] Oxidation using PhIO. [c] Oxidation using Br_2. [d] Oxidation using O_2. [e] Oxidation using Bu_4NNO_2 (for other oxidations see Experimental Section). [f] Yield based on acyl **17a**.

Cp lithiation, acetyl migration, and iron methylation.[18] The required complex **17b** was thus prepared via the reductive 2-propylation of **18** and reaction with trimethyl phosphite[19] (61%). Dehydration of **16a** and **16b** using the exact Hughes procedure with trifluoromethanesulfonic anhydride and tetrafluoroboric acid etherate[13] readily gave **20a** and **23a**. Reaction of **16b** with the anhydride alone gave **23b**.[13] However, dehydration of **17a** and **17b** proved to be more problematical. Attempts to convert **17b** into the tetrafluoroborate salt **23d** resulted in extensive decomposition during isolation. In the optimized reaction **17b** was dehydrated by using trifluoromethanesulfonic anhydride *alone* to provide **23c** (96%) as a stable peach colored solid. The material was authenticated by reaction with methanol to produce the corresponding cationic carbene complex. In the same way **17a** was converted into **20b**, although this preparation was not optimized and the vinylidene was used in situ.

The reactions of the vinylidenes **20** and **23** with imines are summarized in Schemes IV and V and Table II. It is clear that the reaction of the unsubstituted vinylidenes **20a,b** closely paralleled the chromium carbene system in that the intermediate **22** was not isolated. However the dimethylvinylidenes **23a–c** reacted smoothly to give 1:1 adducts. NMR spectra of the products showed that complexes **21** and **24** were formed with poor (4:3–4:1) diastereoselectivities (Fe and C-4 centers). The vinylidene **23c** (entry 8) reacted more readily with imine **8a** in consequence of the lower cone angle and higher π-acidity of the trimethyl phosphite ligand.[1] Additionally, the intermediate **26** was slower to cyclize due to the reduced nucleophilicity of the alkene iron unit.[20] Thus, on mixing at low temperature, **23c** and **8a** reacted to produce the acyclic adduct **26**. This material, much to our surprise, could be

(10) For a review on metal carbene complexes see: Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.
(11) Dötz, K. H.; Kuhn, W.; Ackermann, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1351.
(12) For the synthesis of related α-methylene-β-lactam derivatives see: Commercon, A.; Ponsinet, G. *Tetrahedron Lett.* **1983**, *24*, 3725. Kano, S.; Shibuya, S.; Ebata, T. *J. Chem. Soc., Perkin Trans. 1* **1982**, 257. Adlington, R. M.; Barrett, A. G. M.; Quayle, P.; Walker, A.; Betts, M. J. *Ibid.* **1983**, 605. Ishida, M.; Minami, T.; Agawa, T. *J. Org. Chem.* **1979**, *44*, 2067. Agawa, T.; Ishida, M.; Ohshiro, Y. *Synthesis* **1980**, 933. Minami, T.; Ishida, M.; Agawa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 12. Chiba, K.; Mori, M.; Ban, Y. *Ibid.* **1980**, 770. Mori, M.; Chiba, K.; Okita, M.; Ban, Y. *Ibid.* **1979**, 698. Fletcher, S. R.; Kay, I. T. *Ibid.* **1978**, 903. Corbett, D. F.; Eglington, A. J. *Ibid.* **1980**, 1083. Kano, S.; Ebata, T.; Yuasa, Y.; Shibuya, S. *Heterocycles* **1980**, *14*, 589. Mayrhofer, R.; Otto, H. H. *Synthesis* **1980**, 247. Kano, S.; Ebata, T.; Funaki, K.; Shibuya, S. *Ibid.* **1978**, 746. Alper, H.; Hamel, N. *Tetrahedron Lett.* **1987**, *28*, 3237.
(13) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L.; *Organometallics* **1982**, *1*, 628.
(14) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889.
(15) Green, M.; Westlake D. J. *J. Chem. Soc. A.* **1971**, 367.
(16) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(17) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem.* Soc., *Chem. Commun.* **1984**, 745.
(18) For related rhenium chemistry see: Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.
(19) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.
(20) For recent examples of vinyl iron intermediates in synthesis see: Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940 and references therein.

Scheme V



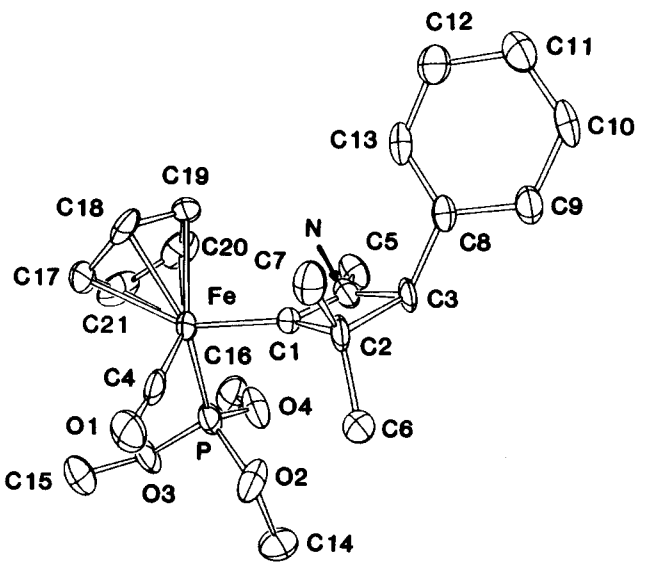


Figure 1. ORTEP drawing of the [*R*(*S*),*S*(*R*)]-carbonyl(η^5-cyclopentadienyl)[2-(4-phenyl-1,3,3-trimethylazetidinylidene)](trimethyl phosphite)iron(II) cation (**24f**). The thermal ellipsoids are drawn at 50% probability level.

isolated by chromatography!! On standing in solution, **26** underwent cyclization to produce **24f**. In the optimum procedure (entry 8), reaction of vinylidene **23c** with **8a** in the presence of *dry* Amberlyst A21 basic resin gave **24f** (74%). In this experiment the intermediate **26** was rapidly cyclized by brief reflux in 1,2-dichloroethane. A blank experiment established that the vinylidene **23c**, which was particularly unstable to acid in the presence of air, readily decomposed to give **27**.[21] This undesirable reaction was, however, suppressed under rigorously anaerobic conditions with the base resin present. Recrystallization of **24f** from methanol gave the *R*(*S*),*S*(*R*) diastereoisomer,[22] the structure of which was determined by an X-ray crystallographic study. The molecular structure of the compound consists of discrete CpFe(CO)($P(OCH_3)_3$)(azetidinylidene)$^+$ cations and $CF_3SO_3^-$ anions (Figure 1). Large thermal vibration parameters of the triflate atoms suggest a significant amount of disorder affecting the anion. The

Table III. Preparation and Oxidation of Bicyclic Azetidinylidene Complexes

entry	vinylidene	2-thiazoline	carbene (%, ds[a])	β-lactam (%)
1	**23c**	**28a**	**29b** (90, 15:1)	**30a** (36)[b]
2	**23d**	**28a**	**29a** (14,[d] 15:1)	
3	**23c**	**28b**	**29c** (72, 8:1)	**30b** (52)[b]
4	**23c**	**28c**	**29d** (58, 6:1 → 10:1)	**30c** (32)[c]

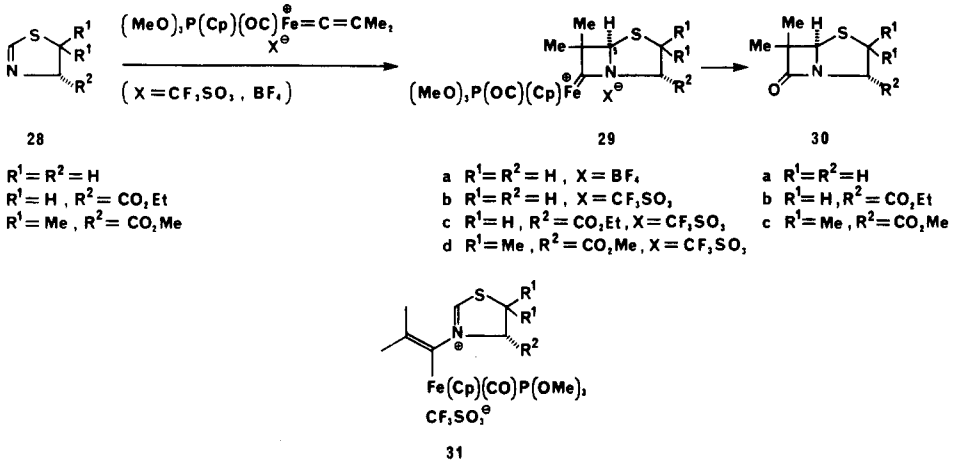
[a] Ratio of diastereoisomers. [b] Oxidation using PhIO. [c] Oxidation using Bu_4NNO_2 (for other oxidations see Experimental Section). [d] Low overall yield based on **17b** (see text).

complex cation contains the CpFe(CO)($P(OCH_3)_3$) fragment bonded through the carbon atom C1 to the azetidinylidene ring system. The Fe–C1 distance of 1.893 (5) Å is longer than the formal Fe–C(sp^2) double-bond length (1.78 Å) but significantly shorter than the single-bond distance expected to be 2.07 Å.[23] The azetidinylidene ring is planar with the N–C1 and N–C3 distances of 1.315 (7) and 1.475 (7) Å, respectively. Similar bond distances were found in the Cr carbonyl complex with 1-methyl-4-phenyl-3(*E*)-(phenylmethylene)azetidinylidene.[9] The C1–C2 and C2–C3 bond lengths seem stretched, a feature that has been observed in several cyclobutane and β-lactam derivatives.[24-26]

