1,3-Dipolar Cycloaddition to Tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron: Rapid Construction of a Spiro[4.5]decane System

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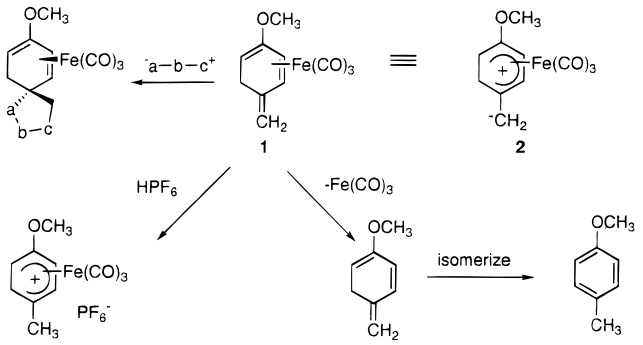
Summary: Tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron ***(1)*** *undergoes 1,3-dipolar cycloaddition reaction regio-, stereo-, and chemoselectively at its exocyclic double bond, yielding a spiro[4.5]-decane system. Reactive 1,3-dipoles with low-lying LUMO's such as nitrile oxides, ozone, diazoacetate, and oxoallyl cation participate well in cycloaddition to give isoxazole, ketone, pyrazoline, and cyclopentanone adducts, respectively. The complex* ***1*** *can be viewed as the synthetic equivalent of synthon* ***2*** *and has been illustrated for the first time as a versatile synthetic intermediate.*

Cycloaddition reactions have been a powerful methodology for ring construction in organic synthesis. Well-known examples include (i) cycloaddition of two 2π reactants that yield four-membered rings,[1] (ii) 1,3-dipolar cycloaddition reactions that yield five-membered rings,[1,2] and (iii) Diels−Alder reactions that yield six-membered rings.[1] Extensive efforts have recently been focused on the organometallic version of cycloaddition reactions, and these again can be subdivided into two major types: (i) the π systems of metal-bonded alkenes and polyenes participating in cycloaddition reactions[1,3,4] and (ii) cycloaddition to the free alkene or polyene within the metal π-complexes.[5,6]

As part of our continuing effort to explore new synthetic applications of tricarbonyliron complexes in organic synthesis, we herein report the first elegant examples of 1,3-dipolar cycloadditions with tricarbonyl-[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]-iron (**1**), which provide convenient access to carbo- and hetero-spiro[4.5]decane systems. The complex **1** has appeared in the literature[7] over the years as a reaction side product due to proton abstraction from tricarbonyl-(4-methoxy-1-methylcyclohexadienyl)iron hexafluorophosphate by base or basic nucleophilic species. We now report complex **1** as an important intermediate for organic synthesis. The inherent advantages of using complex **1** to effect cycloaddition reactions for organic synthesis are manifold: first, the reaction should proceed with a high level of chemoselectivity at the exocyclic double bond; second, lateral coordination of the bulky $Fe(CO)_3$ provides a high degree of stereoselectivity for the incoming 1,3-dipole; third, complex **1** is a synthetic equivalent of synthon **2** which controls the regioselectivity during the reaction; fourth, the $Fe(CO)_3$ acts as a protecting group for the free exocyclic double bond in complex **1**, which upon its removal isomerizes immediately to 4-methylanisole (Scheme 1).

Scheme 1



Results and Discussion

Tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron (**1**) was conveniently prepared in high yield by treating tricarbonyl(4-methoxy-1-methylcyclohexadienyl)iron hexafluorophosphate with triethylamine in THF.[8] It is worthwhile to note that although other bases such as potassium *tert*-butoxide at 0 °C and butyllithium at −78 °C in THF may be used, the yield of **1** was found to decrease. Furthermore, complex **1** was found to be stable when dissolved in ether to enable further manipulation and became very unstable when all the solvent was removed. The ease of handling complex **1** in the presence of a minute amount of solvent makes it a valuable synthetic intermediate.

