

Ring Opening of (Spiro[2.4]hepta-4,6-diene)tricarbonyliron: A Revisit

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(Spiro[2.4]hepta-4,6-diene)tricarbonyliron (**2**) self-converts to the tethered acyl complex (CO)₂FeC(O)CH₂CH₂(η⁵-C₅H₄) (**3**) when refluxed for 1 h in common organic solvents. The reaction of **2** with an external electrophile (CPh₃⁺, H⁺) opens the three-membered ring, resulting in the cation (η⁵-C₅H₄CH₂CH₂R)Fe(CO)₃⁺ whose structure was determined by spectroscopic methods and confirmed by X-ray analysis of the PPh₃ derivative (η⁵-C₅H₄CH₂-CH₃)Fe(CO)₂(PPh₃)⁺. The reaction of **3** with a strong electrophile (CPh₃⁺, Me⁺) affords the rotationally restricted Fe–(alkoxy)carbene cation (CO)₂Fe=C(OR)CH₂CH₂(η⁵-C₅H₄)⁺, which can be converted to the Fe–(anilino)carbene cation (CO)₂Fe=C(NHPh)CH₂CH₂(η⁵-C₅H₄)⁺.

Introduction

In 1958, Hallam and Pauson¹ reported that spiro[2.4]-hepta-4,6-diene (**1**) formed only ring-opened dinuclear complexes upon reaction with Fe(CO)₅ at 140 °C, no mononuclear iron complexes being isolated. In 1968, Depuy, Kobal, and Gibson² reported that **1** reacted with Fe₂(CO)₉ at room temperature in Et₂O to give, in 38% yield, a compound formulated as the iron tricarbonyl complex of spiro[2.4]hepta-4,6-diene (**2**). In 1976, however, Eilbracht³ revealed that the reported complex (**2**) was in actuality the tethered acyl complex (CO)₂FeC(O)CH₂CH₂(η⁵-C₅H₄) (**3**). Mechanistically, the existence of **2** was assumed to be an intermediate in the formation of **3**.

In 1984, Flecker, Grevels, and Hess⁴ reported a much more facile Fe(CO)₃ transfer reagent (η²-*cis*-C₈H₁₄)₂Fe(CO)₃ (**4**), which was demonstrated to transfer a Fe(CO)₃ unit effectively to a variety of bidentate ligands in common organic solvents at or above –35 °C. A number of successful preparations of dieneiron tricarbonyl complexes employing **4** followed in the literature, for example, the preparation of (2-stannylated butadiene)tricarbonyliron⁵ and (substituted cyclohexadiene)tricarbonyliron.⁶ In order to see if the intermediate **2** could be detected, the reaction of **1** with the mild Fe(CO)₃ transfer reagent **4** was examined; the results are presented herein.

Results and Discussion

Generation of 2 by Reaction of 1 with 4. Compound **4** exhibits ν(CO) stretching bands at 2044 (m) and 1966 (vs) cm⁻¹ in *n*-hexane at –40 °C.⁴ When the solution was warmed to room temperature, these characteristic bands disappeared due to decomposition. An equimolar mixture of **1** and **4** in *n*-hexane, after gradual warming from –60 °C to room temperature, shows final ν(CO) stretching bands at 2047 (s), 1983 (s), 1961 (s) cm⁻¹, implying a successful transfer of Fe(CO)₃ and the formation of the iron tricarbonyl complex of spiro[2.4]-hepta-4,6-diene (**2**) (*cf.* (η⁴-C₅H₆)Fe(CO)₃,⁷ IR(*n*-hexane) ν(CO) 2048, 1981, 1974 cm⁻¹).

Self-Conversion of 2 to 3. At room temperature under N₂ atmosphere, compound **2** in THF gradually shows a decrease in the ν(CO) absorption at 2040 cm⁻¹ with an increase at 2020 and 1663 cm⁻¹ (Figure 1). When an equimolar mixture of **1** and **4** in THF under N₂ atmosphere is warmed from –60 °C to room temperature, only **2** is present in solution, as characterized by the IR ν(CO) bands in Figure 1a. After 13 h, the ν(CO) bands of **3** are just discernible, Figure 1b. After 112 h, ν(CO) absorptions due to **3** at 2020, 1964, and 1663 cm⁻¹ are clearly seen, Figure 1c. Comparison of the ν(CO) intensities in Figures 1a and 1c suggests that the loss of **2** after 112 h is about 10–20%. Among the solvents studied, the conversion of **2** to **3** in *n*-hexane is much slower than that in CH₂Cl₂, Et₂O, or THF. Compound **2** is soluble in common organic solvents but it is difficult to purify due to the conversion to **3** and the interference of *cis*-C₈H₁₄, which is a high boiling impurity (bp 145–146 °C) originating from **4**. If brought to reflux for 1 h, compound **2** in solution is fully converted to **3**, whose IR ν(CO) stretching bands are shown in Figure 1d. Compound **3** is not soluble in *n*-hexane or Et₂O but is soluble in THF and chlorinated solvents.

Reactions of 2 with Lewis and Protic Acids. Scheme 1 shows a proposed, intramolecular, ionic rear-

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(1) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 646.

(2) DePuy, C. H.; Kobal, V. M.; Gibson, D. H. *J. Organomet. Chem.* **1968**, *13*, 266.

(3) (a) Eilbracht, P.; Mayser, U. *J. Organomet. Chem.* **1977**, *135*, C26. (b) Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211.

(4) Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

(5) Colson, P.-J.; Franck-Neumann, M.; Sedrati, M. *Tetrahedron Lett.* **1989**, *30*, 2393.

(6) (a) Eilbracht, P.; Hittinger, C.; Kufferath, K. *Chem. Ber.* **1990**, *123*, 1071. (b) Eilbracht, P.; Hittinger, C.; Kufferath, K.; Henkel, G. *Chem. Ber.* **1990**, *123*, 1079. (c) Eilbracht, P.; Hittinger, C.; Kufferath, K.; Schmitz, A.; Gilsing, H.-D. *Chem. Ber.* **1990**, *123*, 1089.

(7) Kochhar, R. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 272.