Although the cycloaddition reactions of the vinylidene **20** and **23** with imines **8** proceeded in reasonable yields, oxidative demetalation[27] to produce the β-lactams proceeded inefficiently. A series of reagents including iodosobenzene, aqueous bromine,[28] pyridine *N*-oxide,[29] and oxygen were examined, but the yields of the resultant β-lactams were hardly satisfactory (Table II). In contrast to neutral metal carbene complexes, there have been few

(21) For a related reaction see Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130.
(22) The relative stereochemistry is incorrectly assigned in a footnote in our preliminary communication. We thank John A. Gladysz for helpful comments. For a discussion of priority rules in such complexes see: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598.
(23) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole: Monterey, CA, 1985.
(24) Sweet, R. M. In *Cephalosporins and Penicillins*; Flynn, E. H., Ed.; Academic Press: New York, 1970; Chapter 7.
(25) Margulis, T. N. *Acta Crystallogr.* **1965**, *19*, 857.
(26) Parthasarathy, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1283.
(27) For examples of the oxidation of carbene complexes see: Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1975**, *97*, 421. Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.
(28) For a related oxidation using bromine see: Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *90*, 1449.
(29) Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2672; **1973**, *95*, 3552.
(30) β-Lactams **25a** and **25d** are known compounds see: Rogalska, E.; Belzecki, C. *J. Org. Chem.* **1984**, *49*, 1397. Moreau, J. L.; Gaudemar, M. *C. R. Acad. Sci., Ser. 2* **1985**, *300*, 399.

Scheme VI



studied of the oxidative demetalation of cationic species.[10] Indeed it is probably that ring scission is complicating the oxidation of **24**.[10] In contrast to these common oxidation reactions, the carbene complex **24f** was readily and cleanly converted into **25a** (72%) by reaction with tetrabutylammonium nitrite[31] in dichloromethane at 7 kbar (entry 8). It is clear from these experiments that monocyclic β-lactams can be prepared from imines by reaction with iron(II) vinylidenes and oxidation. The low diastereoselectivity of the cycloaddition reaction is the result of the intermediacy of vinyl iron intermediates (e.g. **26**) and either (*E*/*Z*) isomerization prior to or low facial selectivity on ring closure.

Preparation of Bicyclic Azetidinylidene Complexes. The stepwise cycloaddition chemistry was extended to the 2-thiazoline derivatives **28a–c**[32] to provide the corresponding bicyclic complexes (Table III, Scheme VI). Since the intermediates **31** in these transformations clearly can not possibly undergo *E,Z* isomerization, the reaction showed considerable facial selectivity in the formation of the final C–C bond. Thus **29b**, which contains two chiral centers (Fe and C5), was formed in a 15:1 ratio; this selectivity is controlled solely by the iron. Since we have been unable to recrystallize **29a** or **29b**, we have been unable to determine which is the major isomer formed in this reaction. Additionally **29c** (8:1) and **29d** (6:1 → 10:1) were produced only as two diastereoisomers. It is reasonable to assume that the azetidinylidene ligands have the exo stereochemistry[33] and the diastereoisomeric ratios result only from the asymmetry at iron. Oxidation of **29b–d** using iodosobenzene (entries 1 and 3) or tetrabutylammonium nitrite (entry 4) smoothly, albeit slowly, gave the corresponding penam derivatives **30a–c**. Consistent with our stereochemical arguments these materials were obtained as single isomers. Assignment as the exo configurations was fully consistent with NMR data and, in particular, with the fact that **30b** was not isomerized by base.[34] It is germane to comment here on yields. In the "cycloaddition" of vinylidenes with imines the yields obtained depend crucially on the ease of isolation and purity of the vinylidene reagent. It is essential that the vinylidene used is solid, acid-free material. Vinylidene **20b** is difficult to prepare and isolate pure whereas **20c** is easily handled.[35] In contrast vinylidene **23c** is readily isolated pure whereas the corresponding tetrafluoroborate **23d** is difficult to manipulate. No doubt these apparent inconsistencies are only the result of crystal packing forces. These results demonstrate that cationic iron(II) vinylidenes behave as ketene surrogates in their reactions with imines and 2-thiazolines. Oxidation of the resultant mono- and bicyclic carbene complexes may be used to prepare both mono- and bicyclic β-lactams.[36]

Experimental Section

Melting points were determined on a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^{1}H NMR spectra were recorded with either tetramethylsilane or chloroform as an internal reference on a Varian EM390A or a Varian XL-400 spectrometer. All ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. UV spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Mass spectra were either recorded on a V-G 7070F mass spectrometer or were recorded by the Midwest Center for Mass Spectrometry. Microanalyses were determined either by Galbraith Laboratories, Knoxville, TN 37921, or by G.D. Searle and Co. Hexane was purified by distillation. THF and Et_2O were dried by distillation under nitrogen from sodium benzophenone ketyl. DMF, CH_2Cl_2, and MeCN were dried by distillation from CaH_2. 1,2-Dichloroethane was dried and distilled from P_4O_{10}. MeOH was distilled from $Mg(OMe)_2$. All tertiary nitrogen bases were dried over and distilled from sodium wire. Amberlyst A21 weakly basic resin was dried by azeotropic removal of the water with benzene under an inert atmosphere of dry nitrogen. All reactions were carried out under dry nitrogen. Chromatography was carried out on Merck Kieselgel 60 (Art. 9385); eluants are given in parentheses.

[3(*E*)-Benzylidene-1-methyl-4-phenylazetidinylidene]pentacarbonylchromium(0) (9a). $Me_4N^+MeC(=Cr(CO)_5)O^-$ (**7**)[8] (200 mg) was dissolved in CH_2Cl_2 (10 mL) at room temperature. A solution of TsCl (123 mg) in CH_2Cl_2 (2 mL) was added

(31) For the use of nitrite salts in nitroso complex formation see: Stevens, R. F.; Yanta, T. J.; Gladfelter, W. I. *J. Am. Chem. Soc.* **1981**, *103*, 4981.

(32) Ito, Y.; Inubushi, Y.; Zenbayashi, M.; Tomita, S.; Saegusa, T. *J. Am. Chem. Soc.* **1973**, *95*, 4447. Bose, A. K.; Manhas, M. S.; Chib, J. S.; Chawla, H. P. S.; Dayal, B. *J. Org. Chem.* **1974**, *39*, 2877. Bell, M. R.; Carlson, J. A.; Oesterlin, R. *J. Org. Chem.* **1972**, *37*, 2733.

(33) Exo refers to the stereochemistry of the alkoxycarbonyl group on the 4-thia-1-azabicyclo[3.2.0]heptylene ligand.

(34) For a related endo to exo isomerization see: Cama, L. D.; Christensen, B. G. *Tetrahedron Lett.* **1978**, 4233.

(35) For the use of **20c** in Claisen chemistry see: Barrett, A. G. M.; Carpenter, N. E. *Organometallics* **1987**, *6*, 2249.

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dropwise with stirring. After 10 min **8a**[37] (308 mg) was added and the reaction mixture was stirred at room temperature for 8 h. Removal of the solvent gave a brown oil which was purified by chromatography on silica (hexane/Et_2O, 100:0–90:10) to give **9a** (72 mg, 26%): mp 163 °C (hexane/Et_2O); IR (CH_2Cl_2) 2060, 1922, 1595, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.16 (m, 10 H), 7.10 (m, 1 H), 6.08 (s, 1 H), 3.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 273.8, 222.9, 217.9, 144.9, 133.2, 132.4, 129.8, 129.4, 129.3, 128.5, 128.4, 127.8, 82.3, 35.3: UV (CH_2Cl_2) λ (ε) 408 (3280), 290 (11 400) nm; mass spectrum (CI), *m/e* (%) 425 (100), 398 (53), 370 (18), 342 (23), 313 (30), 285 (28), 234 (97). Anal. Calcd for $C_{22}H_{15}CrNO_5$: C, 62.12; H, 3.55; N, 3.29. Found: C, 61.78; H, 3.56; N, 3.21.

(2) To **7** (500 mg) in CH_2Cl_2 (25 mL) was added dropwise, with stirring, TsCl (310 mg) in CH_2Cl_2 (5 mL) at room temperature. After 10 min **8a** (432 mg) was added dropwise and stirring was continued for a further 5 min. ^{t}BuOH (10 mL) was added and the reaction mixture stirred for $3^1/_2$ h. Evaporation and chromatography of the residue (hexane/Et_2O, 98:2) gave **9a** (162 mg, 24%).

(3) To **7** (200 mg) in CH_2Cl_2 (12 mL) was added with stirring TsCl (124 mg) in CH_2Cl_2 (1 mL). After 5 min **8a** (162 mg) was added dropwise and stirring continued for 10 min. MeOH (5 mL) was added and the reaction mixture stirred for $3^1/_2$ h. Evaporation and chromatography gave **14** (20 mg, 9%) with spectral data consistent with that previously reported,[11] and **9a** (25 mg, 9%).

