ELSEVIER

Journal of Organometallic Chemistry 487 (1995) 95–104

Journal of Organometallic Chemistry

Reactions of transition-metal η^1-allyl and propargyl complexes with ketenes and some new nonoxidative transition-metal–carbon bond cleaving reactions of the ketene cycloadducts which yield cyclopentenones

Heather L. Stokes, Li Ming Ni, John A. Belot, Mark E. Welker *,[1]

Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, USA

Received 4 May 1994

Abstract

Reactions of cyclopentadienyl iron 2-alkynyl and allyl complexes with ketenes or ketene precursors yield transition-metal substituted cyclopentenones in some cases and new transition-metal substituted allyl complexes in others. The transition metals can subsequently be cleaved from the cyclopentenone containing complexes under a variety of oxidative and nonoxidative reaction conditions.

Keywords: Iron; Allyl complexes; Alkynyl complexes; Ketenes; Cycloadditions; Cyclopentenones

1. Introduction

Cycloaddition reactions between transition-metal 2-alkynyl (**1**) and η^1-allyl complexes (**2**) and unsaturated electrophilic reagents (**3**) have been studied in detail over the last 20 years with the pioneering work in this area having been done by the Rosenblum and Wojcicki groups [1]. These 3 + 2 cycloaddition reactions have been shown to yield transition-metal substituted five-membered-ring heterocycles and carbacycles (**4** and **5**) (Scheme 1) which offer alternative approaches to these ring systems when the metal is subsequently cleaved from the ring [1–3].

Several years ago, we reported a variant of this 3 + 2 cycloaddition reaction which yields transition-metal substituted five-membered-ring thiosulfinate esters [1a]. More recently we have been exploring an example of this reaction first reported by Wojcicki in 1977 [2], involving the cycloaddition of cyclopentadienyl iron dicarbonyl 2-alkynyl complexes (**6**) with diphenyl (**7**) and *t*-butylcyanoketenes (Scheme 2) [3]. This cycloaddition reaction yielded transition-metal substituted cyclopentenones (**9**) and was proposed to proceed through allene complex (**8**) as an intermediate [2]. We became interested in these 3 + 2 cycloaddition reactions involving ketenes with the idea that the ease of preparation of a variety of 2-alkynyl complexes [1,4] and ketenes [5] could make this an attractive route to cyclopentenones. However, for that to be the case, we would have to: (1) work out efficient methods for removing the cyclopentenone formed via cycloaddition from the metal and (2) determine reaction conditions whereby a wide variety of ketenes or ketene equivalents would participate in this reaction. Our efforts along both of these lines are presented in detail here.

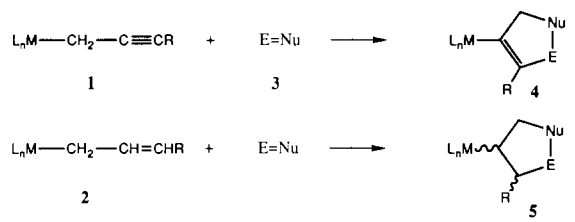
2. Results and discussion

We first repeated Wojcicki's original reported cycloaddition reactions with diphenyl ketene (**7**) on a ten fold increase in size over the original preparation and found that they produce $CpFe(CO)_2$ substituted cyclopentenones (**9a** and **9b**) in very good isolated yield. These complexes (**9a** and **9b**) are air-stable yellow solids which can be chromatographed on alumina or silica gel.

* Corresponding author.

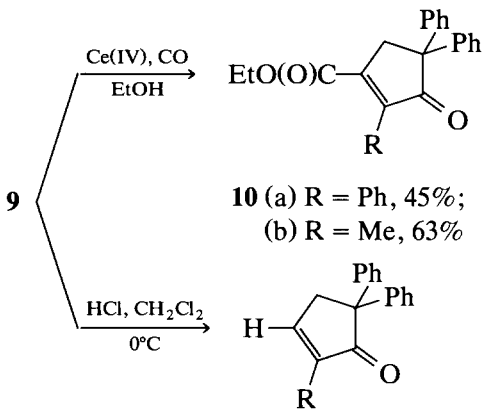
[1] Henry Dryfus Teacher-Scholar Awardee (1994-99)

SSDI 0022-328X(94)05071-I



Scheme 1.

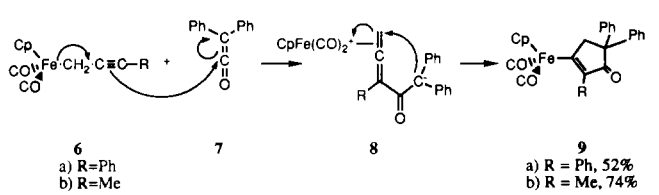
Next we chose to investigate methods for the cleavage of the iron–carbon bonds in complexes (**9a** and **9b**). The methods most often used by organometallic chemists to remove organic ligands from CpFe(CO)(L)(R) complexes are oxidative carboxylation, halogenolysis and protonolysis [6] so not surprisingly, we found that the cyclopentenone framework can be liberated from complexes (**9**) using ceric ammonium nitrate or HCl. Oxidative carboxylation produced 3-carboethoxy-2-cyclopentenones (**10**) in moderate to good yields on a preparatively useful scale (2–4 mmol) and acid cleavage yielded 2-methyl-5,5-diphenyl-2-cyclopentenone (**11**) (53%).



10 (a) R = Ph, 45%;
(b) R = Me, 63%

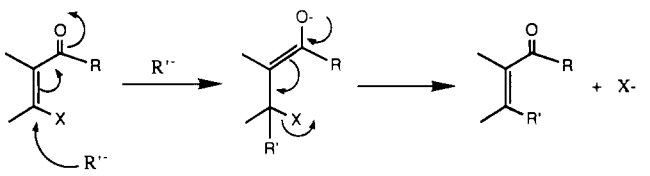
11 (b) R = Me, 53%

While the cleavage reactions mentioned above have been shown to yield useful organic products in many cases, their utility in synthesis is sometimes limited because the reaction conditions are many times harshly acidic or oxidative. Given the number of organic groups that now work with transition-metal complexes containing metal–carbon σ bonds, one area we were particularly interested in exploring in conjunction with this project was new nonoxidative methods for the removal of ligands from transition metals.