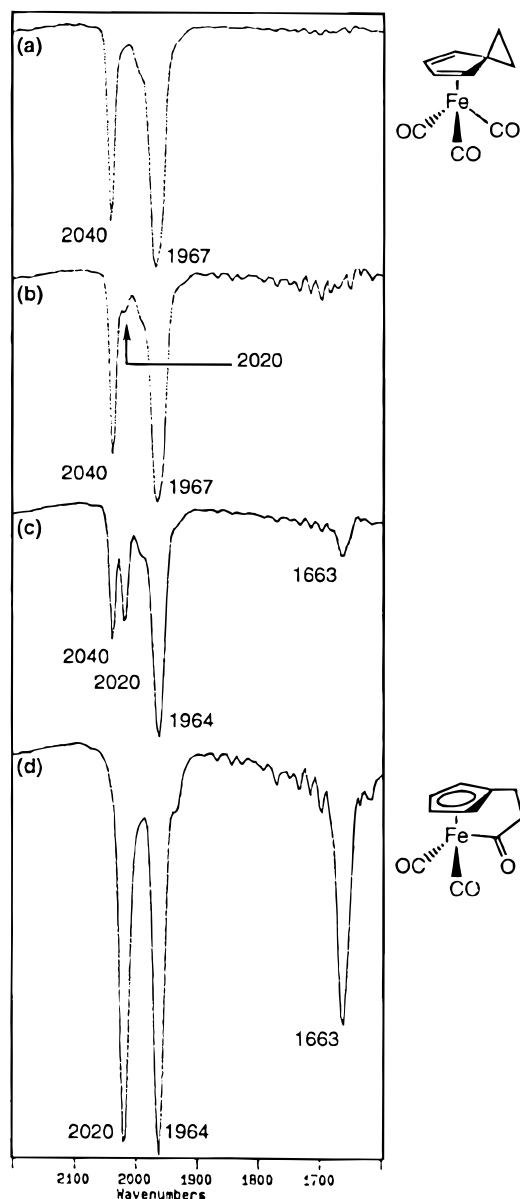


Figure 1. IR $\nu(\text{CO})$ bands of **2** in THF as a function of time: (a) at 0 h, (b) at 13 h, (c) at 112 h. The IR $\nu(\text{CO})$ bands of **3** are shown in d.

ring-opening pathway for the conversion of **2** to **3**, where one ring is opened and another joined. The carbonyl carbon atom plays the role of an electrophile in this mechanism.⁸ The ionic pathway is preferred to the also-plausible homolytic pathway. If indeed ionic, this intramolecular electrophilic ring-opening process at the three-membered ring should be in competition with an intermolecular one by external strong electrophiles.

The reaction of **2** in CH_2Cl_2 with $[\text{Ph}_3\text{C}^+][\text{PF}_6^-]$, included in Scheme 1, produces $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CPh}_3)\text{Fe}(\text{CO})_3]^+[\text{PF}_6^-]$ (**5**· PF_6). The Ph_3C^+ addition opens the three-membered ring, which in turn effectively changes the bonding mode of $\eta^4\text{-Fe}$ to $\eta^5\text{-Fe}$ and the oxidation state of Fe from 0 to +2. The ^1H NMR and IR data are

(8) (a) Wong, A.; Pawlick, R. V.; Thomas, C. G.; Leon, D. R.; Liu, L.-K. *Organometallics* **1991**, *10*, 530. (b) Liu, L.-K.; Sun, C.-H.; Yang, C.-Z.; Wen, Y.-S.; Wu, C.-F.; Shih, S.-Y.; Lin, K.-S. *Organometallics* **1992**, *11*, 972. (c) Liu, L.-K.; Eke, U. B.; Mesubi, M. A. *Organometallics* **1995**, *14*, 3958.

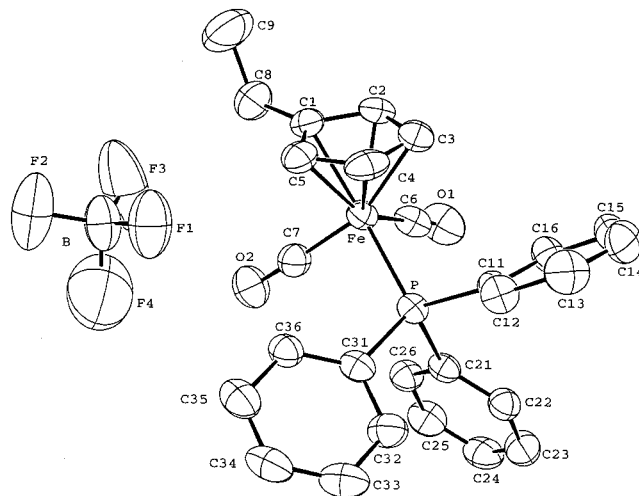


Figure 2. Molecular plot of **9**· BF_4 . The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe–C1 2.116(4), Fe–C2 2.090(4), Fe–C3 2.074(4), Fe–C4 2.098(4), Fe–C5 2.104(4), Fe–C6 1.777(5), Fe–C7 1.774(5), Fe–P 2.2380(15), C1–C8 1.496(7), C8–C9 1.505(8), C6–O1 1.139(6), C7–O2 1.146(6), P–C11 1.817(4), P–C21 1.839(4), P–C31 1.831(4). Selected bond angles (deg): P–Fe–C6 91.74(15), P–Fe–C7 94.00(15), C6–Fe–C7 95.43(21), Fe–C1–C8 129.5(3), C1–C8–C9 110.4(5), Fe–C6–O1 178.5(4), Fe–C7–O2 177.9(4), Fe–P–C11 110.87(13), Fe–P–C21 115.65(14), Fe–P–C31 117.19(15).

in agreement with the structure of **5** (see Experimental Section).

The reaction of **2** in CH_2Cl_2 with electrophilic methylating reagents, $[\text{Me}_3\text{O}^+][\text{BF}_4^-]$, MeSO_3CF_3 , MeI , or $[(\text{MeO})_2\text{CH}^+][\text{PF}_6^-]$ (from 1:1 $[\text{Ph}_3\text{C}^+][\text{PF}_6^-]/(\text{MeO})_3\text{CH}$),⁹ produces acyl **3** in part, which is expected in view of the conversion of **2** to **3**, but no $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{-Me})\text{Fe}(\text{CO})_3]^+[\text{X}^-]$ (**6**· X , $\text{X} = \text{BF}_4$, SO_3CF_3 , I , or PF_6) is formed. With $[\text{Me}_3\text{O}^+][\text{BF}_4^-]$, $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_3)\text{Fe}(\text{CO})_3]^+[\text{BF}_4^-]$ (**7**· BF_4) is formed,¹⁰ and with $[\text{Ph}_3\text{C}^+][\text{PF}_6^-]/(\text{MeO})_3\text{CH}$, **5**· PF_6 is the product.