Pentacarbonyl[1-(1-methoxy-3(*E*)-phenyl-2-propenylidene)]chromium(0) (14). Carbene **15**[10] (300 mg) was dissolved in Et_2O (20 mL) and cooled to −78 °C. After the dropwise addition of *n*-BuLi (1.6 M, 850 μL), the mixture was stirred at −78 °C for 15 min. Addition of this solution by cannula over 40 min to a stirred solution of **8a** (152 mg) in Et_2O (40 mL) at −78 °C gave an orange solution. HCl in Et_2O (0.58 M, 2.25 mL) was added at −78 °C. The reaction mixture was allowed to warm up to room temperature and the solvent removed in vacuo. The residue was purified by chromatography (hexane/Et_2O, 1:0–4:1) to give **14**[11] (48 mg, 12%) with spectral data consistent with that previously reported and recovered **15** (150 mg, 50%).

[2-(3(*E*)-(3-Methylbenzylidene)-1-methyl-4-(3-methylphenyl)azetidinylidene)]pentacarbonylchromium(0) (9b). To **7** (250 mg) in CH_2Cl_2 (12 mL) was added dropwise, with stirring, TsCl (155 mg) in CH_2Cl_2 (3 mL) at room temperature. After 10 min the imine **8b**[37] (269 mg) was added dropwise, and stirring was continued for 5 min. ^{t}BuOH (5 mL) was added dropwise, and the reaction mixture was stirred for $3^1/_2$ h. Evaporation and chromatography (eluant hexane/Et_2O, 98:2) gave **9b** (29 mg, 8%) as an orange powder: mp 112 °C (hexane/Et_2O); IR ($CHCl_3$) 3010, 2060, 1929 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.4–6.9 (m, 9 H), 6.05 (m, 1 H), 3.38 (s, 3 H), 2.38 (s, 3 H), 2.20 (s, 3 H); UV (CH_2Cl_2) λ (ε) 410 (4060), 290 (14 800) nm; mass spectrum (CI), *m/e* (%) 453 (9), 425 (1), 397 (6), 369 (8), 341 (25), 313 (93), 272 (100). Anal. Calcd for $C_{24}H_{19}CrNO_5$: C, 63.58; H, 4.19; N, 3.09. Found: C, 63.60; H, 4.48; N, 3.35.

[2-(3(*E*)-(4-Methylbenzylidene)-1-methyl-4-(4-methylphenyl)azetidinylidene)]pentacarbonylchromium(0) (9c). In exactly the same way **7** (250 mg) and **8c**[37] (250 μL) gave **9c** (30 mg, 8%) as an orange powder: mp 150 °C, dec (hexane/Et_2O); IR (CH_2Cl_2) 3110, 3060, 2980, 2940, 2880, 2041, 1960, 1740, 1690, 1611, 1483, 1422, 1255, 1002 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.3–6.9 (m, 9 H), 6.00 (m, 1 H), 3.42 (s, 3 H), 2.43 (s, 3 H), 2.24 (s, 3 H); UV (CH_2Cl_2) λ (ε) 354 (1410), 302 (6580), 212 (10 000); nm; mass spectrum (EI), *m/e* (%) 453 (22), 397 (18), 369 (22), 341 (67), 313 (35), 272 (53). Mass spectrum *m/e* calcd for $C_{22}H_{19}CrNO_3$: ($M^{\cdot+}$ − 2 CO), 397.0769. Found: ($M^{\cdot+}$ − 2 CO), 397.0774.

3(*E*)-Benzylidene-1-methyl-4-phenyl-2-azetidinone (10a). (1) A solution of **9a** (40 mg) in CH_2Cl_2 (5 mL) was added to PhIO (62 mg). The resulting suspension was stirred for 4 days. The solvent was evaporated and the residue chromatographed (Et_2O) to give **10a** (23 mg, 97%): mp 151 °C ($CHCl_3$); IR ($CDCl_3$) 3095, 3078, 3019, 2902, 1732, 1600, 1578, 1418, 1372, 1308, 1277, 1011 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.32 (s, 5 H), 7.18 (s, 5 H), 6.97 (m, 1 H), 5.18 (m, 1 H), 2.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.4, 141.0, 135.3, 133.1, 129.1, 128.9, 128.4, 127.9, 123.4, 65.5, 26.8; UV (CH_2Cl_2) λ (ε) 272 (45 200) nm; mass spectrum (EI), *m/e* (%) 249 (83), 248 (65), 220 (21), 191 (90), 179 (7), 147 (83), 144 (34), 118 (62). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.92; H, 6.02; N, 5.62. Found: C, 82.05; H, 6.32; N, 5.76.

(2) Carbene **9a** (20 mg) in CH_2Cl_2 (4 mL) was added to pyridine *N*-oxide (45 mg), and the mixture was stirred at room temperature for 7 days. Evaporation and chromatography of the residue (Et_2O) gave **10a** (11 mg, 96%).

3-(3-Methylbenzylidene)-1-methyl-4-(3-methylphenyl)-2-azetidinone (10b). A solution of **9b** (15.7 mg) in CH_2Cl_2 (4 mL) was added to pyridine *N*-oxide (100 mg) at room temperature. After stirring overnight, evaporation and chromatography (Et_2O) gave **10b** (8.2 mg, 85%): mp 141 °C (Et_2O); IR (CH_2Cl_2) 3030, 2928, 2890, 1745, 1610, 1460, 1383, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 3 H), 7.12–7.05 (m, 2 H), 7.01–6.96 (m, 3 H), 6.92 (s, 1 H), 5.14 (s, 1 H), 2.81 (s, 3 H), 2.32 (s, 3 H), 2.18 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 141.3, 138.7, 138.1, 135.6, 133.3, 130.0, 129.8, 128.8, 128.6, 128.4, 126.6, 125.2, 123.5, 65.49, 26.7, 21.4, 21.2; UV (CH_2Cl_2) λ (ε) 275 (9600) nm, mass spectrum (EI), *m/e* (%) 277 (100), 262 (68), 205 (68), 132 (28); mass spectrum *m/e* calcd for $C_{19}H_{19}NO$: ($M^{\cdot+}$), 277.1466. Found: ($M^{\cdot+}$), 277.1463.

3-(4-Methylbenzylidene)-1-methyl-4-(4-methylphenyl)-2-azetidinone (10c). A solution of **9c** (18 mg) in CH_2Cl_2 (4 mL) was added to pyridine *N*-oxide (100 mg) at room temperature. The reaction mixture was stirred overnight. Evaporation and chromatography (Et_2O) gave **10c** (9 mg, 81%): mp 157–158 °C (Et_2O); IR (CH_2Cl_2) 2940, 2890, 1730, 1608, 1382 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2 H, J = 8.0 Hz), 7.14 (d, 2 H, J = 8.0 Hz), 7.05 (d, 2 H, J = 8.0 Hz), 6.98 (d, 2 H, J = 8.0 Hz), 6.93 (s, 1 H), 5.15 (s, 1 H), 2.79 (s, 3 H), 2.31 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 140.6, 139.6, 139.2, 132.9, 131.0, 130.1, 129.7, 128.3, 123.7, 65.6, 26.9, 21.7, 21.7; UV (CH_2Cl_2) λ (ε) 282 (20 400) nm; mass spectrum (CI), *m/e* (%) 278 (100), 186 (22). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.38; H, 6.99; N, 4.81.

(η^5-Acetylcyclopentadienyl)carbonylmethyl(trimethyl phosphite)iron(II) (19). To a stirred solution of ^{i}Pr$_2$NH (123 μL) in THF (1 mL) at 0 °C was added ^{n}BuLi (1.6 M, 552 μL), and the solution was stirred at 0 °C for 20 min. Addition of this solution to **17a**[14] (141 mg) in THF (10 mL) at −78 °C and subsequent stirring for 40 min gave a deep red solution. MeI (60 μL) was added at −78 °C to produce an orange solution. After being warmed to room temperature, the solution was diluted with Et_2O (20 mL) and washed with H_2O (2 × 10 mL). The Et_2O solution was dried (Na_2SO_4) and the solvent removed to give an orange oil. Chromatography (CH_2Cl_2) gave an oil tentatively assigned as **19** (24 mg, 17%): IR (CH_2Cl_2) 3080, 3004, 2960, 2900, 2850, 2812, 1938, 1666, 1620, 1595, 1467, 1374, 1291, 1030 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.14–4.90 (m, 2 H), 4.70–4.48 (m, 2 H), 3.50 (d, 9 H, J = 11 Hz), 2.22 (s, 3 H), −0.15 (d, 3 H, J = 4 Hz); ^{13}C NMR ($CDCl_3$) δ 219.4 (d, J = 46 Hz), 197.2 (d, J = 5 Hz), 92.6, 92.3, 90.9, 89.0, 87.4, 85.8, 84.6, 83.1, 56–52 (m), 10.2, −20.5 to −23.0 (m); mass spectrum (EI), *m/e* (%) 330 (7), 302 (22), 287 (42), 163 (17), 93 (100).