Scheme 2.

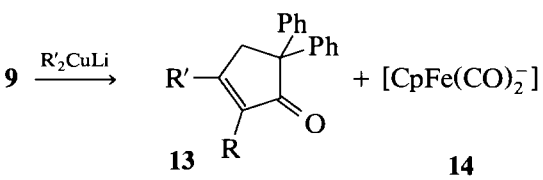
There are many examples in the organic literature of Michael type additions to β-heteroatom substituted α,β-unsaturated carbonyl systems (**12**) which result in the replacement of the β-heteroatom with the Michael nucleophile [7]. Since the $CpFe(CO)_2$ anion could



12

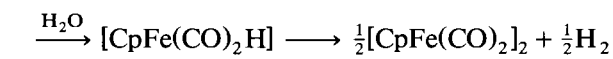
What about X = $CpFe(CO)_2$·?

function as a leaving group (X^-) from the metal substituted cyclopentenones (**9**), we treated these complexes with both Me_2CuLi and Ph_2CuLi and got very high isolated yields of the 3-methyl and 3-phenyl substituted cyclopentenones (**13**). Upon addition of the metallocyclopentenone to the cuprate, the solution turns the characteristic olive-brown color seen when the air sensitive $CpFe(CO)_2^-$ anion (**14**) is generated from $[CpFe(CO)_2]_2$ [8]. Aqueous workup presumably yields iron hydride (**15**) which is known to decompose in the presence of water to yield the $CpFe(CO)_2$ dimer [9] (**16**) which we also isolate (70%, from the reaction of **9b** with Me_2CuLi) in addition to the cyclopentenone. Not only does this reaction replace a metal–carbon bond with a carbon–carbon bond, it also provides us with a transition-metal complex (**16**) which is the original starting material used in the synthesis of the alkynyl complexes (**6**).



13 **14**

(a) from **9a**, R = R′ = Ph, 72%
(b) from **9b**, R = Ph, R′ = Me, 76%
(c) from **9b**, R = R′ = Me, 82%

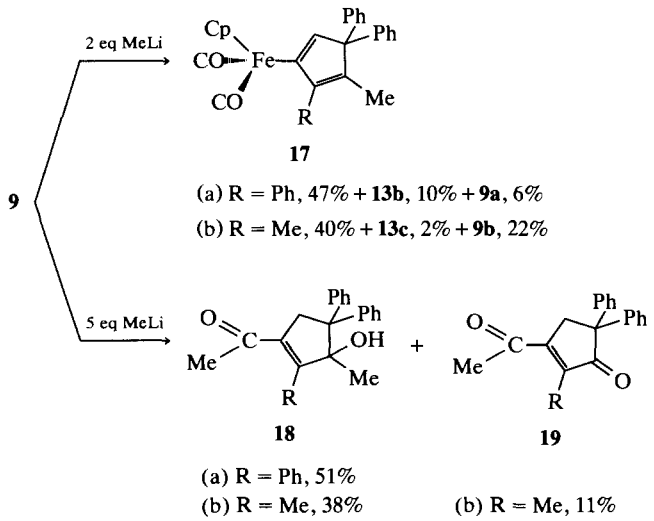


15 **16**

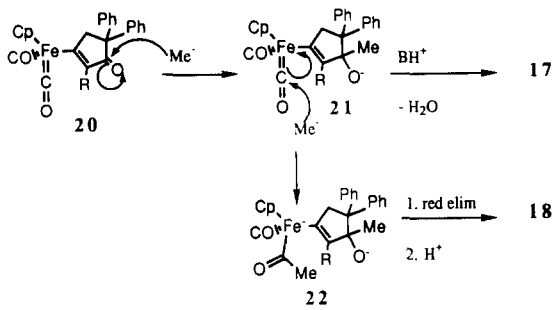
70% from (b)

Given the success of the cuprate experiments outlined above, we became interested in exploring the reactivity of these cyclopentenone complexes (**9a** and **9b**) with other carbon nucleophiles such as alkyl lithiums. There have been some reports of carbon–carbon bond forming reactions occurring when metal carbonyl alkyl complexes have been treated with carbon nucle-

ophiles [10] and we wanted to investigate possible alkyl lithium induced iron–carbon bond cleavages of complexes (**9a** and **9b**). Treatment of **9a** with MeLi (1.2 eq) at 0°C (quenched after 3 min by H_2O) produced **17a** (22%) and recovered **9a** (45%). Treatment of **9a** with MeLi (1.2 eq) at 0°C (2 h) produced **17a** (27%), **18a** (9%), and recovered **9a** (35%). When we increased the amount of MeLi added to **9a** or **9b** to two equivalents for long (3 h) or short (3 min) reaction times, we isolated 2-(cyclopentadienyl iron dicarbonyl) substituted cyclopentadienes (**17**) in 40–50% yield in addition to small amounts of the Michael addition products (**13b** and **13c**) and unreacted **9a** or **9b**. However, when these cyclopentenone complexes (**9a** and **9b**) were treated with a large excess (5 equivalents) of methyl lithium, the major products isolated were 3-acetylcyclopentenols (**18**).