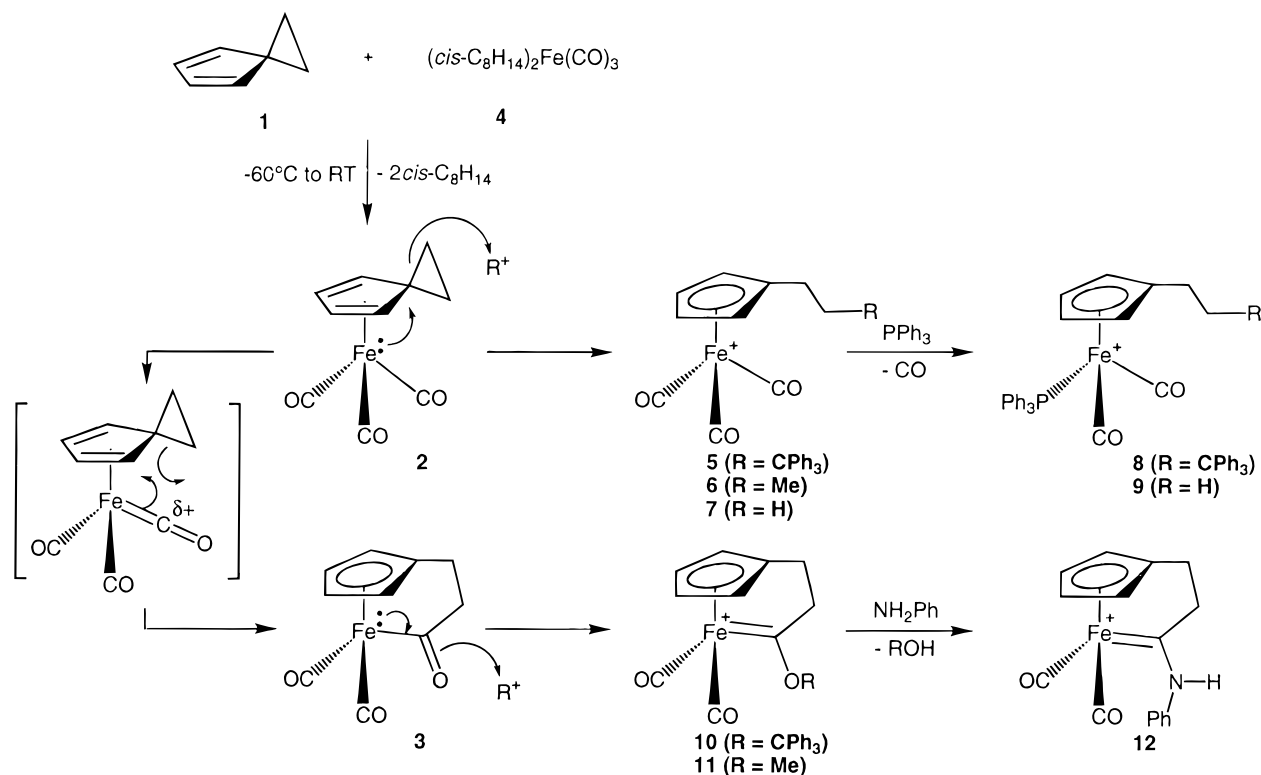
The reaction of **2** in CH_2Cl_2 with excess $\text{HBF}_4\cdot\text{OEt}_2$ yields **7**· BF_4 with IR (CH_2Cl_2) $\nu(\text{CO})$ stretching bands at 2122, 2077, and 2067 cm^{-1} . Cation **7** has a blue shift of ca. 80 cm^{-1} from those of **2** in the IR $\nu(\text{CO})$ stretching bands. The ^1H NMR data of cation **7** are also consistent with the structure: the two Cp resonances at δ 5.82 and 5.67 and the tethered ethyl signals at δ 2.52 (q) and 1.28 (t).

Compounds **5**· PF_6 and **7**· BF_4 were collected as precipitates from the reaction of the respective electrophiles with **2** prepared *in situ* in CH_2Cl_2 . To eliminate *cis*- C_8H_{14} contamination, compounds **5**· PF_6 and **7**· BF_4 were chemically derivatized by stirring equimolar **5**· PF_6 (or **7**· BF_4) and PPh_3 ; initiation with a drop of Et_3N produced 96% $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CPh}_3)]^+[\text{PF}_6^-]$ (**8**· PF_6); or 98% $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_3)]^+[\text{BF}_4^-]$ (**9**· BF_4). A single-crystal X-ray diffraction study of **9**· BF_4 confirms a three-legged piano-stool structure with an ethyl tether arm on the Cp ring (see Figure 2). With

(9) Bodnar, T. W.; Cutler, A. R. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 31.

(10) Me_3O^+ was noted as a proton source rather than a methylating source in H_2O , see: Webb, M. J.; Stewart, R. P.; Graham, W. A. G. *J. Organomet. Chem.* **1973**, *59*, C21.

Scheme 1



Et_3N initiation, the PPh_3 replacement for CO in cations **5** and **7** takes a few seconds to reach completion, due to an electron-transfer-chain catalytic process.¹¹ Without Et_3N initiation, the PPh_3 substitution takes overnight and the yield is much lower.

X-ray Structure of 9·BF₄. An ORTEP molecular plot of **9·BF₄** with relevant bond lengths and angles is given in Figure 2. The cation has a three-legged piano-stool geometry, as found with $[(\eta^5-C_5H_5)Fe(CO)_2(PPh_3)]^+[X^-]$ ($X = C_3(CN)_5$,¹² Cl^{13}). The ethyl arm in **9·BF₄** points away from Fe, as indicated by the torsion angle $Fe-C1-C8-C9$ of $178.8(6)^\circ$, whereby C8 is displaced by $0.097(9)$ Å from the Cp plane in the direction opposite to Fe and C9 is located $1.538(11)$ Å from the Cp plane.