Carbonyl(η^5-cyclopentadienyl)(2-methylpropanoyl)(trimethyl phosphite)iron(II) (17b). A solution of **18** (15.26 g) in THF (300 mL) was added to 6% sodium amalgam (92.6 g). The mixture was stirred vigorously at room temperature for 9 days. The brown solution was separated from the excess amalgam by cannula and cooled to −78 °C, ^{i}PrBr (16.1 mL) was added rapidly, and the resulting solution stirred at −78 °C for 2 h. After being warmed to room temperature, the crude reaction mixture was filtered through silica (eluant hexane) to give the impure isopropyliron complex (12.86 g). This material was dissolved in $(MeO)_3P$ (21.2 g) and was stirred at room temperature for 24 h. Chromatography (hexane/EtOAc, 1:0–9:1) gave **17b** (18.31 g, 62% overall): IR (thin film) 2980, 2960, 2879, 2870, 1928, 1605, 1453, 1360, 1180, 1026 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 4.67 (s, 5 H), 3.66 (d, 9 H, J = 12 Hz), 3.13 (m, 1 H), 1.02 (d, 3 H, J = 7 Hz), 0.86 (d, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 219.4 (d, J = 46 Hz), 166.8, 85.06, 62.1, 52.9 (d, J = 1.8 Hz), 19.7, 19.3; UV (CH_2Cl_2) λ (ε) 338 (6760), 248 (13 200), 210 (31 200) nm; mass spectrum (EI), *m/e* (%) 344 (1), 313 (1), 301 (30), 245 (100), 121 (18). Anal. Calcd

(37) Cromwell, N. H.; Babson, R. D.; Harris, C. E. *J. Am. Chem. Soc.* **1943**, *65*, 312.

for $C_{13}H_{21}FeO_5P$: C, 45.34; H, 6.10. Found: C, 45.26; H, 6.14.

Carbonyl(η^5-cyclopentadienyl)(2-methylpropenylidene)(trimethyl phosphite)iron(II) Trifluoromethanesulfonate (23c). The iron acyl **17b** (1.29 g) was dissolved in Et_2O (250 mL) and cooled to −78 °C. Trifluoromethanesulfonic anhydride (1.89 mL) was added dropwise, and the reaction mixture was stirred vigorously for 1 h at −78 °C. Warming up to room temperature and further stirring for 7 h gave a peach precipitate. The ethereal solution was removed by cannula, and the remaining solid was washed with Et_2O (2 × 100 mL). Drying of the solid *in vacuo* (10^{-2} mmHg) gave the vinylidene **23c** (1.49 g, 96%) as a fine pink powder: IR (CH_2Cl_2) 3110, 2952, 2913, 2843, 2020, 1715, 1700, 1430, 1259, 1160, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 5 H), 3.79 (d, 9 H, J = 12 Hz), 1.87 (s, 6 H). The material, which was used directly without further purification, was authenticated by reaction with methanol. Thus the vinylidene **23c** (152 mg) was dissolved in MeOH (5 mL) at room temperature and the resulting solution stirred for 30 min. Evaporation and chromatography ($MeOH/CH_2Cl_2$, 0:1–1:24) gave carbonyl(η^5-cyclopentadienyl)[1-(1-methoxy-2-methylpropanylidene)](trimethyl phosphite)iron(II) trifluoromethanesulfonate (156 mg, 96%) as a red oil: IR (CH_2Cl_2) 2948, 2843, 1980, 1600, 1450, 1285, 1228, 1160, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (s, 5 H), 4.72 (s, 3 H), 3.82 (m, 1 H), 3.77 (d, 9 H, J = 11.6 Hz), 1.07 (d, 3 H, J = 6.8 Hz), 1.01 (d, 3 H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 85.7, 69.4, 62.3, 54.4, 19.9, 19.6; mass spectrum (FAB), m/e (%) 359 (100), 331 (72), 245 (69), 207 (31), 175 (33), 121 (24). Mass spectrum (FAB) m/e calcd for $C_{14}H_{24}FeO_5P$: (M^+), 359.0710. Found: (M^+), 359.0702.

[2-(3(*E*)-Benzylidene-1-methyl-4-phenylazetidinylidene)]carbonyl(η^5-cyclopentadienyl)(triphenylphosphine)iron(II) Tetrafluoroborate (21a). The vinylidene **20a** (300 mg), prepared according to the literature procedure from **16a**,[13] was cooled in a liquid-nitrogen bath, and **8a** (2 mL) was condensed into the flask. The mixture was warmed to −15 °C with stirring and left at this temperature for 3 days to produce a brown-yellow solution. The product was precipitated by slow addition of dry hexane (20 mL) and then washed with hexane (2 × 20 mL). The crude product was chromatographed (silica deactivated with 5% H_2O: CH_2Cl_2/Et_2O, 0:1–1:0) to give crude **21a** (220 mg, 46%) as a golden foam: IR ($CDCl_3$) 3035, 2978, 2870, 1968, 1605, 1487, 1440, 1068, 1064 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 8.0–6.2 (m, 26 H), 5.90 (m, 1 H), 4.90 (s, 5 H), 3.50 (s, 3 H). This material proved to be impossible to purify further and was therefore authenticated via oxidation. Thus PhIO (114 mg) was added to **21a** (110 mg) in CH_2Cl_2 (10 mL). After the solution was stirred at room temperature for 6 h, more PhIO (41 mg) was added and the resulting suspension was stirred for 2 days. Evaporation and chromatography (Et_2O) gave **10a** (29 mg, 77%) as a white crystalline solid. The material was identical in all respects with that prepared via the chromium carbene **9a**.

Carbonyl(η^5-cyclopentadienyl)[2-(4-phenyl-1,3,3-trimethylazetidinylidene)](triphenylphosphine)iron(II) Tetrafluoroborate (24a). Vinylidene **23a**[13] (250 mg) was dissolved in CH_2Cl_2 (9 mL) and cooled to −78 °C. Imine **8a** (54 mg) in CH_2Cl_2 (1 mL) was added dropwise, and the reaction mixture was stirred for 30 min at −78 °C. After warming to room temperature, the reaction was allowed to stir overnight. Evaporation and chromatography of the residue (silica deactivated with 5% H_2O; CH_2Cl_2/Et_2O, 0:1–1:0) gave **24a** (157 mg, 52%), a 3:1 mixture of diastereoisomers, as a golden foam: IR ($CDCl_3$) 3060, 2978, 2930, 1963, 1737, 1604, 1528, 1436, 1260, 1161, 1061, 1030 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) major diastereoisomer, δ 8.0–6.9 (m, 18 H), 6.6–6.4 (m, 2 H), 5.56 (s, 1 H), 4.95 (s, 5 H), 3.23 (s, 3 H), 1.41 (s, 3 H), 0.67 (s, 3 H); minor diastereoisomer, δ 8.0–6.9 (m, 18 H), 6.6–6.4 (m, 2 H), 5.19 (s, 1 H), 4.98 (s, 5 H), 3.30 (s, 3 H), 1.05 (s, 3 H), 0.54 (s, 3 H); UV (CH_2Cl_2) λ (ϵ) 320 (2900), 270 (9750), 263 (10 300), 256 (10 200), 234 (17 100) nm; mass spectrum (FAB), m/e 584, 556, 491, 383, 294, 185. Mass spectrum (FAB) m/e calcd for $C_{36}H_{35}FeNOP$: (M^+), 584.1805. Found: (M^+), 584.1798.

Carbonyl(η^5-cyclopentadienyl)[2-(4-phenyl-1,3,3-trimethylazetidinylidene)](triphenylphosphine)iron(II) Trifluoromethanesulfonate (24b). Vinylidene **23b**, prepared according to the literature procedure[13] from **16b** (100 mg), was dissolved in CH_2Cl_2 and hexane (1:1; 5 mL), and to this was added **8a** (48 mg). The resulting solution was allowed to stand for 4 days at −15 °C. Evaporation and chromatography (silica deactivated with 5% H_2O; CH_2Cl_2/Et_2O, 0:1–1:0) gave **24b** (85 mg, 58%) as a golden oil. The ^1H NMR spectra for this material was identical with the previous fully characterized tetrafluoroborate **24a**.

Carbonyl(η^5-cyclopentadienyl)[2-(4-(3-methylphenyl)-1,3,3-trimethylazetidinylidene)](triphenylphosphine)iron(II) Tetrafluoroborate (24c). Vinylidene **23a** (156 mg) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78 °C. Imine **8b** (37 mg) was added, and the reaction was stirred at −78 °C for 50 min. After being warmed to room temperature, the reaction was stirred for 3 days. Evaporation and chromatography (silica deactivated with 5% H_2O; CH_2Cl_2/Et_2O, 0:1–2:3) gave **24c** (60 mg, 31%): IR (CH_2Cl_2) 3030, 2980, 2930, 2870, 1960, 1600, 1592, 1530, 1481, 1436, 1270, 1190, 1050 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) major diastereoisomer, δ 8.0–6.9 (m, 19 H), 5.46 (s, 1 H), 4.94 (s, 5 H), 3.28 (s, 3 H), 2.3 (s, 3 H), 1.36 (s, 3 H), 0.98 (s, 3 H); minor diastereoisomer, δ 8.0–6.9 (m, 19 H), 5.10 (s, 1 H), 4.88 (s, 5 H), 2.22 (s, 1 H), 0.66 (s, 3 H), 0.48 (s, 3 H); UV (CH_2Cl_2) λ (ϵ) 316 (1640), 269 (6370), 264 (6830), 257 (6690), 231 (15 200) nm; mass spectrum (FAB), m/e 598, 570, 383, 308, 280. Mass spectrum m/e calcd for $C_{37}H_{37}FeNOP$: (M^+), 598.1962. Found: (M^+), 598.1934.