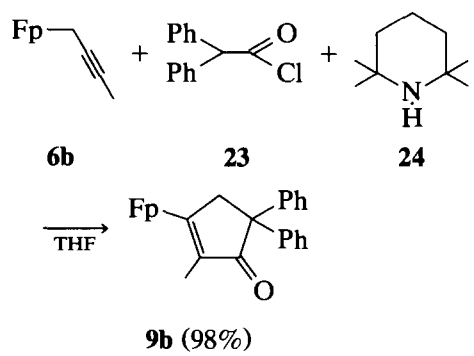


These nonstoichiometric reactions of methyl lithium with **9a** and **9b** were unexpected and may be due to alkyl lithium aggregation since the tetrameric alkyl lithium aggregates have been shown to give quite different results when treated with 1–4 equivalents of electrophiles [11]. To explain the formation of these two different types of products (**17** and **18**), we envision possible reaction pathways as outlined below. We assume that methyl lithium would rapidly attack the α,β-unsaturated carbonyl system in **20** in a 1,2 fashion to generate an intermediate of structure (**21**). In the presence of a large excess of methyl lithium, a rapid attack on a complexed CO would yield acetyl complex (**22**) which could undergo reductive elimination to generate **18**. Isolation of some acetyl substituted cyclopentenone (**19**) would indicate that attack at the metal carbonyl can be competitive with attack on the cyclopentenone carbonyl [10]. In the absence of a large excess of methyl lithium, elimination of the tertiary alcohol formed after protonation of **21** on workup (addition of MeLi to a solution of **9b** in d_8 THF does not generate **17b** directly) to yield cyclopentadienes (**17**) is the major reaction path. As expected complexes **17** were unaffected by MeLi and can be ruled out as possible precursors to **18**. In principle, these reactions could also be expected to produce iron anion (**14**) if performed under an atmosphere of CO, so iron recovery may also prove possible here.



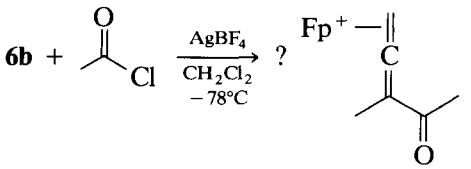
With a number of possible methods for iron–carbon bond cleavages available for cyclopentenones, we next began to explore cycloadditions with other ketenes or ketene equivalents and this chemistry proved to be much more difficult than expected. Since the butynyl complex (**6b**) was qualitatively more reactive than **6a**, we chose to use it in this chemistry. Realizing that we needed to replace the 5,5-diphenyl cyclopentenone substitutents with groups more amenable to subsequent synthetic manipulation, we first decided to prepare another isolable ketene, trimethylsilylketene [12], as an alternative cycloaddition partner. Unfortunately, complex **6b** proved unreactive toward TMS ketene over a temperature range of −78 to 100°C in a range of solvents. Temperatures higher than 100°C cause significant decomposition of **6b**.

Since ketenes are routinely generated from acid chlorides (using hindered amine bases) in the presence of potential nucleophiles [5], we next decided to investigate the possibility of in situ generation of ketenes in the presence of **6b**. Initially, we were very optimistic about this approach, when treatment of **6b** and diphenylacetylchloride (**23**) with 2,2,6,6-tetramethylpiperidine (**24**) produced cyclopentenone complex (**9b**) in 98% isolated yield. Unfortunately, this reaction did



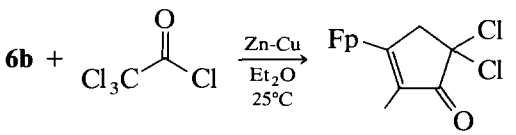
not prove general and when cyclohexanecarbonyl chloride, acetyl chloride, chloroacetyl chloride or dichloroacetyl chloride were treated with base (hindered amines

or Al_2O_3) in the presence of **6a** or **6b** over temperature ranges of −78 to 25°C in a range of solvents, we saw complex mixtures of products and only occasionally isolated small amounts of material that had ^1H NMR spectra consistent with a cyclopentenone structure. We next treated a mixture of complex (**6b**) and acetyl chloride with $AgBF_4$ in CH_2Cl_2 at −78°C [13] in hopes of generating the expected cationic allene complex intermediate (**25**) which could subsequently be deprotonated to yield the desired cyclopentenone complex. This acyl cation generation prodecure had been used to effect acylations in the presence of dicobalthexacarbonyl alkyne complexes [13] and allene complexes similar to **25** have been generated by treatment of propargyl complexes with electrophilic BF_4 salts or by allene ligand exchange with the Fp isobutylene complex [14]. However, we again only obtained a complex mixture of products.



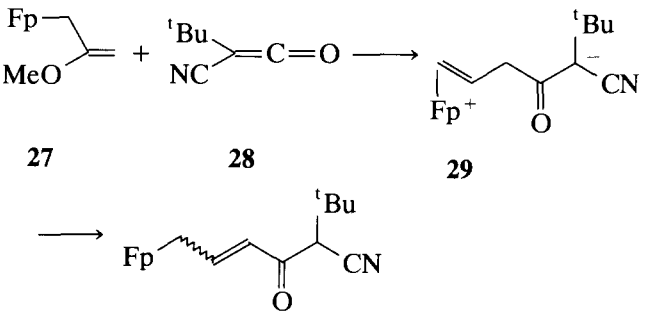
25

Our last attempt at ketene 3 + 2 cycloaddition of complex **6b** involved reductive rather than base induced ketene generation. Complex **6b** and trichloroacetyl chloride were treated with a ZnCu couple to generate dichloroketene [15] in situ. The desired cyclopentenone complex (**26**) was isolated but the yield was disappointing and failed to improve when Lewis bases were added to complex the $ZnCl_2$ generated in this reaction.

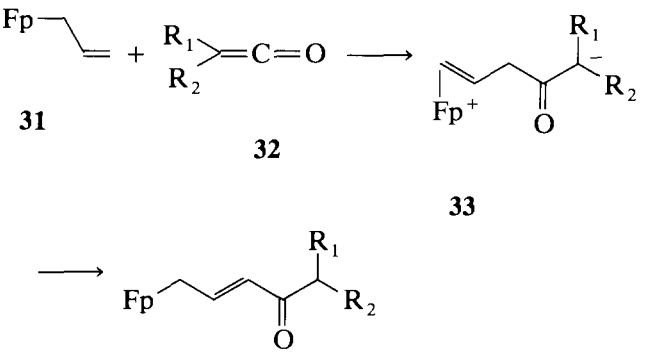


26 (6%)

Changes in the metal propargyl or allyl complex's coordination spheres then seemed to be a logical area to explore in an effort to discover complexes which would react cleanly with a variety of ketenes or ketene equivalents. We decided to prepare cyclopentadienyl iron monocarbonyl monophosphite propargyl and allyl complexes based on observations originally made by the Baker and Rosenblum groups discussed below. In 1982, Baker and co-workers reported that enol ether complex (**27**) reacted with *t*-butylcyanoketene but the products were addition/proton transfer products (**30**) rather than a 3 + 2 cycloaddition product [16]. These products (**30**) were postulated to arise from proton transfer reactions of intermediate (**29**) and the rates of these acid-base reactions are presumably faster than cycloaddition.