Reactions of 3 with Lewis and Protic Acids. The reaction of **3** with $[Ph_3C^+][PF_6^-]$ in CH_2Cl_2 yields partial conversion to the carbene $[(CO)_2Fe=C(OCPh_3)CH_2CH_2-(\eta^5-C_5H_4)^+][PF_6^-]$ (**10·PF₆**), as judged from the new IR $\nu(CO)$ bands at 2068 and 2024 cm^{-1} . Treatment of **3** with $[(MeO)_2CH^+][PF_6^-]$ in CH_2Cl_2 results in the carbene $[(CO)_2Fe=C(OMe)CH_2CH_2(\eta^5-C_5H_4)^+][PF_6^-]$ (**11·PF₆**); reaction of **3** with $[Me_3O^+][BF_4^-]$ gives the same carbene with a BF_4^- anion, **11·BF₄** (Scheme 1). It is reported that the reaction of $(\eta^5-C_5H_5)Fe(CO)_2C(O)Me$ with a methylating reagent gives rise to the carbene $[(\eta^5-C_5H_5)Fe(CO)_2=C(OMe)Me^+][PF_6^-]$ (IR (CH_2Cl_2) $\nu(CO)$ 2060 , 2014 cm^{-1}).¹⁴ Compound **3** does not react with MeI to produce a carbene. Also shown in Scheme 1, the Fe-(methoxy)carbene cation **11** proceeds smoothly to a Fe-(anilino)carbene cation $(CO)_2Fe=C(NHPh)CH_2-$

$CH_2(\eta^5-C_5H_4)^+$ (**12**) upon reaction with NH_2Ph , in analogy to the known preparation of Fp-(amino)carbenes from Fp-(methoxy)carbenes, $Fp = (\eta^5-C_5H_5)Fe(CO)_2$.¹⁵ In such a transformation, the IR $\nu(CO)$ bands are red-shifted, the shifts being from 2072 and 2028 cm^{-1} in **11** to 2054 and 2011 cm^{-1} in **12**, giving evidence for more back-bonding from Fe to the CO ligands in **12**. As a consequence, a cationic Fe-(anilino)carbene is more stable than a cationic Fe-(methoxy)carbene.¹⁶ Crystals of **12·PF₆** suitable for X-ray diffraction analysis were grown from MeOH/THF by slow evaporation. A diffraction study confirms the structure of **12·PF₆** (Figure 3). In the reaction of **11** with NH_2Et as detailed elsewhere,¹⁷ the cationic Fe-(diethylamino)carbene $[(CO)_2Fe=C(NEt_2)CH_2CH_2(\eta^5-C_5H_4)^+][BF_4^-]$ is obtained.

The IR spectrum of **3** does not change when compound **3** is mixed with 1 equiv of $HBF_4 \cdot OEt_2$, suggesting that there is little Fe-(hydroxy)carbene cation formation. Interestingly anionic $(CO)_2ReC(O)CH_2CH_2(\eta^5-C_5H_4)^-$, the isolobal Re analog of neutral **3**, reacts with $HBF_4 \cdot OEt_2$ to give rise to the corresponding neutral Re-(hydroxy)carbene $(CO)_2Re=C(OH)CH_2CH_2(\eta^5-C_5H_4)$ that is in equilibrium with the Re-hydride $(CO)_2(H)ReC(O)CH_2CH_2(\eta^5-C_5H_4)$.¹⁸ When **3** was added to neat CF_3CO_2H , transient IR $\nu(CO)$ bands were seen at 2129 , 2081 , 2042 , and 2011 cm^{-1} , but the latter two disap-

(14) (a) Bodnar, T.; LaCroze, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (d) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

(15) Rueck-Braun, K.; Kuehn, J.; Schollmeyer, D. *Chem. Ber.* **1996**, *129*, 937.

(16) Petz, W. *Iron-Carbene Complexes*; Springer-Verlag: Berlin, Germany, 1993.

(17) Fu, Y.-T.; Liu, L.-K. *Bull. Inst. Chem., Acad. Sin.* **1997**, *44*, 7.

(18) Casey, C. P.; Czerwinski, C. J.; Hayashi, R. K. *J. Am. Chem. Soc.* **1995**, *117*, 4189.

(11) Pevear, K. A.; Banaszak Holl, M. M.; Carpenter, G. B.; Rieger, A. L.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1995**, *14*, 512 and references within.

(12) Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 629.

(13) Riley, P. E.; Davis, R. E. *Organometallics* **1983**, *2*, 286.

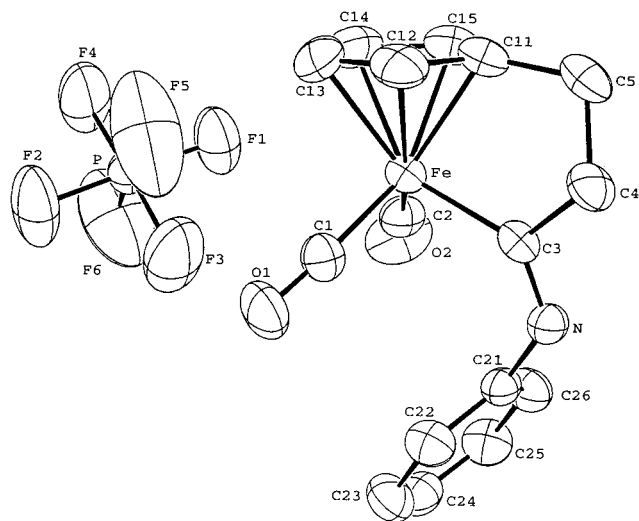
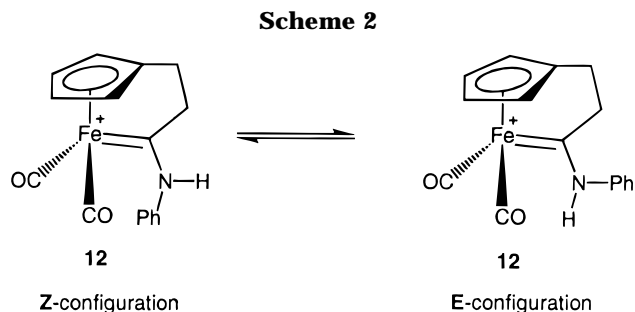


Figure 3. Molecular plot of $12 \cdot \text{PF}_6$. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe–C1 1.769(5), Fe–C2 1.770(5), Fe–C3 1.933(5), Fe–C11 2.084(4), Fe–C12 2.090(4), Fe–C13 2.112(5), Fe–C14 2.108(5), Fe–C15 2.093(5), N–C3 1.296(6), N–C21 1.436(5), C1–O1 1.139(6), C2–O2 1.143(6), C3–C4 1.522(6), C4–C5 1.519(7), C5–C11 1.497(7). Selected bond angles (deg): C1–Fe–C2 94.18(23), C1–Fe–C3 95.61(20), C2–Fe–C3 96.92(20), C3–N–C21 127.0(4), Fe–C1–O1 176.8(4), Fe–C2–O2 176.2(5), Fe–C3–N 131.4(3), Fe–C3–C4 115.3(3), N–C3–C4 113.3(4), C3–C4–C5 110.5(4), C11–C5–C4 106.9(4), Fe–C11–C5 114.6(3).

peared within minutes. Attempts to isolate and characterize the protonated **3** species were unsuccessful.