Carbonyl(η^5-cyclopentadienyl)[2-(4-(4-methylphenyl)-1,3,3-trimethylazetidinylidene)](triphenylphosphine)iron(II) Tetrafluoroborate (24d). Vinylidene **23a** (155 mg) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78 °C. Imine **8c** (40 μL) was added and the reaction stirred at −78 °C for 50 min. After being warmed to room temperature, the reaction was stirred for 2 days. Evaporation and chromatography (silica deactivated with 5% H_2O; CH_2Cl_2/Et_2O, 0:1–2:3) gave **24d** (73 mg, 38%) as an oil: IR (CH_2Cl_2) 1960, 1580, 1528, 1480, 1435, 1271, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major diastereoisomer, δ 7.8–6.8 (m, 17 H), 6.36 (m, 2 H), 5.49 (s, 1 H), 4.92 (s, 5 H), 3.20 (s, 3 H), 2.30 (s, 3 H), 1.37 (s, 3 H), 0.68 (s, 3 H); minor diastereoisomer, δ 7.8–6.8 (m, 19 H), 5.09 (s, 1 H), 4.98 (s, 5 H), 3.28 (s, 3 H), 2.34 (s, 3 H), 0.99 (s, 3 H), 0.54 (s, 3 H); UV (CH_2Cl_2) λ (ϵ) 262 (10 100), 240 (2690), 235 (15 800) nm; mass spectrum (FAB), m/e 598, 570, 383, 308, 280. Anal. Calcd for $C_{37}H_{37}BF_4FeNOP$: C, 64.82; H, 5.40; N, 2.04. Found: C, 64.76; H, 5.33; N, 1.68. Mass spectrum (FAB) m/e calcd for $C_{37}H_{37}FeNOP$: (M^+), 598.1962. Found: (M^+), 598.1963.

Carbonyl(η^5-cyclopentadienyl)[2-(4-(2(*E*)-phenylethenyl)-1,3,3-trimethylazetidinylidene)](triphenylphosphine)iron(II) Tetrafluoroborate (24e). Vinylidene **23a** (153 mg) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78 °C. Imine **8d** (80 mg) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred at −78 °C for 50 min. After the mixture was warmed to room temperature, stirring was continued for 4 days. Evaporation and puification by chromatography (silica deactivated with 5% H_2O; CH_2Cl_2/Et_2O 0:1–2:3) gave **24e** (84 mg, 33%) as a 4:1 mixture of diastereoisomers: IR (CH_2Cl_2) 3035, 2970, 2936, 2880, 1962, 1633, 1537, 1440, 1272, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70–7.16 (m, 21 H), 6.59 (m, 1 H), 5.64 (m, 1 H), 4.94 (s, 5 H), 3.10 (s, 3 H), 1.28 (s, 3 H), 0.76 (s, 3 H); UV (CH_2Cl_2) λ (ϵ) 328 (4100), 294 (4900), 258 (15 300), 236 (14 500), 215 (9600) nm; mass spectrum (FAB), m/e 610, 582, 383, 348, 320, 279, 162. Mass spectrum (FAB) m/e calcd for $C_{38}H_{37}FeNOP$: (M^+), 610.1962. Found: (M^+), 610.1955.

4-Phenyl-1,3,3-trimethyl-2-azetidinone (25a). (1) To **24a** (38.6 mg) in CH_2Cl_2 (7 mL) was added PhIO (62 mg), and the suspension was stirred overnight. Evaporation and chromatography (Et_2O) gave **25a** (1.5 mg, 14%) as a colorless oil. All spectral data were consistent with that previously published[30] for this compound.

(2) The crude carbene complex **24a**, prepared from the vinylidene **23a** (48 mg), was dissolved in CH_2Cl_2 (4 mL) cooled to 0 °C, and wet bromine (3 drops) was added. The solution was stirred at 0 °C for 7 h, washed with water (2 × 15 mL), and chromatographed (Et_2O) to give **25a** (3.2 mg, 19%) as a colorless oil.

(3) Oxidation of **24a** (from **23a** (532 mg) and **8a** (126 mg)) in CH_2Cl_2 with oxygen at −78 °C for 36 h, followed by chromatography (Et_2O), gave **25a** (36 mg, 19%).

4-(4-Methylphenyl)-1,3,3-trimethyl-2-azetidinone (25c). To **24d** (39 mg) in CH_2Cl_2 (7 mL) was added PhIO (62 mg). After the mixture was stirred overnight at room temperature, the solvent was removed and the residue chromatographed (Et_2O) to give **25c** (1.6 mg, 14%): IR (CH_2Cl_2) 3030, 3021, 2970, 2932, 2871, 1755, 1599, 1518, 1463, 1428, 1395 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.30–6.90 (m, 4 H), 4.28 (s, 1 H), 2.87 (s, 3 H), 2.36 (s, 3 H), 1.42 (s, 3 H), 0.78 (s, 3 H); mass spectrum (EI), *m/e* (%) 203 (19), 188 (15), 146 (66), 134 (48), 132 (52), 131 (100), 105 (15), 91 (34).

4-(3-Methylphenyl)-1,3,3-trimethyl-2-azetidinone (25b). Oxidation of the crude carbene **24c**, from the vinylidene **23a** (97 mg), using bromine at 0 °C for 6 h, followed by workup and chromatography (Et_2O) gave **25b** (2.8 mg, 8%) as a colorless oil: IR ($CDCl_3$) 3040, 2982, 2920, 2878, 1738, 1672, 1610, 1463, 1445, 1428, 1397, 1263, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–6.90 (m, 4 H), 4.20 (s, 1 H), 2.79 (s, 3 H), 2.31 (s, 3 H), 1.35 (s, 3 H), 0.70 (s, 3 H); mass spectrum (EI), *m/e* (%) 203 (15), 188 (2), 146 (71), 131 (100), 117 (17), 91 (27). Mass spectrum (EI) *m/e* calcd for $C_{13}H_{17}NO$: ($M^{\bullet+}$), 203.1310. Found: ($M^{\bullet+}$), 203.1314.

4-[2(*E*)-Phenylethenyl]-1,3,3-trimethyl-2-azetidinone (25d). Oxidation of the crude carbene **24e**, from the vinylidene **23a** (70 mg) and imine **8d** (37 mg), in CH_2Cl_2 (1 mL) with oxygen at −78 °C for 48 h, followed by evaporation and chromatography (Et_2O) gave **25d** (8.0 mg, 29%): IR (thin film) 3090, 3065, 3040, 2967, 2938, 1743, 1655, 1603, 1582, 1428, 1397, 973, 742, 696 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.4–7.2 (m, 5 H), 6.66 (d, 1 H, *J* = 15 Hz), 6.13 (dd, 1 H, *J* = 15, 9 Hz) , 3.80 (d, 1 H, *J* = 9 Hz), 2.79 (s, 3 H), 1.36 (s, 3 H), 1.17 (s, 3 H); mass spectrum (EI), *m/e* 215, 200, 144, 91, 77. Mass spectrum (EI) *m/e* calcd for $C_{14}H_{17}NO$: ($M^{\bullet+}$), 215.1310. Found: ($M^{\bullet+}$), 215.1312.

[1-(*N*-Benzylidene-*N*-methylammonio)-2-methyl-1-propenyl]carbonyl(η⁵-cyclopentadienyl)(trimethyl phosphite)iron(II) Trifluoromethanesulfonate (26). The vinylidene **23c** (75 mg) was dissolved in CH_2Cl_2 (4 mL) and cooled to −78 °C. Imine **8a** (19 μL) was added and the reaction stirred at −78 °C for 30 min. After being warmed to room temperature, the crude mixture was chromatographed (CH_2Cl_2/MeOH, 1:0–24:1) to give **26** (71 mg, 80%) as an oil: IR (CH_2Cl_2) 3070, 2962, 2863, 1960, 1622, 1435, 1160, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (br s, 1 H), 8.04 (m, 2 H), 7.43 (m, 3 H), 4.62 (s, 5 H), 3.89 (s, 3 H), 3.42 (d, 9 H, *J* = 11 Hz), 1.96 (s, 3 H), 1.48 (s, 3 H). Mass spectrum (FAB) *m/e* calcd for $C_{21}H_{29}FeNO_4P$: (M^+), 446.1183. Found: (M^+), 446.1197. This material was observed to undergo slow cyclization upon standing to product **24f**; thus the mass spectral data probably represented the cyclic species **24f**.

Carbonyl(η⁵-cyclopentadienyl)[2-(4-phenyl-1,3,3-trimethylazetidinylidene)](trimethyl phosphite)iron(II) Trifluoromethanesulfonate (24f). (1) The vinylidene **23c** (124 mg) was dissolved in CH_2Cl_2 (20 mL) and cooled to −78 °C. Imine **8a** (40 μL) was added dropwise with stirring. After 30 min the reaction mixture was allowed to warm to room temperature and was stirred in the dark for 8 days. The solvent was removed under a stream of dry nitrogen, and the residue was purified by chromatography (CH_2Cl_2/MeOH, 1:0–24:1) to give **24f** (51 mg, 36%): IR (CH_2Cl_2) 2970, 2865, 1982, 1536, 1455, 1448, 1425, 1228, 1153, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) minor isomer, δ 7.5–7.3 (m, 3 H), 7.1–6.9 (m, 2 H), 5.23 (s, 1 H), 4.98 (s, 5 H), 3.75 (d, 9 H, *J* = 11 Hz) 3.41 (s, 3 H), 1.33 (s, 3 H), 0.78 (s, 3 H); major isomer, δ 7.5–7.3 (m, 3 H), 7.1–6.9 (m, 2 H), 5.41 (s, 1 H), 5.04 (s, 5 H), 3.79 (d, 9 H, *J* = 11 Hz), 3.38 (s, 3 H), 1.42 (s, 3 H), 0.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) minor isomer, δ 277.2 (d, *J* = 35 Hz), 215.6 (d, *J* = 43 Hz), 132.6, 129.0, 126.2, 84.3, 83.9, 60.2, 54.1 (d, *J* = 8 Hz), 37.3, 23.2, 20.0; major isomer: δ 275.0 (d, *J* = 36 Hz), 215.6 (d, *J* = 43 Hz), 133.2, 128.7, 128.5, 126.5, 83.9, 83.5, 60.5, 53.8 (d, *J* = 6 Hz), 36.5, 24.0, 18.7; UV (CH_2Cl_2) λ (ε) 293 (2300), 268 (3200) nm; mass spectrum (FAB), *m/e* 446, 418 294, 286, 245, 121. Mass spectrum (FAB) *m/e* calcd for $C_{21}H_{29}FeNO_4P$: (M^+), 446.1183. Found: (M^+) 446.1197. Anal. Calcd for $C_{22}H_{29}F_3FeNO_7PS$: C, 44.37; H, 4.87; N, 2.35. Found: C, 44.58; H, 4.90; N, 2.34.