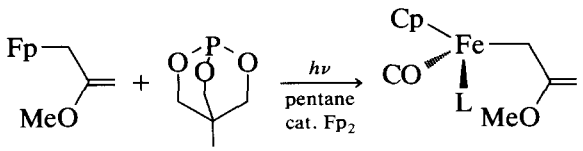


Also in 1982, Rosenblum and co-workers reported that the simple iron allyl (**31**) reacted with alkyl and aryl phenyl ketenes (**32**, R_1 = Me, Et, Ph, R_2 = Ph) to yield proton transfer (**34**) (10–30%) rather than cycloaddition products [17].

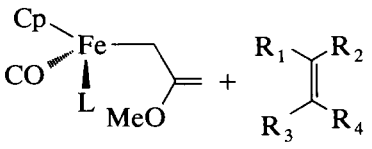


In 1983, Baker et al. in chemistry analogous to that reported by Rosenblum in 1980 [18], reported the reaction of the 2-methoxy substituted allyl (**27**) with bulky phosphite (**35**) to yield chiral racemic allyl complex (**36**) (70%) [19]. Unlike **27**, complex **36** reacted with a variety of electron deficient alkenes via a 3 + 2 cycloaddition to produce transition metal substituted cyclopentenes (**38/39**). In contrast to the reactions of the analogous $CpFe(CO)_2$ methoxy substituted allyl (**27**) [18,19], linear hydrogen transfer products were minor products if isolated at all. Cationic alkene intermediates presumably formed here would be more stable (increased backbonding) and less electrophilic than Fp(alkene) cations and yet the products here are those of cyclization rather than proton transfer. If proton transfer products arise via an intermolecular reaction, then this may be just a steric effect where the bulky phosphite ligand retards proton transfer and cyclization becomes the major reaction pathway. Additionally, with this phosphite (**35**) the pKa of protons α to the alkene in cationic alkene complexes increases by 9 relative to the Fp complexes and this would also retard proton transfer [18,19]. Based on these observations, we anticipated that chiral iron propargyl and allyl complexes should react with ketenes or ketene equiva-

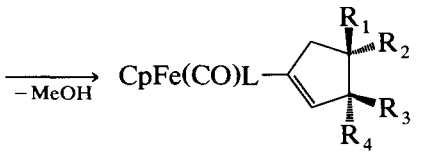
lents to yield 3 + 2 cycloaddition products rather than proton transfer products.



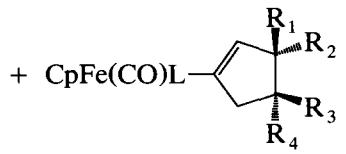
27 35 36, L = 35, 70%



36 37

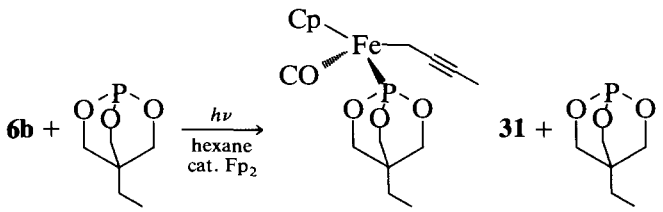


38

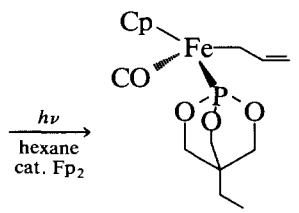


39

To initiate this study, we prepared chiral at iron propargyl (**41**) and allyl complexes (**42**) using a commercially available phosphite (Strem) (**40**) analogous to the one used by Baker [19] and Rosenblum [18]. The photolyses proved straightforward and produced the desired complexes (**41** and **42**) in good isolated yield (63 and 69%) as air-stable yellow-orange solids.

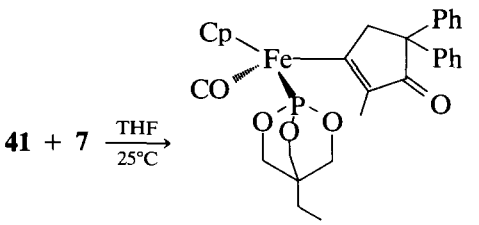


40 41 (63%)



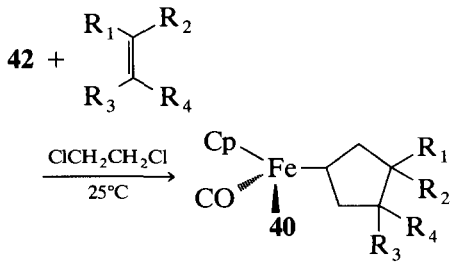
42 (69%)

We initiated our study of ketene cycloaddition chemistry of these complexes by treating propargyl complex (**41**) with diphenyl ketene and found that **41** did react with this ketene in a 3 + 2 cycloaddition reaction to produce cyclopentenone complex (**43**) in 46% yield. Unfortunately, **41** like **6b**, proved unreactive toward TMS ketene and **41** reacted with diketene to produce a complex mixture of products which were isolated in poor mass balance.



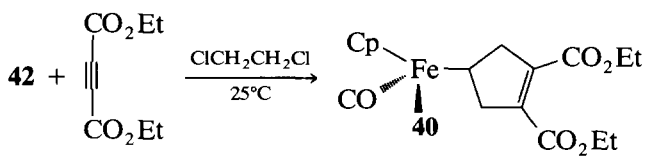
43 (46%)

Since alkenes are much more reactive to electrophilic attack than alkynes, we then decided to concentrate our cycloaddition efforts on allyl complex (**42**) [20]. We first confirmed that this allyl complex (**42**) would participate in 3 + 2 cycloaddition reactions similar to those reported for **36** above by treating **42** with tetracyanoethylene, diethylmethylenemalonate, and diethylacetylenedicarboxylate. We isolated the expected 3 + 2 cycloaddition products (**44–46**) in all cases. The cycloaddition to produce **45** turned out to be quite diastereoselective producing a 11.2:1 mixture of diastereomers. The relative stereochemistry of the major diastereomer was not determined since it was not relevant to the study underway.