The first 1,3-dipolar cycloaddition reactions attempted were between diazomethane and benzyl azide with complex **1**. These reactions did not give any cycloadducts. The exocyclic double bond of complex **1** must be considered electron rich, as it is equivalent to synthon **2**, which undergoes protonation readily to regenerate the salt. Thus, the exocyclic double bond should behave as a nucleophilic species in 1,3-dipolar cycloaddition reactions. According to Sustmann classifications,[9] electron-rich alkenes should favor interaction between its HOMO and the 1,3-dipole LUMO's during cycloaddition reaction. Within this context, only those 1,3-dipoles having a low-lying LUMO, described as type III, will

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(1) Trost, B. M., Fleming, I., Eds. In *Comprehensive Organic Synthesis;* Pergamon Press, Oxford, U.K., 1991; Vol. 5.
(2) Padwa, A. In *1,3-Dipolar Cycloaddition Reactions:* Wiley: New York, 1984; Vol. 1 and 2.
(3) Davis, R.; Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 405.
(4) Rigby, J. H. *Acc. Chem. Res.* **1993**, *26*, 579.
(5) Green, M.; Heathcock, S.; Wood, P. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1564.
(6) Goldschmidt, Z.; Antebi, S.; Cohen, D.; Goldberg, I. *J. Organomet. Chem.* **1984**, *273*, 347.
(7) Pearson, A. J. In *Iron Compounds In Organic Synthesis:* Academic Press: London, 1994; Chapter 5, p 113.
(8) Pearson, A. J.; Perrior, T. R. *J. Organomet. Chem.* **1985**, *285*, 253.
(9) Sustmann, R. *Tetrahedron Lett.* **1971**, 2721.

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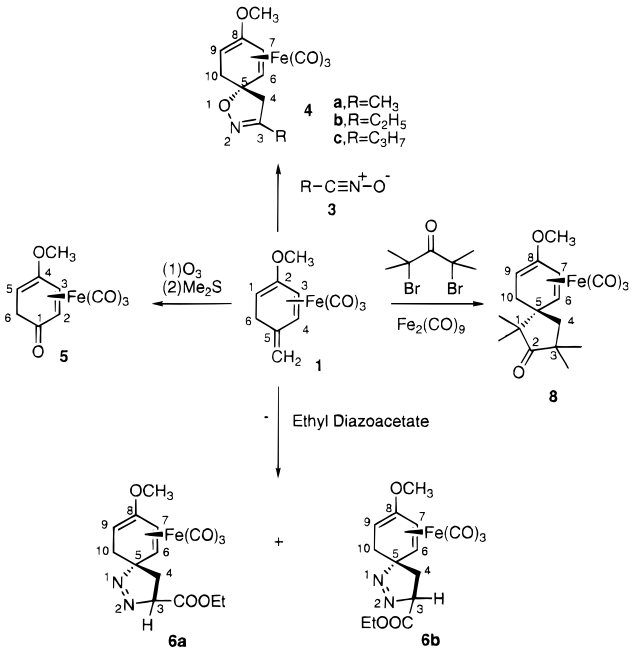
Scheme 2. 1,3-Dipolar Cycloaddition Reactions of 1



react with complex **1**, thus explaining the failure of the above intermolecular reactions.

FMO theory predicts that nitrile oxides should readily react with electron-rich alkenes.[10] There are several procedures for the preparation of nitrile oxides. Our initial conditions employed oxidation of alkoxyimine with sodium hypochlorite[11] to generate the nitrile oxide in situ for reaction with **1**, and this led to decomposition. We next examined the generation of nitrile oxide by heating nitroalkanes with phenyl isocyanate in benzene,[12] followed by addition of **1** in a one-pot reaction. Treatment of **1** with the nitrile oxides **3a**−**c** generated from nitroethane, nitropropane, and nitrobutane with this method resulted in the chemo-, regio-, and stereospecific addition to the exocyclic π-system, affording exclusively hetero-spiro[4.5]decane cycloadducts **4a**−**c**, respectively, in greater than 70% yield (Scheme 2). The regioselectivity can be determined from the ^{13}C NMR spectra, which showed the quaternary spirocyclic carbon at around 88 ppm for **4a**−**c**. The stereoselective approach of the 1,3-dipole from the opposite face of $Fe(CO)_3$ was based on the ^{1}H NMR for complex **4b**, which showed the C-4 methylene protons at a lower field of δ 2.60 and 2.90. This is consistent with the deshielding effect caused by the $Fe(CO)_3$ group. Furthermore, the two hydrogens of the methylene group are nonequivalent. The proton projecting closer into the space of $Fe(CO)_3$ is more deshielded. Thus, the methylene protons of the ethyl substituent at C-3 in complex **4b**, which have the same chemical environment as the C-4 methylene protons but are not affected by the $Fe(CO)_3$ group, have a higher chemical shift at δ 2.30. This tentatively allowed us to assume exo attack of the nitrile oxide with complex **1,** similar to the result reported for the acyclic triene complex.[13] Interestingly, complex **1** failed to react with benzonitrile oxide, probably due to the increased stabilization of the carbocation and the raising of the LUMO by the benzyl substituent. The cycloaddition of **1** is thus very prone to the electronic effect of the 1,3-dipoles.