(2) Vinylidene **23c** (560 mg) was dissolved in $ClCH_2CH_2Cl$ (50 mL) and was transferred to a flask previously purged with dry nitrogen containing dry Amberlyst A21 resin (~500 mg). Imine **8a** (150 μL) was added in a dropwise manner. The reaction was stirred at room temperature for 1 h prior to refluxing for 2 h. The reaction mixture was filtered, and the solvent was removed *in vacuo* to give an orange oil. Chromatography (CH_2Cl_2/MeOH, 1:0–96:4) gave **24f** (515 mg, 74%) as a 8:5 mixture of diastereoisomers. Recrystallization from methanol gave the minor diastereoisomer, mp 213–214 °C dec.

Dicarbonyl(η⁵-cyclopentadienyl)(trimethyl phosphite)iron(II) Trifluoromethanesulfonate (27). A solution of vinylidene **23c** (99 mg) in CH_2Cl_2 (4 mL) was cooled to −78 °C and dry O_2 was bubbled through the solution for 30 min. The flow of gas was stopped and the solution warmed up to room temperature over 20 min. Evaporation and chromatography (CH_2Cl_2/MeOH, 1:0–24:1) gave **27** (47 mg, 50%) as a white solid: mp 195 °C (CH_2Cl_2); IR (CH_2Cl_2) 3130, 3080, 2980, 2865, 2069, 2026, 1458, 1420, 1228, 1161, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.53 (s, 5 H), 3.87 (d, 9 H, *J* = 11.6 Hz); ^{13}C NMR ($CDCl_3$) δ 206.3 (d, *J* = 38 Hz), 87.3, 55.2 (d, *J* = 9.3 Hz); UV (CH_2Cl_2) λ (ε) 324 (560), 213 (14 000) nm; mass spectrum (FAB), *m/e* 301, 273, 245, 121. Anal. Calcd for $C_{11}H_{14}F_3FeO_8PS$: C, 29.30; H, 3.11. Found: C, 29.40; H, 3.09.

[2-(3(*E*)-Benzylidene-1-methyl-4-phenylazetidinylidene)]carbonyl(η⁵-cyclopentadienyl)(trimethyl phosphite)iron(II) Trifluoromethanesulfonate (21b). The iron acyl **17a**[15] (266 mg) was dissolved in Et_2O (30 mL) and cooled to −78 °C. Trifluoromethanesulfonic anhydride (141 μL) was added in a dropwise manner and the reaction mixture stirred for 60 min at −78 °C, before it was allowed to warm to room temperature. The solvent was removed by cannula and the remaining precipitate washed with Et_2O (2 × 5 mL). The remaining solid was evaporated to dryness in vacuo and dissolved in CH_2Cl_2 (3 mL). Imine **8a** (200 μL) was added at −78 °C resulting in an immediate color change from orange to red. The solution was allowed to warm to room temperature and stirred overnight. Evaporation and chromatography of the residual oil (CH_2Cl_2) gave **21b** (58 mg, 11%) as a 2:1 mixture of diastereoisomers: IR (CH_2Cl_2) 3125, 3020, 2912, 1972, 1730, 1686, 1605, 1494, 1423, 1231, 1161, 1036 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) major diastereoisomer, δ 7.40–7.00 (m, 11 H), 6.40 (m, 1 H), 5.02 (s, 5 H), 3.63 (d, 9 H, *J* = 12 Hz), 3.33 (s, 3 H); minor diastereoisomer, δ 7.40–7.00 (m, 11 H), 6.42 (m, 1 H), 5.02 (s, 5 H), 3.68 (d, 9 H, *J* = 12 Hz), 3.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) major diastereoisomer (minor diastereoisomer), δ 216.4 (d, *J* = 40 Hz), 132.8, 132.2, 130.2, 130.0, 129.6, 129.1, 129.0, 128.9, 128.4, 128.2, 109.3, 84.8, 82.5, (82.6), 54.2 (d, *J* = 7 Hz), 36.4 (36.2); UV (CH_2Cl_2) λ (ε) 369 (2400), 303 (13 100), 212 (20 800) nm; mass spectrum (FAB), *m/e* 506, 478, 386, 354, 313, 245, 162, 121. Mass spectrum (FAB) *m/e* calcd for $C_{26}H_{29}FeNO_4P$: (M^+), 506.1183. Found: (M^+), 506.1160.

Oxidation of Carbene 24f. (1) Oxidation of **24f** (49.5 mg) in dry EtOH (3 mL) using PhIO (92 mg) for 8 days at room temperature, followed by chromatography (Et_2O), gave **25a** (5 mg, 32%) identical spectroscopically with that previously obtained.

(2) A solution of **24f** (140 mg) and Bu_4NNO_2 (672 mg) in CH_2Cl_2 (20 mL) was pressurized at 6.5 kbar for 60 h. Evaporation and chromatography (Et_2O) gave **25a** (31 mg, 72%).

Oxidation of Carbene 21b. Oxidation of **21b** (33.4 mg) in dry ethanol (3 mL) using PhIO (56 mg) for 7 days at room temperature followed by evaporation and chromatography (Et_2O) gave **10a** (6 mg, 47%), identical spectroscopically with that obtained previously.

Carbonyl(η⁵-cyclopentadienyl)[7-(6,6-dimethyl-4-thia-1-azabicyclo[3.2.0]heptylidene)](trimethyl phosphite)iron(II) Tetrafluoroborate (29a). To the iron acyl **17b** (142 mg) in Et_2O (20 mL) at −78 °C was added trifluoromethanesulfonic anhydride (208 μL) in a dropwise manner. Subsequent addition of $HBF_4 \cdot Et_2O$ (120 μL) at −78 °C before warming to room temperature and stirring for 8 h gave an orange/pink precipitate. The supernatant layer was removed by use of a cannula, and the remaining solid was washed with Et_2O (3 × 20 mL) and dried in vacuo. The crude vinylidene **23d** (108 mg, 64%) was dissolved in $ClCH_2CH_2Cl$ (20 mL) and transferred to a flask, previously purged with dry nitrogen, containing Amberlyst A21 resin (20 mg). 2-Thiazoline (**28a**)[32] (28 mg) in $ClCH_2CH_2Cl$ (1 mL) was added and the mixture stirred for 10 min at room temperature prior to refluxing for 2 h. The solution was filtered and the solvent was removed to leave an orange oil. Chromatography (CH_2Cl_2/MeOH, 1:0–24:1) gave **29a** as a tan solid (27 mg, 14% overall): All spectral

data corresponding to the cationic moiety were identical with that obtained for the trifluoromethanesulfonate salt **29b**. Anal. Calcd for $C_{18}H_{25}BF_4FeNO_4PS$: C, 38.02; H, 4.99; N, 2.79. Found: C, 38.08; H, 5.00; N, 2.75.

Carbonyl(η^5-cyclopentadienyl)[7-(6,6-dimethyl-4-thia-1-azabicyclo[3.2.0]heptylidene)](trimethyl phosphite)iron(II) Trifluoromethanesulfonate (29b). The vinylidene **23c** (333 mg) in $ClCH_2CH_2Cl$ (40 mL) was added to Amberlyst A21 resin (~500 mg). 2-Thiazoline (**28a**)[32] (75 mg) in $ClCH_2CH_2Cl$ (2 mL) was added dropwise and the reaction mixture was stirred for 10 min at room temperature. The solution was refluxed for 2 h, filtered, and evaporated. The resultant orange oil was chromatographed (CH_2Cl_2/MeOH, 1:0–24:1) to give **29b** (354 mg, 90%) as a mixture of isomers (15:1): IR (CH_2Cl_2) 2960, 2860, 1982, 1740, 1603, 1542, 1155, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major isomer, δ 5.06 (s, 1 H), 5.01 (s, 5 H), 4.30 (m, 1 H), 3.90 (m, 1 H), 3.76 (d, 9 H, J = 11.2 Hz), 3.42 (m, 1 H), 3.18 (m, 1 H), 1.42 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR ($CDCl_3$) major isomer, δ 284.9 (m), 214.9 (d, J = 42 Hz), 84.7, 58.7, 54.1 (d, J = 8.2 Hz), 49.2, 34.4, 23.3, 19.1; UV (CH_2Cl_2) λ (ϵ) 315 (910), 273 (1030) nm; mass spectrum (FAB), m/e 414, 386, 327, 262, 245. Mass spectrum (FAB) m/e calcd for $C_{16}H_{25}FeNO_4PS$: (M^+), 414.0591. Found: (M^+), 414.0592. Anal. Calcd for $C_{17}H_{25}F_3FeNO_7PS_2$: C, 36.24; H, 4.47; N, 2.49. Found: C, 36.12; H, 4.48; N, 2.44.