44 $R_1 = R_2 = R_3 = R_4 = CN$, 64%

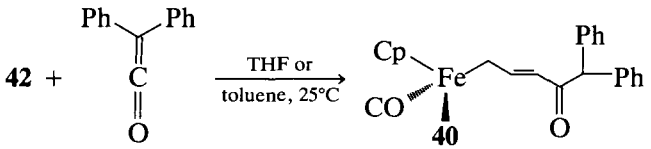
45 $R_1 = R_2 = CO_2Et$, $R_3 = R_4 = H$, 54%



46 38%

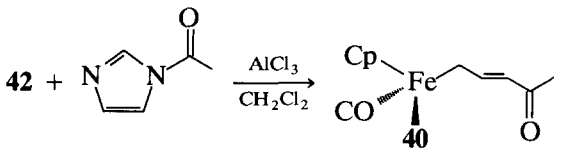
We then treated allyl complex (**42**) with diphenyl ketene in both THF (25°C, 1 h or −78°C, 4 h) and toluene and in all cases observed a clean reaction which produced the proton transfer product (**47**) rather than the 3 + 2 cycloaddition product. Complex (**42**) like **6a** and **6b** also proved to be unreactive toward TMS ketene. Generating diphenyl ketene in situ from diphenylacetyl chloride and tetramethylpiperidine (TMP) as described above for complex **6b** also pro-

duced only complex (**47**). Treating **42** with acetyl chloride and tetramethylpiperidine at 25°C in THF led to recovery of unreacted **42**. Likewise, treatment of **42** with cyclohexanecarbonyl chloride and TMP at 0 and 25°C in toluene lead to recovery of **42**. Heating this solution resulted in decomposition of **42**.



47 42%

Lastly, we tried an acyl imidazole (**48**) [21] as a ketene precursor in hopes that the expected imidazole by-product might induce the desired 3 + 2 cycloaddition but we instead isolated the proton transfer product (**49**) (20%). The crude product ^{1}H NMR showed only **49** and unreacted **42** (1 : 2).



49

48

3. Summary

Cyclopentadienyl iron dicarbonyl propargyl complexes participate in 3 + 2 cycloaddition reactions with diphenyl ketene (isolated or generated in situ) in good yield. The cyclopentenone ring thus generated can be removed from the iron under a variety of reaction conditions some of which yield recovered iron complexes as well as cyclopentenones. These same propargyl complexes react with dichloroketene but fail to yield isolable cyclopentenone complexes with a variety of other ketenes or ketene precursors. Cyclopentadienyl iron monocarbonyl monophosphite alkynyl complex (**41**) reacted with diphenyl ketene to produce the desired 3 + 2 cycloadduct in modest yield. Cyclopentadienyl iron monocarbonyl monophosphite allyl complex (**42**) reacted with ketenes or ketene equivalents but produced proton transfer rather than 3 + 2 cycloaddition products also in modest yield. Unfortunately, the switch from dicarbonyl to chiral at iron complexes here did not lead to a change from proton transfer to cycloaddition products as it had done with electron deficient alkenes [18,19]. Performing these reactions under high dilution conditions or using CpFe(diphos) alkynyl complexes [22] might solve this problem but the isolated yields observed here did not encourage us to pursue this line of thought any further.

4. Experimental section

4.1. General

All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR. All absorptions are expressed in parts per million relative to tetramethylsilane. Infrared (IR) spectra were obtained using a Perkin Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, Georgia. High resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, University of Nebraska-Lincoln. Low resolution EI mass spectra were obtained on a Hewlett Packard 5989 GC/MS system. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise noted. Cyclopentadienyliron dicarbonyl dimer was purchased from Strem Chemicals and used as received. Phenyl lithium and methyl lithium solutions and copper iodide were purchased from Aldrich Chemical Company and used as received. $CpFe(CO)_2CH_2C{\equiv}CR$ (R = CH_3) [**4a**] and (R = Ph) [**4b**] were synthesized according to literature procedures via addition of a THF solution of the appropriate metal anion to a THF solution of the appropriate 2-alkynyl chloride or bromide. Diphenyl ketene was prepared according to a literature procedure [23].

4.2. Synthesis of 2-phenyl and 2-methyl-3-(cyclopentadienyl dicarbonyl iron)-5,5-diphenyl-2-cyclopentenone (9a and 9b)

Iron 2-alkynyl complexes were prepared in a manner analogous to that reported by Wojcicki and co-workers [2] except they were performed on a scale about 10 times largers than that reported by Wojcicki. The iron 2-alkynyl complexes (**6a**, **b**) (2.446 g, 0.01063 mol of **6b**, 2.84 g, 0.0097 mol of **6a**) were dissolved in CH_2Cl_2 (40 ml) and to the solution was added diphenyl ketene (2.90 g, 0.0149 mol; 2.64 g, 0.0136 mol) in benzene (20 ml) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo and the crude product was chromatographed on alumina. Elution with 1 : 3 CH_2Cl_2 : petroleum ether afforded an air-stable yellow solid (**9a** or **b**). **9a** (2.452 g, 5.04 mmol, 52%): ^{1}H NMR ($CDCl_3$) (lit. [2]) 7.17–7.42 (m, 15H), 4.71 (s, 5H), 3.84 (s, 2H). **9b** (3.338 g, 7.87 mmol, 74%): ^{1}H NMR ($CDCl_3$) (lit. [2]) 7.34–7.15 (m, 10H), 4.92 (s, 5H), 3.66 (q, J = 2.0 Hz, 2H), 1.96 (t, J = 2.0 Hz, 3H).