X-ray Structure of $12 \cdot \text{PF}_6$. Figure 3 shows the ORTEP plot of $12 \cdot \text{PF}_6$ with relevant bond lengths and angles. The X-ray structure shows that ring closure produces a moderately strained system in comparison with rotationally unrestricted $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ carbene complexes. The alkyl tether of the Cp ring of $12 \cdot \text{PF}_6$ is bent down *ca.* 10° toward Fe (Cp(centroid)–C1–C8 = $170.1(4)^\circ$), while in untethered systems, an alkyl arm on the ring is normally positioned away from the metal center. The carbene C atom has sp^2 bonding, indicated by the fact that the sum of angles around C10 is 360° . The interplanar angle between the carbene C and the neighboring atoms and the planar anilino N and the neighboring atoms is only $1.1(2)^\circ$, indicative of a resonance, indeed, between the carbene C atom and the attached anilino N atom. The resonance does not extend to the phenyl group, however. The phenyl group is positioned far from coplanarity with the carbene plane or the anilino N plane, the respective interplanar angles with the phenyl group being *ca.* $76.9(2)^\circ$ and $77.0(2)^\circ$. A vertical molecular mirror plane as defined by Fe, Cp(centroid), C_{ipso} of the Cp ring, and the midpoint of two carbonyl C atoms is only $13.3(2)^\circ$ with the carbene plane, placing the carbene plane in an approximately upright position. The C–N bond of $1.296(6)$ Å suggests a partial double-bond character. In this regard, the X-ray structure of $12 \cdot \text{PF}_6$ is in a *Z*-configuration, the torsion angle Fe–C10–N–C11 being $2.2(2)^\circ$. Ring strain also narrows the angle between Cp(centroid), the Fe atom, and the carbene C atom to $117.1(1)^\circ$, as compared to $121.2(2)$ – $124.3(2)^\circ$ angles in the three-legged piano-stool $(\eta^5\text{-C}_5\text{H}_5)\text{FeL}_3$ systems. The rota-



tionally restricted Re–(methoxy)carbene $(\text{CO})_2\text{Re}=\text{C}(\text{OMe})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ also shows a bending of the alkyl tether toward the Re by 9° and a decrease of the angle between Cp(centroid), the Re atom, and the carbene C atom (111.8°).¹⁸

Rotational Isomers of $12 \cdot \text{PF}_6$. The ^1H NMR spectrum of $12 \cdot \text{PF}_6$ in acetone- d_6 indicates the presence of two isomers at room temperature. One isomer has ^1H peaks for the Cp ring protons and the methylene protons at δ 5.85, 5.44, 3.87, and 2.61 ($C_{3,4}$, $C_{2,5}$, C_α , C_β), while the other isomer has peaks at δ 5.79, 5.35, 4.10 and 2.64, with an integration ratio of 54:46 between the two, respectively. The numerical atom numbering is applied to the Cp ring, whereas the Greek letters refer to positions relative to the carbene C atom. The two isomers were not assigned to a specific *Z*- or *E*-configuration (Scheme 2). The Fe=C bond in resonance with the planar N atom results in a relatively strong C–N bond. Due to the restricted rotation around the C–N bond, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-(\text{amino})\text{carbene}$ complexes can usually be obtained as a mixture of rotational isomers provided that the amino substituents are unsymmetrical; $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(i\text{-Pr})\text{NHPh}^+$ was reported to have a C–N bond rotational barrier of 77 ± 2 kJ/mol.¹⁹

Conclusion

The iron tricarbonyl complex of spiro[2.4]hepta-4,6-diene, **2**, converts to the tethered acyl **3**. Compounds **2** and **3** act differently toward Lewis and protic acids. Opening of the three-membered ring occurs in the reaction of **2** with Lewis and protic acids, resulting in compounds with a $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_3^+$ fragment. In contrast, **3** reacts with Lewis and protic acids to form Fe–carbene compounds.

Experimental Section

General. All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.²⁰ IR spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 882 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with chemical shifts reported in δ values relative to the residual solvent resonance of CDCl_3 (^1H , 7.24 ppm; ^{13}C , 77.0 ppm). FAB mass spectra were obtained on a VG system, model 70–250S spectrometer. Microanalytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer independently operated by the Institute of Chemistry, Academia Sinica. The melting points were measured on a Yanaco

(19) Fehlhammer, W. P.; Hirschmann, P.; Mayr, A. *J. Organomet. Chem.* **1982**, 224, 153.

(20) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1981.

micro melting point apparatus. Compounds **1** and **4** were synthesized according to procedures in the literature.^{4,21} All reagents including $[\text{Me}_3\text{O}^+][\text{BF}_4^-]$, MeSO_3CF_3 , $[\text{Ph}_3\text{C}^+][\text{PF}_6^-]$, and $(\text{MeO})_3\text{CH}$ were obtained from commercial sources and used without further purification.

(η^4 -Spiro[2.4]hepta-4,6-diene)Fe(CO)₃ (2**).** Compound **1** (0.18 g, 2.0 mmol) in THF (10 mL) was slowly added to a stirred solution of **4** (0.72 g, 2.0 mmol) in THF (100 mL) at -60°C . After the mixture was stirred for 2 h at -60°C , the solution was gradually warmed to room temperature, giving **2**, quantitatively, in solution, which was ready for use in further reactions. IR (THF) $\nu(\text{CO})$: 2039 (s), 1966 (s, br) cm^{-1} . Similar solutions of **2** were prepared in *n*-hexane and CH_2Cl_2 . IR (*n*-hexane) $\nu(\text{CO})$: 2047 (s), 1983 (s), 1961 (s) cm^{-1} . IR (CH_2Cl_2) $\nu(\text{CO})$: 2040 (s), 1971 (s, br) cm^{-1} . Using CD_2Cl_2 as the solvent, the ^1H NMR spectrum of **2** was obtained. ^1H NMR (CD_2Cl_2): δ 5.73 (b, 2H), 2.90 (b, 2H), 0.90 (t, $J = 7.8$ Hz, 2H), 0.32 (t, $J = 7.8$ Hz, 2H).