Carbonyl(η^5-cyclopentadienyl)[7-(2-(ethoxycarbonyl)-6,6-dimethyl-4-thia-1-azabicyclo[3.2.0]heptylidene)](trimethyl phosphite)iron(II) Trifluoromethanesulfonate (29c). Vinylidene **23c** (180 mg) in $ClCH_2CH_2Cl$ (20 mL) was added to Amberlyst A21 resin (20 mg). The mixture was cooled to −23 °C, and ethyl 2-thiazoline-4-carboxylate (**28b**)[32] (92.7 mg) in $ClCH_2CH_2Cl$ (1 mL) was added. After 10 min the reaction mixture was allowed to warm to room temperature. After stirring for a further 10 min, the solution was refluxed for 2 h. Filtration, evaporation, and chromatography (CH_2Cl_2/MeOH, 1:0–24:1) gave **29c** (174 mg, 72%) as an orange oil containing an 8:1 mixture of diastereoisomers: IR (CH_2Cl_2) 3050, 2980, 1990, 1750, 1430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) minor isomer, δ 5.53 (s, 1 H), 5.28 (m, 1 H), 5.06 (s, 5 H), 4.30 (q, 2 H, J = 7.2 Hz), 3.73 (d, 9 H, J = 11.2 Hz), 3.61 (m, 1 H), 3.52 (m, 1 H), 1.43 (s, 3 H), 1.35 (t, 3 H, J = 7 Hz), 1.21 (s, 3 H); major isomer, δ 5.45 (m, 1 H), 5.41 (s, 1 H), 5.07 (s, 5 H), 4.36 (q, 2 H, J = 6.8 Hz), 3.80 (d, 9 H, J = 11.2 Hz), 3.72 (m, 1 H), 3.41 (m, 1 H), 1.46 (s, 3 H), 1.37 (t, 3 H, J = 7.2 Hz), 1.16 (s, 3 H); ^{13}C NMR ($CDCl_3$) major isomer, δ 294.0 (d, J = 37 Hz), 214.4 (d, J = 42 Hz), 166.9, 85.2, 84.1, 63.3, 62.8, 60.9, 54.6 (d, J = 8 Hz), 37.4, 23.7, 19.3, 14.0; UV (CH_2Cl_2) λ (ϵ) 311 (6350), 288 (6830), 209 (28300) nm; mass spectrum (FAB), m/e 486, 458, 334, 280, 266, 245, 216, 121. Mass spectrum (FAB) m/e calcd for $C_{19}H_{29}FeNO_6PS$: (M^+), 486.0802. Found: (M^+), 486.0801.

Carbonyl(η^5-cyclopentadienyl)[7-(2-(methoxycarbonyl)-3,3,6,6-tetramethyl-4-thia-1-azabicyclo[3.2.0]heptylidene)](trimethyl phosphite)iron(II) Trifluoromethanesulfonate (29d). Vinylidene **23c** (660 mg) in $ClCH_2CH_2Cl$ (80 mL) was added to Amberlyst A21 resin (~500 mg) followed by methyl 5,5-dimethyl-2-thiazoline-4-carboxylate (**28c**)[32] (236 mg) in $ClCH_2CH_2Cl$ (1 mL) while stirring. After 10 min the solution was refluxed for 10 min. Evaporation and chromatography (CH_2Cl_2/MeOH, 1:0–24:1) gave **29d** (520 mg, 58%) as a 6:1 mixture of diastereoisomers: IR (CH_2Cl_2) 3040, 3000, 2945, 2840, 1988, 1752, 1440, 1220, 1157, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 1 H), 5.03 (s, 5 H), 4.77 (s, 1 H), 3.92 (s, 3 H), 3.80 (d, 9 H, J = 11.2 Hz), 1.96 (s, 3 H), 1.54 (s, 3 H), 1.49 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 289.8 (d, J = 36 Hz), 214.7 (d, J = 42 Hz), 167.4, 84.9, 84.0, 71.5, 62.9, 60.7, 54.6 (d, J = 8 Hz), 53.3, 31.2, 27.3, 24.0, 20.1; UV (CH_2Cl_2) λ (ϵ) 308 (1710), 272 (1750), 224 (4540) nm; mass spectrum (FAB), m/e 500, 472, 348. Mass spectrum (FAB) m/e calcd for $C_{20}H_{31}FeNO_6PS$: (M^+), 500.0958. Found: (M^+), 500.0895. Anal. Calcd for $C_{21}H_{31}F_3FeNO_9PS_2$: C, 38.84; H, 4.81; N, 2.16. Found: C, 39.21; H, 5.04; N, 2.02.

[2*R*(*S*),5*S*(*R*)]-Ethyl 6,6-Dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-3-carboxylate (30b). The carbene complex **29c** (23 mg) in EtOH (2 mL) was added to PhIO (40 mg). The reaction mixture was stirred at room temperature for 4 days and evaporated. Chromatography (CH_2Cl_2) gave **30b** (4.3 mg, 52%): IR (CH_2Cl_2) 3040, 2955, 2923, 2880, 1778, 1748, 1460, 1444, 1418, 1388, 1320 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.92 (s, 1 H), 4.88 (dd, 1 H, J = 7.0, 1.8 Hz), 4.20 (q, 2 H, J = 7.2 Hz), 3.42 (dd, 1 H, J = 11.8, 1.8 Hz), 3.23 (dd, 1 H, J = 11.8, 7.0 Hz), 1.48 (s, 3 H), 1.28 (t, 3 H, J = 7.2 Hz), 1.20 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 179.2, 168.5, 73.1, 62.0, 59.3, 55.7, 39.2, 28.8, 22.9, 14.3; mass spectrum (EI), m/e (%) 229 (8), 161 (10), 128 (19), 101 (87), 86 (39), 70 (100). Mass spectrum (EI) m/e calcd for $C_{10}H_{15}NO_3S$: ($M^{+\cdot}$), 229.0772. Found: (M^+), 229.0775.

Table IV. Crystal Data

formula	$C_{22}H_{29}F_3FeNO_7PS$
mol wt	595.35
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.963 (2)
b, Å	13.424 (2)
c, Å	9.505 (2)
α, deg	110.64 (2)
β, deg	99.76 (2)
γ, deg	85.27 (2)
V, Å^3	1290 (1)
Z	2
μ(Mo Kα), cm^{-1}	8.1
radiatn	graphite-monochromated Mo Kα, λ = 0.71069 Å
2θ range, deg	4–45
unique data	3345
unique data with $I > 3\sigma(I)$	2533
no. of variables	325
R	0.061
R_w	0.082
GOF	1.95

Determination of Stereochemistry of the β-Lactam (30b). Penam **30b** (2.3 mg) was dissolved in dry $CDCl_3$ (1 mL) containing Et_3N (0.3 mg). After 7 days there was no change in the 400-MHz NMR spectrum.

(2*R*,5*S*)-Methyl 7-Oxo-3,3,6,6-tetramethyl-4-thia-1-azabicyclo[3.2.0]heptane-3-carboxylate (30c). (1) Oxidation of the carbene complex **29d** (37 mg) in MeOH (2 mL) using PhIO (63 mg) for 22 days followed by evaporation and chromatography (CH_2Cl_2) gave **30c** (1.6 mg, 13%): IR (CH_2Cl_2) 2964, 2940, 2880, 1765, 1720, 1440, 1390, 1366, 1282, 1213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1 H), 4.37 (s, 1 H), 3.74 (s, 3 H), 1.59 (s, 3 H), 1.48 (s, 3 H), 1.44 (s, 3 H), 1.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 178.8, 169.0, 74.7, 68.7, 56.1, 52.6, 39.1, 32.7, 27.0, 23.4, 19.3; mass spectrum (EI), m/e 243, 175, 174. Mass spectrum (EI) m/e calcd for $C_{11}H_{17}NO_3S$: ($M^{+\cdot}$), 243.0929. Found: ($M^{+\cdot}$), 243.0921.

(2) A solution of **29d** (195 mg), Bu_4NNO_2 (1.3 g) and CH_2Cl_2 (15 mL) was pressurized at 6.6 kbar for 96 h. Evaporation and chromatography (CH_2Cl_2) gave **30c** (23 mg, 32%).

6,6-Dimethyl-4-thia-1-azabicyclo[3.2.0]heptane (30a). A solution of **29b** (149 mg) in dry EtOH (15 mL) was reacted with PhIO (294 mg) for 2 days at room temperature. Evaportion and chromatography on silica (CH_2Cl_2) gave **30a** (15 mg, 36%): IR (film) 2960, 2925, 2855, 1775, 1495, 1260; ^1H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1 H), 4.12 (ddd, 1 H, J = 12, 6.4, 2 Hz), 3.07 (ddd, 1 H, J = 10.8, 6.4, 2 Hz), 2.98 (ddd, 1 H, J = 10.8, 9.6, 6.4 Hz), 2.76 (ddd, 1 H, J = 12, 9.6, 6 Hz), 1.45 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 72.5, 55.1, 46.0, 36.0, 22.8, 18.3.