Ozone is another classical dipolar molecule with a very low-lying LUMO[14] which reacts with electron-rich alkene to generate 1,2,3-trioxolone; this compound rearranges to ozonide and can be cleaved by oxidation or reduction. Reaction of **1** with ozone followed by reductive cleavage was found to give tricarbonyl(4-methoxycyclohexa-2,4-dienone)iron (**5**) in reasonable yield (40%) (Scheme 2). This reaction was complicated by the presence of free oxygen in the generation of ozone, which upon warming of the reaction mixture to room temperature causes partial decomposition. This is a relatively rare example of $Fe(CO)_3$ complexes withstanding manipulation under such strong oxidative conditions at low temperatures.[15] Complex **5** has been previously obtained from the hydrolysis of tricarbonyl[(1−5-η)-2,5-dimethoxycyclohexadienyl]iron fluoroborate.[16] Our new method provides an easier access to **5**, which is a tautomer of hydroquinone upon decomplexation and should serve as another important synthetic intermediate.[16]

With these fundamental precedents in hand, we have reexamined the 1,3-dipolar reaction of complex **1** with the more reactive diazo ketones. Diazoacetates bearing acceptor substituents are known to add to electron-rich alkenes.[17] While diazomethane did not react, ethyl diazoacetate[18] was found to react with complex **1** to give a Δ^1-pyrazoline cycloadduct. Ethyl diazoacetate was assumed to attack anti to the bulky $Fe(CO)_3$ group, and a mixture of two diastereoisomeric spiropyrazoline adducts, **6a**,**b** (Scheme 2), was obtained in a 1.2:1 ratio. The diastereomeric ratio was readily determined from the ^{1}H NMR integral ratio for the Δ^1-pyrazoline methine protons at δ 4.97 and 5.35 for **6a**,**b**, respectively. The ambivalent nature of diazo ketones may also give rise to two regioisomeric cycloadducts. The preferential regiospecific attack of the exocyclic double bond in **1** at the electrophilic carbon center of diazo ketone leading to the formation of **6a**,**b** was deduced from the ^{13}C NMR, which showed spiro C-5 at δ 140. The ^{1}H NMR peaks for the C-4 protons in the diastereoisomeric mixture were also found at a rather lower field than expected, δ 3.05 and 2.86, probably due to deshielding by the $Fe(CO)_3$ group, indicating the exo approach of diazo ketone. The C-3 methine proton that has the lower chemical shift must be influenced by the 2,5-dienyl−$Fe(CO)_3$ group and was tentatively assigned as complex **6b**. The reaction is thus regio- and stereoselective with respect to **1** but non-facial selective with respect to the *si* and *re* faces of the diazo ketone, giving rise to two diastereoisomeric products. When a mixture of **6a**,**b** was heated at reflux in toluene, only **6b** was recovered in 40% yield. Thus, **6b** was assigned as the thermodynamically more stable product. The Δ^1-pyrazoline ad-

(10) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 7287.
(11) Grudmann, C.; Grunanger, P. In *The Nitrile Oxides*: Springer-Verlag: Berlin, 1971.
(12) Mukaiyama, T.; Hoshino, T. *J. Am. Chem. Soc.* **1960**, *82*, 5339.
(13) Gall, T. L.; Lellouche, J.-P.; Toupet, L.; Beaucourt, J.-P. *Tetrahedron Lett.* **1989**, 6517.
(14) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 7301.
(15) Neumann, M. F.; Kastler, A. *Synlett* **1995**, 61.
(16) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc. Perkin Trans. 1* **1973**, 1882.
(17) Huisgen, R.; Reissig, H. U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 330.
(18) Womack, B.; Nelson, N. B. In *Organic Syntheses;* Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. III, p 392.

duct **6a**,**b** did not undergo the facile hydrogen shift to form the Δ^2-pyrazoline, or the elimination of nitrogen to give cyclopropanes which was found to occur frequently in these reactions. The sensitivity of these cycloaddition reactions to the electronic effect of the substituent in 1,3-dipole compounds is again fully consistent with the requirement of a low-lying LUMO. Formation of the initial cycloadduct can be explained by a pronounced HOMO−LUMO interaction between the reactants. We next examined the cycloaddition of **1** with diazoacetophenone, which similarly gave two diastereomeric mixtures of products **7a**,**b**, as deduced from their crude ^{1}H NMR. These products were found to be unstable, which on preparative chromatography gave decomposition products.