*4.3. Preparation of 3-carboethoxy-2,5,5-triphenyl-2-cyclopentenone (**10a**) and 3-carboethoxy-2-methyl-5,5-diphenyl-2-cyclopentenone (**10b**)*

Iron cyclopentenone complexes (**9a** or **b**) (2–4 mmol) were dissolved in dichloromethane : ethanol (1 : 1, 20 ml) and the solution was cooled to −78°C. Ceric ammonium nitrate (2.5 eq) was dissolved in ethanol (60 ml) and this solution was also cooled to −78°C. Both solutions were degassed with CO and then the Ce(IV) solution was transferred to the iron complex solution using a double ended needle under CO. The mixture was then allowed to stir under CO (balloon) for 0.75 h at −78°C followed by 0.75 h at 25°C. The solvent was removed by rotary evaporation and the crude products were chromatographed on alumina (dichloromethane : petroleum ether, 1 : 1) to yield **10a** as a light yellow solid: mp 87–89°C (dichloromethane : petroleum ether), IR ($CDCl_3$) 3063, 2982, 1715, 1601 cm^{-1}; ^1H NMR ($CDCl_3$) 7.38–7.18 (m, 15H), 4.22 (q, $J = 6.7$ Hz, 2H), 3.72 (s, 2H), 1.19 (t, $J = 6.7$ Hz, 3H). Anal. Calc. for $C_{26}H_{22}O_3$; C: 81.65, H: 5.80. Found; C: 81.45, H: 5.89 and **10b** as a yellow gum: IR ($CDCl_3$) 3064, 2985, 1714, 1643, 1600, 1580, 1494 cm^{-1}; ^1H NMR ($CDCl_3$) 7.35–7.10 (m, 10H), 4.33 (q, $J = 7.3$ Hz, 2H), 3.56 (q, $J = 2.5$ Hz, 2H) 2.12 (t, $J = 2.5$ Hz, 3H), 1.38 (t, $J = 7.3$ Hz, 3H). Anal. Calc. for $C_{21}H_{20}O_3$; C: 78.75, H: 6.25. Found; C: 78.76, H: 6.31.

*4.4. Synthesis of 2-methyl-5,5-diphenyl-2-cyclopentenone (**11**)*

To iron cyclopentenone complex (**9b**) (0.5 mmol) in CH_2Cl_2 (40 ml) at 0°C, con. HCl (5 eq) was added. After 1 h at 0°C and 12 h at 25°C, the solvent was removed under reduced pressure and the residue chromatographed on silica gel (4 : 1, petroleum ether : EtOAc) to yield **11** as a yellow solid: mp 45–50°C, IR ($CDCl_3$) 3156, 1702, 1644, 470, 1382, 1096, 938 cm^{-1}; ^1H NMR ($CDCl_3$) 7.44 (m, 1H), 7.33–7.18 (m, 10H), 3.36 (p, $J = 2.6$ Hz, 2H), 1.85 (t, $J = 2.6$ Hz, 3H). Anal. Calc. for $C_{18}H_{16}O$; C: 87.05, H: 6.50. Found; C: 86.98, H: 6.51.

*4.5. Reactions of cuprates with cyclopentenone complexes (**9a** and **b**). Preparation of 2,3,5,5-tetraphenyl-2-cyclopentenone (**13a**), 3-methyl-2,5,5-triphenyl-2-cyclopentenone (**13b**), and 2,3-dimethyl-5,5-diphenyl-2-cyclopentenone (**13c**)*

Copper iodide (2 mmol) was added to THF (6 ml) in a flame dried flask under nitrogen. After cooling to −10°C, alkyl lithium (4 mmol) was added via syringe. The solution was then stirred for 0.5 h at −10°C and iron complex (**4**) (0.5–1 mmol, dissolved in THF (9 ml) was added dropwise to the cuprate. The solution was allowed to stir at 0°C for 2 h after this addition. The reaction was then quenched by the addition of a saturated NaCl solution (20 ml) and extracted with diethyl ether (3 × 20 ml). The extracts were dried (Na_2SO_4) and the solvent removed by rotary evaporation. The crude product was chromatographed on silica gel (10 : 1, petroleum ether : acetone) to yield **13a** as a light yellow gum; IR ($CDCl_3$) 3062, 3031, 2959, 2928, 1710, 1599, 1495, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) 7.55–7.12 (m, 20H), 3.90 (s, 2H). EI MS 386 (32), 357 (11), 310 (100), 267 (16). EI HRMS Calc. for $C_{29}H_{22}O$: 386.1671; Found: 386.1671; **13b** as a white solid m.p.: 145–147°C (acetone/petroleum ether), IR ($CDCl_3$) 3065, 2950, 1710, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) 7.46–7.21 (m, 15H), 3.48 (s, 2H), 2.29 (s, 43H). EI HRMS Calc. for $C_{24}H_{20}O$: 324.1513; Found: 324.1513. Anal. Calc. for $C_{24}H_{20}O$; C: 88.89; H: 6.17. Found; C: 88.78, H: 6.19 and **13c** as a light yellow waxy solid: m.p. 49–51°C (acetone/petroleum ether), IR ($CDCl_3$) 3063, 2962, 2926, 1697, 1651, 1601, 1580, 1493 cm^{-1}; ^1H NMR ($CDCl_3$) 7.36–7.10 (m, 10H), 3.29 (s, 2H) 2.11 (s, 3H), 1.76 (s, 3H). Anal. Calc. for $C_{19}H_{18}O$; C: 87.02, H: 6.87. Found; C: 86.77, H: 6.97.