X-ray Data Collection and Structure Determination of Carbonyl(η^5-cyclopentadienyl)[2-(4-phenyl-1,3,3-trimethylazetidinylidene)](trimethyl phosphite)iron(II) Trifluoromethanesulfonate (24f). A yellow crystal of dimensions 0.34 × 0.22 × 0.16 mm was used for the X-ray structure determination. All measurements were performed on an Enraf-Nonius CAD4 diffractometer at −120 °C using Mo Kα radiation (λ = 0.71069 Å). Accurate cell parameters were determined by least-squares refinement applied to the setting angles of 24 high-angle relfections. Experimental details are given in Table IV. Intensities of three standard reflections were remeasured every 3 h of X-ray exposure showing no significant decay. Intensity data were subsequently corrected for Lorentz–polarization and absorption effects. Empirical absorption corrections were obtained from psi scans of six Bragg reflections. The transmission factors ranged 0.68–1.00.

All calculations were performed on a VAX11/730 computer with the TEXSAN 2.0 crystallographic software package.[38] The

Table V. Positional Parameters for 24f

atom	x	y	z
Fe	0.61633 (7)	0.29179 (5)	0.10962 (8)
S	0.1962 (2)	0.2476 (1)	0.6486 (2)
P	0.7269 (1)	0.1561 (1)	0.0030 (2)
F1	0.1929 (9)	0.0489 (4)	0.4697 (7)
F2	0.1008 (9)	0.1596 (5)	0.3663 (5)
F3	0.0309 (8)	0.1104 (7)	0.5173 (9)
O1	0.4363 (4)	0.1561 (3)	0.1365 (5)
O2	0.7389 (4)	0.0761 (4)	0.0921 (5)
O3	0.6828 (4)	0.0893 (3)	−0.1711 (4)
O4	0.8669 (4)	0.1699 (4)	−0.0053 (5)
O5	0.2349 (6)	0.2079 (5)	0.7670 (6)
O6	0.3090 (7)	0.2719 (8)	0.600 (1)
O7	0.125 (1)	0.336 (5)	0.646 (1)
N	0.8177 (4)	0.3536 (3)	0.3710 (5)
C1	0.7113 (4)	0.3087 (4)	0.3022 (6)
C2	0.6845 (5)	0.2951 (4)	0.4509 (6)
C3	0.8120 (4)	0.3527 (4)	0.5246 (6)
C4	0.5084 (5)	0.2092 (4)	0.1298 (6)
C5	0.9162 (5)	0.3920 (5)	0.3200 (6)
C6	0.6948 (6)	0.1793 (4)	0.4449 (7)
C7	0.5711 (5)	0.3514 (5)	0.5056 (7)
C8	0.8127 (4)	0.4610 (4)	0.6458 (6)
C9	0.8586 (5)	0.4725 (4)	0.7978 (6)
C10	0.8543 (5)	0.5706 (5)	0.9101 (6)
C11	0.8076 (5)	0.6586 (4)	0.8770 (6)
C12	0.7648 (5)	0.6495 (4)	0.7265 (7)
C13	0.7676 (5)	0.5515 (4)	0.6139 (6)
C14	0.8169 (7)	−0.0208 (5)	0.052 (1)
C15	0.5585 (7)	0.0605 (5)	−0.2336 (7)
C16	0.9103 (6)	0.1837 (6)	−0.1296 (9)
C17	0.4861 (7)	0.3511 (5)	−0.0273 (8)
C18	0.4946 (5)	0.4222 (4)	0.1218 (7)
C19	0.6142 (5)	0.4583 (4)	0.1639 (6)
C20	0.6808 (6)	0.4085 (5)	0.0435 (8)
C21	0.5981 (9)	0.3420 (5)	−0.0766 (7)
C22	0.1395 (9)	0.1386 (6)	0.4868 (8)

Table VI. Selected Bond Lengths (Å) for 24f

Fe–P	2.137 (2)	N–C5	1.455 (7)
Fe–C1	1.893 (5)	C1–C2	1.565 (7)
Fe–C4	1.764 (7)	C2–C3	1.584 (7)
Fe–C17	2.069 (6)	C2–C6	1.531 (8)
Fe–C18	2.094 (5)	C2–C7	1.475 (8)
Fe–C19	2.109 (5)	C3–C8	1.503 (8)
Fe–C20	2.092 (6)	C8–C9	1.405 (8)
Fe–C21	2.081 (6)	C8–C13	1.387 (8)
P–O2	1.572 (5)	C9–C10	1.375 (8)
P–O4	1.580 (5)	C10–C11	1.366 (8)
P–O3	1.590 (4)	C11–C12	1.393 (8)
O1–O4	1.130 (7)	C12–C13	1.374 (8)
O2–C14	1.465 (8)	C17–C21	1.37 (1)
O3–C15	1.417 (8)	C17–C18	1.39 (1)
O4–C16	1.420 (9)	C18–C19	1.380 (8)
N–C1	1.315 (7)	C19–C20	1.40 (1)
N–C3	1.475 (7)	C20–C21	1.41 (1)

structure was solved by direct methods (MITHRIL).[39] The full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave a final R of 0.061 (R_w = 0.082) for 2533 reflections with $I > 3\sigma(I)$ and 325 variables. The $CF_3SO_3^-$ cation was affected by disorder, and the thermal parameters of the F and O atoms were high. The disorder contributed to somewhat higher than usual values of the R factors.

All hydrogen atoms were located from difference Fourier maps and were included in the final stage of refinement as fixed contributors to the structure factors. The final difference map showed two higher peaks ca. 1 e/Å^3 high located near the disordered cation. Final positional parameters are listed in Tables V–VII.

Table VII. Selected Bond Angles (deg) for 24f

P–Fe–C1	91.2 (1)	N–C3–C2	85.4 (3)
P–Fe–C4	90.9 (2)	N–C3–C8	114.7 (4)
C1–Fe–C4	93.7 (2)	C2–C3–C8	119.2 (4)
Fe–P–O2	109.8 (2)	Fe–C4–O1	176.8 (5)
Fe–P–O3	117.7 (2)	C9–C8–C13	117.9 (5)
Fe–P–O4	120.0 (2)	C8–C9–C10	120.1 (5)
P–O2–C14	122.2 (5)	C9–C10–C11	121.3 (5)
P–O3–C15	124.0 (4)	C10–C11–C12	119.5 (5)
P–O4–C16	124.9 (4)	C11–C12–C13	119.5 (5)
C1–N–C3	98.4 (4)	C12–C13–C8	121.7 (5)
C1–N–C5	133.4 (5)	C18–C17–C21	109.6 (6)
C3–N–C5	128.1 (4)	C17–C18–C19	106.9 (6)
N–C1–C2	91.8 (4)	C18–C19–C20	109.0 (5)
C6–C2–C7	113.5 (5)	C19–C20–C21	107.0 (6)
C1–C2–C3	84.4 (4)	C17–C21–C20	107.5 (6)

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Registry No. **7**, 15975-93-6; **8a**, 622-29-7; **8b**, 17972-15-5; **8c**, 17972-13-3; **8d**, 116910-43-1; **9a**, 97879-05-5; **9b**, 97879-06-6; **9c**, 97879-07-7; **10a**, 97879-03-3; **10b**, 97889-72-0; **10c**, 97879-04-4; **14**, 88034-35-9; **15**, 20540-69-6; **17a**, 77307-42-7; **17b**, 109863-58-3; **18**, 12154-95-9; **19**, 116926-27-3; **20a**, 80642-55-3; **21a**, 109492-24-2; **21b** (isomer 1), 117019-41-7; **21b** (isomer 2), 117019-39-3; **23a**, 80642-54-2; **23b**, 71163-57-0; **23c**, 109863-62-9; **23d**, 116926-31-9; **24a** (isomer 1), 109527-58-4; **24a** (isomer 2), 109464-77-9; **24b** (isomer 1), 109863-70-9; **24b** (isomer 2), 109863-68-5; **24c** (isomer 1), 109527-60-8; **24c** (isomer 2), 109464-81-5; **24d** (isomer 1), 109464-79-1; **24d** (isomer 2), 109582-48-1; **24e** (isomer 1), 109527-62-0; **24e** (isomer 2), 109464-83-7; **24f** (isomer 1), 109863-70-9; **24f** (isomer 2), 117019-37-1; **25a**, 29668-85-7; **25b**, 116910-44-2; **25c**, 116926-30-8; **25d**, 116910-45-3; **26**, 109863-64-1; **27**, 96021-13-5; **28a**, 504-79-0; **28b**, 51932-25-3; **28c**, 58134-39-7; **29a** (isomer 1), 117019-35-9; **29a** (isomer 2), 117020-21-0; **29b** (isomer 1), 109956-72-1; **29b** (isomer 2), 109863-72-1; **29c** (isomer 1), 109956-74-3; **29c** (isomer 2), 109863-74-3; **29d** (isomer 1), 109863-57-2; **29d** (isomer 2), 109956-70-9; **30a**, 103910-44-7; **30b**, 109863-75-4; **30c**, 116910-46-4; carbonyl(η^5-cyclopentadienyl)[1-(1-methoxy-2-methylpropanylidene)](trimethylphosphite)-iron(II) trifluoromethanesulfonate, 116926-29-5.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances, and bond angles for **24f** (5 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

(38) Swepston, P. N. TEXSAN Crystallographic Program Package; Molecular Structure Corp.: College Station, TX, 1986.

(39) Gilmore, G. N. MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data; University of Glasgow: Glasgow, Scotland, 1983.