Self-Conversion of 2 to (CO)₂FeC(O)CH₂CH₂(η^5 -C₅H₄) (3**).** A solution of **2** (2.0 mmol) in THF (100 mL), prepared *in situ* as described previously, was refluxed for 1 h before the solvent was removed under vacuum. The dark brown residue was purified by SiO_2 column chromatography, eluting with ethyl acetate/*n*-hexane (1:5) to give **3** (0.25 g, 1.1 mmol, 55%) as a yellow solid after the eluate was dried. IR (CH_2Cl_2) $\nu(\text{CO})$: 2024 (s), 1966 (s), 1645 (m) cm^{-1} . ^1H NMR (CDCl_3): δ 5.06 (b, 2H), 4.72 (b, 2H), 3.44 (t, $J = 7.6$ Hz, 2H), 2.15 (t, $J = 7.6$ Hz, 2H); ^1H NMR (acetone-*d*₆): δ 5.37 (t, $J = 1.8$ Hz, 2H), 4.91 (t, $J = 1.8$ Hz, 2H), 3.40 (t, $J = 7.6$ Hz, 2H), 2.18 (t, $J = 7.6$ Hz, 2H) (lit.²² IR (KBr) $\nu(\text{CO})$ 2000, 1960, 1940, 1915, 1640, 1620 cm^{-1} . ^1H NMR (C_6D_6) δ 5.08 (t, $J = 2$ Hz, 2H), 4.72 (t, $J = 2$ Hz, 2H), 3.46 (t, $J = 7.5$ Hz, 2H), 2.17 (t, $J = 7.5$ Hz, 2H). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{FeO}_3$: C, 51.77; H, 3.98. Found: C, 51.68; H, 3.51.

[Fe(CO)₃(η^5 -C₅H₄CH₂CH₂CPh₃)⁺][PF₆⁻] (5**-PF₆).** To a solution of **2** (2.0 mmol) in CH_2Cl_2 (100 mL), prepared *in situ*, was slowly added $\text{Ph}_3\text{C}^+\text{PF}_6^-$ (2.33 g, 6.0 mmol) in CH_2Cl_2 (50 mL). After the mixture was stirred overnight, the reaction mixture was concentrated to about 50 mL and diluted with Et_2O (300 mL) to precipitate **5**-PF₆, that was then recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ as a yellow solid (0.58 g, 0.94 mmol, 47%). Mp: 188°C (dec). IR (CH_2Cl_2) $\nu(\text{CO})$: 2122 (s), 2079 (s), 2069 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.35–7.09 (m, 15H), 5.69 (b, 2H), 5.41 (b, 2H), 2.89 (t, $J = 7.1$ Hz, 2H), 2.28 (t, $J = 7.1$ Hz, 2H). MS: m/z 475 (cation). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{F}_6\text{FeO}_3\text{P}$: C, 56.15; H, 3.74. Found: C, 55.29; H, 3.81.

Reactions of 2 with Methylating Reagents. (a) With [Me₃O⁺][BF₄⁻]. To a slurry of $[\text{Me}_3\text{O}^+][\text{BF}_4^-]$ (0.89 g, 6.0 mmol) in CH_2Cl_2 (50 mL) was added a solution of **2** (2.0 mmol) in CH_2Cl_2 (100 mL), prepared *in situ*. After the mixture was stirred overnight, the reaction mixture was concentrated to about 10 mL and diluted with Et_2O (100 mL) to obtain a precipitate, which was washed with CHCl_3 . After recrystallization from $\text{MeOH}/\text{Et}_2\text{O}$ as a yellow solid, the compound was identified to be **7**-BF₄ (0.07 g, 0.22 mmol, 11%) based on the following spectroscopic data. IR (CH_2Cl_2) $\nu(\text{CO})$: 2122 (s), 2077 (s), 2067 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 5.82 (s, 2H), 5.67 (s, 2H), 2.52 (q, $J = 7.4$ Hz, 2H), 1.28 (t, $J = 7.4$ Hz, 3H).

(b) With MeI. To a solution of **2** (2.0 mmol) in CH_2Cl_2 (100 mL), prepared *in situ*, was added MeI (0.84 g, 6.0 mmol). The mixture was monitored with IR, revealing only a gradual growth of $\nu(\text{CO})$ bands at 2024, 1966, 1645 cm^{-1} and a concurrent decrease of bands at 2041 and 1970 cm^{-1} , indicative of self-conversion of **2** to **3** only.

(c) With MeSO₃CF₃. To a solution of **2** (2.0 mmol) in CH_2Cl_2 (100 mL), prepared *in situ*, was added MeSO_3CF_3 (0.98 g, 6.0 mmol). The IR $\nu(\text{CO})$ bands immediately changed to 2024 (s), 1966 (s), 1645 (m) cm^{-1} , indicative the formation of **3**.

(d) With [(MeO)₂CH⁺][PF₆⁻]. A solution of **2** (0.46 g, 2.0 mmol) in CH_2Cl_2 (10 mL), prepared *in situ*, was added to a solution of $[(\text{MeO})_2\text{CH}^+][\text{PF}_6^-]$ in CH_2Cl_2 (40 mL), prepared *in situ* by mixing in CH_2Cl_2 $[\text{Ph}_3\text{C}^+][\text{PF}_6^-]$ (0.78 g, 2.0 mmol) and $(\text{MeO})_3\text{CH}$ (0.27 mL, 2.5 mmol). After the mixture was stirred overnight, the reaction mixture was concentrated to about 50 mL and diluted with Et_2O (150 mL) to obtain a precipitate, which was washed with sufficient CHCl_3 . After recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, the yellow solid was found to be **5**-PF₆ (0.38 g, 0.62 mmol, 31%) by the following spectroscopic data. IR (CH_2Cl_2) $\nu(\text{CO})$: 2122 (s), 2079 (s), 2069 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.35–7.09 (m, 15H), 5.68 (s, 2H), 5.41 (s, 2H), 2.89 (t, $J = 7.6$ Hz, 2H), 2.28 (t, $J = 7.8$ Hz, 2H).