*4.6. Treatment of $CpFe(CO)_2$-substituted cyclopentenones (**9a** and **b**) with 2 eq methyl lithium*

*4.6.1. Synthesis of 2-(cyclopentadienyl iron dicarbonyl)-4-methyl-3,5,5-triphenylcyclopentadiene (**17a**)*

Iron complex (**9a**) (0.177 g, 0.364 mmol) was dissolved in THF (7 ml) in a flame dried flask under nitrogen and the solution was cooled to 0°C. Methyl lithium (0.56 ml of a 1.4 M solution in diethyl ether, 0.784 mmol) was added dropwise to the iron complex and then the solution was allowed to stir 3 h at 0°C. Saturated NaCl workup (20 ml), ether extraction (3 × 20 ml), Sodium sulfate drying and rotary evaporation yielded a crude product which was chromatographed on silica gel (230–400 mesh) 10 : 1 (petroleum ether : acetone) to yield **17a** as a yellow gum (0.082 g, 47%) IR ($CDCl_3$) 3060, 3028, 2962, 2927, 2021, 1955, 1651, 1597, 1487, 1441 cm^{-1}; ^1H NMR ($CDCl_3$) 7.49–7.15 (m, 15H), 6.51 (s, 1H), 4.48 (s, 5H), 1.59 (s, 3H). EI HRMS Calc. for $C_{31}H_{24}O_2Fe$: 484.1124. Found: 484.1124. Continued elution of this column yielded **13b** (0.012 g, 10%) followed by unreacted **9a** (0.010 g, 6%). When the reaction was run under identical conditions except the saturated NaCl solution was added 3 min after the MeLi, **17a** was isolated in 43% yield.

*4.6.2. Synthesis of 2-(cyclopentadienyliron dicarbonyl)-3,4-dimethyl-5,5-diphenylcyclopentadiene (**17b**)*

Iron complex (**9b**) (0.167 g, 0.394 mmol) was dissolved in THF (10 ml) in a flame dried flask under nitrogen and cooled to 0°C. Methyl lithium (0.56 ml of a 1.4 M solution in diethyl ether, 0.784 mmol) was

added and the solution was stirred for 3 min at 0°C. The reaction was then quenched and worked up and the crude product chromatographed on silica gel as described above for **17a** to yield **17b** as a yellow-brown gum (0.066 g, 40%) IR ($CDCl_3$) 3060, 3028, 2969, 2921, 2016, 1966, 1646, 1597, 1506, 1488 cm^{-1}; ^1H NMR ($CDCl_3$) 7.32–7.09 (m, 10H), 6.49 (s, 1H) 4.80 (s, 5H), 1.98 (s, 3H), 1.71 (s, 3H); EI HRMS Calc. for $C_{26}H_{22}O_2Fe$: 422.0969; Found: 422.0977. Continued elution yielded **13c** (0.003 g, 2%) and recovered starting material **9b** (0.037 g, 22%).

4.7. Reactions of complexes (9a and b) with 5 eq methyl lithium

4.7.1. Synthesis of 3-acetoxy-1-methyl-2,5,5-triphenyl-2-cyclopenten-1-ol (18a)

Iron complex (**9a**) (0.169 g, 0.348 mmol) was dissolved in THF (7 ml) in a flame dried flask under nitrogen. Methyl lithium (1.24 ml of a 1.4 M solution in diethyl ether, 1.736 mmol) was added and the solution was stirred for 3 min before being quenched with saturated NaCl as above. Workup and silica gel chromatography 10:1 (petroleum ether:acetone) as described above yielded **18a** as a light yellow gum (0.065 g, 51%) IR ($CDCl_3$) 3550, 3059, 3029, 2982, 2930, 1674, 1598, 1495, 1443 cm^{-1}; ^1H NMR ($CDCl_3$) 7.55–7.10 (m, 15H), 3.43 (apparent q, AB CH_2, $J = 19.0$ Hz, 2H), 2.11 (s, 1H, exchanges w/D_2O), 1.84 (s, 3H), 1.23 (s, 3H). EI HRMS Calc. for $C_{26}H_{24}O_2$: 368.1785. Found: 368.1772. Anal. Calc. for $C_{26}H_{24}O_2$; C: 84.78, H: 6.52. Found; C: 84.57, H: 6.60.

4.7.2. Synthesis of 3-acetoxy-1,2-dimethyl-5,5-diphenyl-2-(cyclopenten-1-ol (18b) and 3-acetoxy-2-methyl-5,5-diphenyl-2-cyclopentenone (19)

Iron complex (**9b**) (0.195 g, 0.46 mmol) was dissolved in THF (10 ml) and cooled to 0°C. Methyl lithium (1.64 ml of a 1.4 M solution in diethyl ether, 2.30 mmol) was then added and the reaction quenched after 3 min by the addition of saturated NaCl solution as above. The usual workup and silica gel chromatography (15:1, petroleum ether:acetone) yielded (**19**) (0.014 g, 11%) as a yellow gum: IR ($CDCl_3$) 3063, 2930, 1709, 1675, 1206 cm^{-1}; ^1H NMR ($CDCl_3$) 7.43–7.09 (m, 10H), 3.56 (d, $J = 2.1$ Hz, 2H), 2.52 (s, 3H), 2.09 (t, $J = 2.1$ Hz, 3H). EIMS 290(100) 204 (46); HRMS calc. for $C_{20}H_{18}O_2$: 290.1307; Found: 290.1308; followed by **18b** (0.053 g, 0.15 mmol, 38%) as a light yellow gum: IR ($CDCl_3$) 3561, 3061, 3035, 2980, 2936, 1679, 1652, 1602, 1492, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) 7.52–7.20 (m, 10H), 3.28 (apparent q, AB CH_2, $J = 16.7$ Hz, 2H), 2.36 (s, 3H), 2.17 (s, 1H, exchanges w/D_2O), 2.16 (s, 3H), 1.12 (s, 3H). EI MS 306(56), 263(100), 191(76), 176(89); HRMS calc. for $C_{21}H_{22}O_2$: 306.1620; Found: 306.1618.

4.8. Reaction of complex 6b with diphenylacetylchloride / TMP

The iron 2-alkynyl complex (**6b**) (0.210 g, 0.913 mmol) and diphenylacetylchloride (Aldrich) (0.400 g, 1.73 mmol) were dissolved in THF (5 ml) at 0°C. Tetramethylpiperidine (440 μl, 2.61 mmol) was added to the solution and the reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was filtered through celite, the solvent was removed in vacuo and the crude product was chromatographed on alumina. Elution with 1:3 CH_2Cl_2: petroleum ether and solvent removal in vacuo afforded an air-stable yellow solid (**9b**) (0.384 g, 0.905 mmol, 98%) identical by spectroscopic comparison to the material reported above.