An important issue in organic synthesis is the ability to form carbon−carbon bonds, and the usefulness of **1** to serve as a template in 1,3-dipolar cycloaddition to give spiro[4.5]spirodecane must be demonstrated. Noyori[19] has shown that α,α′-dibromo ketone undergoes debromination with $Fe_2(CO)_9$ to give a reactive oxoallyl cation which undergoes a wide array of cycloaddition reactions. We now disclose that complex **1** undergoes cycloaddition with the oxoallyl cation generated from 2,4-dibromo-2,4-dimethylpentan-3-one and $Fe_2(CO)_9$ to give **8** in good yield, with complete chemo- and stereoselectivity at the exocyclic double bond (Scheme 2). The bulkiness of the oxoallyl cation-Fe(CO)$_n$ complex must surely ensure the anti attack. Furthermore, the nonequivalency of the C-4 methylene protons at a rather low field of δ 1.98 and 1.78 also indirectly indicates the anti attack.

Conclusion

The exocylic double bond in tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron (**1**) has been shown to undergo a wide array of 1,3-dipolar cycloaddition reactions. Our results represent a significant advance in the further exploitation of organoiron complexes as useful intermediates for organic synthesis. This synthetic sequence offers an attractive method for the rapid construction of the spiro[4.5]decane system. The dramatic requirement of a low-lying LUMO in the 1,3-dipolar compounds to achieve cycloaddition reactions with **1** has also been demonstrated. In all the cases examined, the reactions proceed with clean chemo-, regio-, and stereoselectivity.

Experimental Section

General Considerations. All the reactions were performed under an atmosphere of dry nitrogen. Solvents were dried over Na/benzophenone (benzene, THF, diethyl ether) and CaH_2 (CH_2Cl_2) and were freshly distilled prior to use. Infrared spectra were recorded on a BioRad FTS-40 instrument, and all NMR spectra were recorded on a Varian VXR-300 spectrometer. High-resolution mass spectra were obtained using a JEOL JMS-HX100 mass spectrometer. Preparative TLC was performed on silica gel. Tricarbonyl[(1−5-η)-4-methoxy-1-methylcyclohexa-2,4-dienyl]iron hexafluorophosphate,[5] ethyl diazoacetate,[18] and diazoacetophenone were prepared according to literature procedures.

Tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron (1). Triethylamine (2 mL) was added to a vigorously stirred suspension of tricarbonyl[(1−5-η)-4-methoxy-1-methylcyclohexa-2,4-dienyl]iron hexafluorophosphate (407 mg, 1 mM) in THF (20 mL) at 0 °C for 2 h. The solvent was mostly removed under vacuum (but not totally), followed by addition of ice-cold water and extraction with ether. This gave **1** as a yellowish orange oil. Yield: 258 mg, 98%. IR (υ_{max}, $CHCl_3$): 2047, 1970, 1483, 1227 cm^{-1}. ^{1}H NMR: δ 5.13 (dd, 1H, J = 6.5 and 2.5 Hz), 4.77 (s, 1H), 4.33 (s, 1H), 3.63 (s, 3H), 3.46 (m, 1H), 3.19 (d, 1H, J = 6.5), 2.38 (m, 2H). ^{13}C NMR: δ 210.7, 157.6, 139.2, 102.9, 66.2, 55.9, 54.4, 51.6, 30.3. Mass: m/z 262 (M^+), 234, 206, 178. Exact mass: found m/z 263.0004 (M^+), calcd for $C_{11}H_{11}O_4Fe$ 236.0003.

General Procedure for the 1,3-Dipolar Cycloaddition of Nitrile Oxide to 1. Phenyl isocyanate (108 mL, 2 mM) and **1** (288 mg, 1.1 mM) dissolved in benzene (10 mL) was added dropwise to a solution of the nitro compound (1.1 mM) containing 5−8 drops of triethylamine in benzene (10 mL). The reaction started, and *sym*-diphenylurea precipitated. After 1 h, the reaction mixture was refluxed for 1 h and left to react overnight at room temperature. The reaction mixture was filtered, and the benzene solution was washed with water, followed by brine, and dried over $MgSO_4$ (anhydrous). The solvent was removed under vacuum and the crude product chromatographed on a silica gel plate (20 × 20 cm) using benzene/hexane (5:1).