[Fe(CO)₃(η^5 -C₅H₄CH₂CH₃)⁺][BF₄⁻] (7**-BF₄).** To a solution of **2** (2.0 mmol) in CH_2Cl_2 (100 mL), prepared *in situ*, was slowly added $\text{HBF}_4\cdot\text{OEt}_2$ (0.53 g, 6.0 mmol). After the mixture was stirred overnight, the reaction mixture was concentrated to about 50 mL and diluted with Et_2O (300 mL) to precipitate **7**-BF₄, which was recrystallized from $\text{MeOH}/\text{Et}_2\text{O}$ as a yellow solid (0.17 g, 0.52 mmol, 26%). Mp: 203°C (dec). IR (CH_2Cl_2) $\nu(\text{CO})$: 2122 (s), 2077 (s), 2067 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 5.82 (s, 2H), 5.67 (s, 2H), 2.52 (q, $J = 7.4$ Hz, 2H), 1.28 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 202.2 (CO), 119.0 (Cp, C_{ipso}), 89.2 (Cp), 88.0 (Cp), 21.1 (CH₂), 14.1 (Me). MS: m/z 233 (cation). Anal. Calcd for $\text{C}_{10}\text{H}_9\text{BF}_4\text{FeO}_3$: C, 37.55; H, 2.84. Found: C, 37.24; H, 2.66.

[Fe(CO)₂(PPh₃)(η^5 -C₅H₄CH₂CH₂CPh₃)⁺][PF₆⁻] (8**-PF₆).** A solution of **5**-PF₆ (0.28 g, 0.45 mmol) and PPh₃ (0.12 g, 0.45 mmol) in CH_3CN (30 mL) was treated with a drop of NEt_3 . An IR measurement indicated that the transformation was complete after a few seconds. The solvent was then removed, and the residue was re-dissolved in a minimum amount of CH_2Cl_2 and diluted with Et_2O to precipitate **8**-PF₆ (0.37 g, 0.43 mmol, 96%) as a yellow solid. Mp: 203 – 206°C (dec). IR (CH_3CN) $\nu(\text{CO})$: 2051 (s), 2008 (s) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 61.9. ^1H NMR (CDCl_3): δ 7.53–7.43 (m), 7.35–7.01 (m), 5.01 (b, 2H), 4.97 (b, 2H), 2.78 (t, $J = 7.9$ Hz, 2H), 2.09 (t, $J = 7.9$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 209.6 (d, $J_{\text{P-C}} = 23.6$ Hz, CO), 146.0 (C_{ipso}, CPh), 132.8 (d, $J_{\text{P-C}} = 9.7$ Hz, *o*-C, PPh), 132.3 (*p*-C, PPh), 130.8 (d, $J_{\text{P-C}} = 51.6$ Hz, C_{ipso}, PPh), 129.9 (d, $J_{\text{P-C}} = 10.4$ Hz, *m*-C, PPh), 129.0 (*o*-C, CPh), 128.2 (*m*-C, CPh), 126.3 (*p*-C, CPh), 111.4 (C_{ipso}, Cp), 89.8 (Cp), 86.9 (Cp), 56.7 (CPh), 40.9 (Cp-CH₂CH₂), 24.0 (Cp-CH₂CH₂). MS: m/z 710 (cation). Anal. Calcd for $\text{C}_{46}\text{H}_{38}\text{F}_6\text{FeO}_2\text{P}_2$: C, 64.65; H, 4.48. Found: C, 64.94; H, 4.86.

[Fe(CO)₂(PPh₃)(η^5 -C₅H₄CH₂CH₃)⁺][BF₄⁻] (9**-BF₄).** A solution of **7**-BF₄ (0.26 g, 0.81 mmol) and PPh₃ (0.21 g, 0.81 mmol) in CH_3CN (50 mL) was treated with a drop of NEt_3 . An IR measurement indicated that the conversion was complete after a few minutes; the solvent was then removed, and the residue was re-dissolved in a minimum amount of MeOH and diluted with Et_2O to precipitate **9**-BF₄ (0.44 g, 0.79 mmol, 98%) as a yellow solid. Mp: 186 – 188°C . IR (CH_3CN) $\nu(\text{CO})$: 2052 (s), 2008 (s) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 62.1. ^1H NMR (CDCl_3): δ 7.57–7.55 (m, 9H), 7.39–7.31 (m, 6H), 5.26 (b, 2H), 5.03 (b, 2H), 2.42 (q, $J = 7.4$ Hz, 2H), 1.18 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 209.8 (d, $J_{\text{P-C}} = 23.6$ Hz, CO), 132.7 (d, $J_{\text{P-C}} = 10.3$ Hz, *o*-C, Ph), 132.1 (*p*-C, Ph), 131.0 (d, $J_{\text{P-C}} = 51.5$ Hz, C_{ipso}, Ph), 129.7 (d, $J_{\text{P-C}} = 10.8$ Hz, *m*-C, Ph), 113.4 (C_{ipso}, Cp), 89.2 (Cp), 86.0 (Cp), 20.4 (CH₂), 13.9 (Me). MS: m/z 467 (cation). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{BF}_4\text{FeO}_2\text{P}$: C, 58.53; H, 4.37. Found: C, 58.30; H, 4.26. The crystals suitable for X-ray diffraction analysis were grown from $\text{CH}_2\text{Cl}_2/\text{n}$ -hexane by a slow evaporation method.

Reaction of 3 and Ph₃C⁺PF₆⁻. To a solution of **3** (0.46 g, 2.0 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of $\text{Ph}_3\text{C}^+\text{PF}_6^-$ (1.55 g, 4.0 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred for 2 h and was constantly monitored by IR, revealing the following $\nu(\text{CO})$ bands: 2123 (m), 2068 (s), 2024 (s), 1968 (s), 1649 (m) cm^{-1} . The $\nu(\text{CO})$ bands at 2068 (s) and 2024 (s) were assigned to $[(\text{CO})_2\text{Fe}=\text{C}(\text{OCPh}_3)\text{CH}_2\text{CH}_2$

(21) (a) Alder, K.; Ache, H.-J.; Flock, F. H. *Chem. Ber.* **1960**, *93*, 1888. (b) Wilcox, C. F.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866. (22) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429.

Table 1. Crystallographic Data and Refinement Details for $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_3)^+][\text{BF}_4^-]$ (9**·**BF**₄) and $[(\text{CO})_2\text{Fe}=\text{C}(\text{NHPH})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)^+][\text{PF}_6^-]$ (**12**·**PF**₆)**

	9 · BF ₄	12 · PF ₆
formula	C ₂₇ H ₂₄ BF ₄ FeO ₂ P	C ₁₆ H ₁₄ F ₆ FeNO ₂ P
fw	554.10	453.10
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.0297(24)	10.819(10)
<i>b</i> (Å)	17.5912(15)	15.769(5)
<i>c</i> (Å)	13.774(7)	10.965(4)
β (deg)	70.62(3)	70.83(5)
<i>V</i> (Å ³)	2521.1(14)	1767.0(18)
<i>Z</i>	4	4
<i>F</i> (000)	1135.85	911.86
<i>D</i> _{calc} (g cm ⁻³)	1.460	1.703
temp (K)	298	298
μ (cm ⁻¹)	7.1	10.1
λ (Mo K α) (Å)	0.710 69	0.710 69
cryst dimens (mm)	0.44 × 0.22 × 0.09	0.25 × 0.38 × 0.75
2 θ (max)	50.0	50.0
diffractometer	Nonius CAD-4	Nonius CAD-4
scan mode	$\theta/2\theta$	$\theta/2\theta$
data range	-12 < <i>h</i> < 13, 0 < <i>k</i> < 20, 0 < <i>l</i> < 16	-12 < <i>h</i> < 12, 0 < <i>k</i> < 18, 0 < <i>l</i> < 13
no. of unique reflns	4432	3097
no. of obs	2673, <i>I</i> ₀ > 2.5 σ (<i>I</i> ₀)	2709, <i>I</i> ₀ > 2.5 σ (<i>I</i> ₀)
abs corr	yes	yes
transmission factors	0.914–1.000	0.914–1.000
total no. of atoms	60	41
no. of params	326	245
weights	counting-statistics	counting-statistics
weight modifier	0.01	0.01
<i>R</i>	0.040	0.056
<i>R</i> _w	0.044	0.080
goodness of fit	1.69	5.20
max Δ/σ	0.019	0.005
γ (2nd ext coeff × 10 ⁴)	0.3(2)	10(1)
<i>D</i> -map		
highest peak (e Å ⁻³)	0.520	1.090
deepest hole (e Å ⁻³)	-0.310	-0.710

($\eta^5\text{-C}_5\text{H}_4$)⁺][PF₆⁻], **10**·PF₆. The attempted work-up failed to yield the desired carbene, only **3** was recovered.

$[(\text{CO})_2\text{Fe}=\text{C}(\text{OMe})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)^+][\text{PF}_6^-]$ (**11**·**PF**₆). A solution of **3** (0.46 g, 2.0 mmol) in CH₂Cl₂ (10 mL) was added to a solution of [(MeO)₂CH⁺][PF₆⁻] in CH₂Cl₂ (40 mL), prepared *in situ* according to the procedure described for the attempted preparation of **6**·PF₆. The reaction mixture was stirred for 2 h and then diluted with Et₂O (300 mL) to precipitate **11**·PF₆ as a yellow solid (0.71 g, 1.81 mmol, 91%). Mp: 119–121 °C. IR (CH₂Cl₂) ν (CO): 2072 (s), 2028 (s) cm⁻¹. ¹H NMR (CD₂-Cl₂): δ 5.67 (2H), 5.26 (2H), 4.55 (3H), 4.06 (2H), 2.71 (2H). MS: *m/z* 247 (cation). Anal. Calcd for C₁₁H₁₁F₆FeO₃P: C, 33.70; H, 2.83. Found: C, 33.13; H, 2.72.

$[(\text{CO})_2\text{Fe}=\text{C}(\text{NHPH})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)^+][\text{PF}_6^-]$ (**12**·**PF**₆). NH₂Ph (0.19 g, 2.0 mmol) was added to a solution of **11**·PF₆

(0.78 g, 2.0 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 1 h and then diluted with Et₂O (300 mL) to yield [(CO)₂Fe=C(NHPH)CH₂CH₂($\eta^5\text{-C}_5\text{H}_4$)⁺][PF₆⁻] (**12**·**PF**₆) as a yellow solid (0.85 g, 1.88 mmol, 94%). Mp: 209–212 °C. IR (CH₂Cl₂) ν (CO): 2054 (s), 2011 (s) cm⁻¹. ¹H NMR (acetone-*d*₆): δ 7.60–7.34 (m, 10H), 5.85 (t, *J* = 1.8 Hz, 2H), 5.79 (t, *J* = 1.9 Hz, 2H), 5.44 (t, *J* = 1.9 Hz, 2H), 5.35 (t, *J* = 1.9 Hz, 2H), 4.10 (t, *J* = 7.5 Hz, 2H), 3.87 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H). ¹³C{¹H} NMR (acetone-*d*₆): δ 264.9, 264.1 (Fe=C), 211.4, 211.3 (CO), 141.5, 138.5, 130.3, 130.2, 129.8, 129.7, 126.9, 125.4, 86.8 (Cp), 83.9 (Cp), 83.5 (Cp), 68.1, 63.0, 23.6, 22.5. MS: *m/z* 308 (cation). Anal. Calcd for C₁₆H₁₄F₆FeNO₂P: C, 42.41; H, 3.11, N 3.09. Found: C, 42.52; H, 3.13; N, 2.99. The crystals of **12**·PF₆ suitable for X-ray diffraction analysis were grown from MeOH/THF by a slow evaporation method.

X-ray Structure Analysis. A summary of crystal data and refinement details for **9**·**BF**₄ and **12**·**PF**₆ is given in Table 1. Diffraction intensities were measured with background counts made for one-half the total scan time on each side of the peak. Three standard reflections, measured after every hour, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz–polarization and absorption (empirical ψ corrections). The structures were solved by direct methods, MULTAN.²³ Calculations and full-matrix least-squares refinements were performed utilizing the NRCVAX program package.²⁴ All non-H atoms were refined with anisotropic thermal parameters with all hydrogen atoms fixed (C–H = 1.00 Å, N–H = 0.85 Å) at the anisotropic convergence stage. Scattering factor curves of Fe, P, F, O, N, C, and H were taken from ref 25.²⁵

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Supporting Information Available: Tables of crystallographic data and refinement details, positional and anisotropic thermal parameters, bond distances and angles, and torsion angles for **9**·**BF**₄ and **12**·**PF**₆ (15 pages). Ordering information is given on any current masthead page.

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(23) Main, P. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Database*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon: Oxford, U.K., 1985; pp 206–215.

(24) Gabe, E. J.; Le Page, Y.; Lee, F. L. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Database*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon: Oxford, U.K., 1985; pp 167–174.

(25) *International Tables for X-ray Crystallography*, Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, U.K. (current distributor D. Reidel, Dordrecht, The Netherlands), 1974; Vol. 4, Tables 2.2A and 2.3.1D.