By this procedure were prepared the following compounds.

Tricarbonyl{(6−9-η)-3-methyl-8-methoxy-1,2-oxaazaspiro[4.5]deca-2,6,8-triene}iron (4a). The reaction was performed using nitroethane. Yield: 65% as a yellowish oil. IR (υ_{max}): 2048, 1969, 1493, 1238 cm^{-1}. ^{1}H NMR: δ 5.17 (dd, 1H, J = 6.5, 2.1 Hz), 3.67 (s, 3H), 3.27 (m, 1H), 2.96 and 2.72 (d each, 2H, J = 17 Hz), 2.48 (d, 1H, J = 6.5 Hz), 2.32 and 2.12 (d each, 2H, 15 Hz), 1.93 (s, 3H). ^{13}C NMR: δ 210.3, 154.78, 140.9, 89.0, 65.2, 54.5, 53.9, 52, 50.5, 42.4, 13.4. Mass: m/z 319 (M^+), 291, 263, 235, 194, 179. Exact mass: found m/z 319.0144 (M^+), calcd for $C_{13}H_{13}O_5NFe$ 319.0139.

Tricarbonyl{(6−9-η)-3-ethyl-8-methoxy-1,2-oxaazaspiro[4.5]deca-2,6,8-triene}iron (4b). The reaction was performed using nitropropane. Yield: 70% as a yellowish oil. IR (υ_{max}): 2051, 1971, 1494, 1229 cm^{-1}. ^{1}H NMR: δ 5.18 (dd, 1H, J = 6.5, 2.5 Hz), 3.68 (s, 3H), 3.27 (m, 1H), 2.95 and 2.72 (d each, 2H, J = 17 Hz), 2.49 (d, 1H, J = 6.5 Hz), 2.31 and 2.12 (d each, 2H, J = 15 Hz), 2.30 (q, 2H, J = 7.8 Hz), 1.13 (t, 3H, J = 7.8 Hz). ^{13}C NMR: δ 210.3, 159.4, 140.9, 88.7, 65.2, 54.5, 53.9, 50.5, 50.2, 42.3, 21.5, 10.8. Mass: m/z 333 (M^+), 305, 277, 249, 194, 179. Exact mass: found m/z 333.0292 (M^+), calcd for $C_{14}H_{15}O_5NFe$ 333.0295.

Tricarbonyl{(6−9-η)-3-propyl-8-methoxy-1,2-oxaazaspiro[4.5]deca-2,6,8-triene}iron (4c). The reaction was performed with nitrobutane. Yield: 75% as a yellowish oil. IR (υ_{max}): 2048, 1974, 1492, 1236 cm^{-1}. ^{1}H NMR: δ 5.18 (dd, 1H, J = 6.5, 2.5 Hz), 3.67 (s, 3H), 3.27 (m, 1H), 2.93 and 2.70 (d each, 2H, J = 17 Hz), 2.48 (d, 1H, J = 6.5 Hz), 2.28 and 2.12 (d each, 2H, J = 15 Hz), 2.27 (t, 2H), 1.56 (m, 2H), 0.94 (t, 3H). ^{13}C NMR: δ 210.2, 158.3, 140.9, 88.6, 65.2, 54.4, 53.9, 50.5, 50.3, 42.3, 29.8, 19.6, 13.6. Mass: m/z 347 (M^+), 319, 291, 263, 194, 179. Exact mass: found m/z 347.0450 (M^+), calcd for $C_{15}H_{17}O_5NFe$ 347.0451.

Tricarbonyl[(2−5-η)-4-methoxycyclohexa-2,4-dienone]iron (5). A solution of **1** (262 mg, 1 mM) in dichloromethane (20 mL) was cooled to −78 °C and ozone bubbled through the solution for 1 h. The resulting bluish solution was reduced with dimethyl sulfide and worked up using a standard procedure. The crude product was chromatographed on a silica gel plate (20 × 20 cm) using benzene/hexane (5:1) as solvent. Yield: 40% as yellowish crystals, mp 63−64 °C. IR (υ_{max}): 2063, 1984, 1675, 1234 cm^{-1}. ^{1}H NMR: δ 5.56 (dd, 1H, J = 6.5 and 2.5 Hz), 3.78 (s, 3H), 3.51 (m, 1H), 2.87 (d, 1H, J = 6.5 Hz), 2.46 and 2.30 (d each, 2H, J = 16 Hz). Mass: m/z 264 (M^+), 236, 208, 180, 124. Exact mass: found m/z 263.9717 (M^+), calcd for $C_{10}H_8O_5Fe$ 263.9718.

Tricarbonyl{(6−9-η)-3-(carboethoxy)-8-methoxy-1,2-diazaspiro[4.5]deca-1,6,8-triene}iron (6a,b). To a solution

(19) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61.

of **1** (550 mg, 2.1 mM) in dichloromethane (25 mL) was added ethyl diazoacetate[18] (285 mg, 2.5 mM), and refluxed for 15 h. The reaction mixture was filtered through Celite and the solution concentrated in vacuo. Further purification by preparative thin-layer chromatography on silica gel (20 × 20 cm) using benzene/hexane (4:1) gave a diastereoisomeric mixture of products **6a,b**. Yield: 81% as a yellowish oil.

6b: IR (υ_{max}): 2050, 1965, 1740, 1492 cm^{-1}. ^1H NMR: δ 5.35 (t, 1H, $J = 7.0$ Hz), 5.17 (dd, 1H, $J = 6.5$, 1.5 Hz), 4.13 (q, 2H), 3.65 (s, 3H), 3.50 (m, 1H), 3.20 (d, 1H, $J = 6.5$ Hz), 3.05 (m, 2H), 2.40 (m, 2H), 1.23 (t, 3H). ^{13}C NMR: δ 210.5, 171.6, 140.3, 139.2, 110.0, 65.8, 55.9, 54.4, 51.1, 33.4, 31,1, 14.1. Mass: m/z 376 (M^+), 348, 320, 292, 264, 192. Exact mass: found m/z 349.0477 ($M^+ - CO$), calcd for $C_{14}H_{17}O_5N_2Fe$ ($M^+ - CO$) 349.0482.

6a: ^1H NMR: δ 5.17 (dd, 1H, $J = 6.5$, 1.5 Hz), 4.92 (t, 1H, $J = 7.2$ Hz), 4.13 (q, 2H), 3.65 (s, 3H), 3.50 (m, 1H), 3.31 (d, 1H, $J = 6.5$ Hz), 2.86 and 2.78 (d each, 2H, $J = 7.2$ Hz), 2.40 and 2.27 (d each, $J = 14.5$ Hz), 1.26 (t, 3H).

When a mixture of **6a**,**b** was refluxed in toluene for 24 h, only **6b** was recovered from the reaction mixture in 40% yield.

Tricarbonyl{(6−9-η)-2-oxo-1,1,3,3-tetramethyl-8-methoxyspiro[4.5]deca-6,8-diene (8). Diiron nonacarbonyl (2 mM) was placed in a round-bottom flask and the system flushed with dry nitrogen. To this was added a mixture of dry benzene (40 mL), **1** (524 mg, 2 mM), and 2,4-dibromo-2,4-dimethylpentan-3-one (272 mg, 1 mM); this mixture was refluxed under nitrogen for 8 h and then cooled to ambient temperature. The resulting precipitate was filtered through Celite and the filtrate concentrated under vacuo. The crude product (278 mg, 86%) was subjected to preparative TLC (20 × 20 cm) using benzene/hexane as solvent (5:1). Yield: 78% as a yellowish oil. IR (υ_{max}): 2050, 1965, 1740, 1231 cm^{-1}. ^1H NMR: δ 5.16 (dd, 1H, $J = 6.5$, 1.5 Hz), 3.64 (s, 3H), 3.29 (m, 1H), 2,40 (d, 1H), 1.98 (d, 1H, $J = 13.5$ Hz), 1.87 (d, 1H, $J = 14.5$ Hz), 1.79 (d, 1H, $J = 13.5$ Hz), 1.70 (d, 1H, $J = 14.5$ Hz), 1.13, 1.02, 1.00, 0.83 (s each, 12H). ^{13}C NMR: δ 225.8, 211.2, 140.3, 63.7, 55.7, 54.4, 53.2, 50.8, 48.8, 48.9, 46.1, 40.3, 28.6, 26.5, 23.0, 19.0. Mass: m/z 374, 346, 318, 290, 178, 121. Exact mass: found m/z 374.0799, calcd for $C_{18}H_{22}O_5Fe$ 374.0810 (M^+).

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