4.9. Synthesis of 2-methyl-3-(cyclopentadienyl dicarbonyl iron)-5,5-dichloro-2-cyclopentenone (26)

Under N_2, trichloroacetyl chloride (0.690 g, 3.79 mmol) in anhydrous diethyl ether (10 ml) was added dropwise to 1-(cyclopentadienyl dicarbonyl iron)-2-butyne (**6b**) (0.432 g, 1.88 mmol) and activated zinc[15] (0.365 g) in anhydrous diethyl ether (50 ml) over 2 h at 0°C. The reaction mixture was then allowed to warm to room temperature and stir for 4 h and monitored by alumina TLC for the disappearance of starting material. Washed successively with water (20 ml), saturated $NaHCO_3$ (20 ml) and saturated NaCl (20 ml), the organic layer was then dried over Na_2SO_4 and filtered. Upon the removal of solvent in vacuo, the residue was chromatographed on an alumina preparative TLC plate. Elution with 1:1 CH_2Cl_2/petroleum ether afforded 2-methyl-3-(cyclopentadienyl dicarbonyl iron)-5,5-dichloro-2-cyclopentenone (**26**) as a yellow gum. (0.038 g, 0.111 mmol, 6%). IR ($CDCl_3$), 2032, 1981, 1694, 1549, 1281, 939 cm^{-1}; ^1H NMR ($CDCl_3$) 4.95 (s, 5H), 3.78 (q, $J = 1.0$ Hz, 2H), 2.01 (t, $J = 1.0$ Hz, 3H). EI HRMS Calc. for $C_{13}H_{10}O_3Cl_2Fe$: 339.9356; Found: 339.9370.

4.10. Preparation of CpFe(CO)[P(OCH$_2$)$_3$CEt](2-butyne) (41)

Cyclopentadienyl iron dicarbonyl anion was generated by stirring cyclopentadienyl dicarbonyl iron dimer (7.026 g, 0.020 mol) under argon in THF (150 ml) with a 1% sodium amalgam followed by treatment of the anion with 2-butyne tosylate (8.269 g, 0.036 mol) in THF (150 ml) to generate the Fp butyne complex as described previously [4a]. The crude Fp butyne (**6b**) was dissolved in ca. 100 ml of hexane and the solution was filtered into the photolysis flask. Thirty milligrams of $[CpFe(CO)_2]_2$ and 4-ethyl-2,6,7-trioxa-1-phosphatricyclo-[2.2.2]-octane (4.4 g, 0.027 mol) were then added. Immediately upon completion of degassing, the solution was photolyzed for 15 minutes with a 150 W

Sylvania flood lamp during which time, an orange solid precipitated. The solution was stirred for thirty minutes at 25°C. The cyclopentadienyl monocarbonyl caged phosphite 2-butyne iron compound (**41**) was collected by vacuum filtration and washed with hexane (6.141 g, 0.0169 mol, 63%). m.p.: 119–120°C, IR (C_6D_6) 2974, 2945, 2914, 1941, 1038 cm^{-1}. ^1H NMR (C_6D_6) 4.62 (s, 5H), 3.57 (d, 6H, $J = 6.9$ Hz), 1.82 (s, 3H), 1.75 (m, 1H), 0.2 (q, 2H, $J = 8.3$ Hz), 0.1 (t, 3H, $J = 8.3$ Hz). HRMS calcd. for $[C_{15}H_{21}O_3PFe]$ (M^+–CO): 336.0577 Found: 336.0563.

4.11. Preparation of $CpFe(CO)[P(OCH_2)_3CEt](allyl)$ (42)

Cyclopentadienyl dicarbonyl iron dimer (8.127 g, 22.96 mmol) was reduced using a 1% sodium amalgam in THF (120 ml) and the iron dicarbonyl anion produced was treated with allyl chloride as previously described [24]. The yellow Fp allyl complex was dissolved in hexane (100 ml) and filtered, degassed (N_2) and then photolyzed with 4-ethyl-2,6,7-trioxa-1-phosphatricyclo-[2.2.2]-octane (4.1 g, 25.28 mmol) for 15 min with a 150 W Sylvania flood lamp. During the photolysis, an orange solid precitated from the hexane. The reaction was stirred for 0.5 h at 25°C before the cyclopentadienyl monocarbonyl 2-propene iron complex (**42**) (6.166 g, 0.0175 mol, 69%) was collected by vacuum filtration. m.p.: 76–77°C, IR (C_6D_6) 2972, 2955, 2886, 1931, 1034 cm^{-1}. ^1H NMR (C_6D_6) 6.67–6.42 (m, 1H), 5.12 (dd, 1H, $J = 16.4$, 2.6 Hz), 4.87 (dd, 1H, $J = 9.8$, 2.6 Hz), 4.45 (s, 5H), 3.63 (d, 6H, $J = 4.7$ Hz), 2.50–2.20 (m, 2H) 0.25 (q, 2H, $J = 7.2$ Hz), 0.10 (t, 3H, $J = 7.2$ Hz). Anal. calc. for $C_{15}H_{21}O_4PFe$; C: 51.16, H: 6.01. Found C: 51.23, H: 6.06.

4.12. Reaction of iron alkynyl complex (41) with diphenyl ketene

Diphenyl ketene (0.050 g, 0.26 mmol) was dissolved in THF (5 ml) and cooled to 0°C. Iron complex (**41**) (0.100 g, 0.27 mmol) was dissolved in ca. 2 ml of THF and added dropwise to the diphenyl ketene. The solution was allowed to warm to 25°C overnight and the solvent was removed by rotary evaporation to yield a red oil which was chromatographed on silica (Et_2O) to obtain **43** as an orange solid (0.067 g, 0.12 mmol, 46%). IR ($CDCl_3$) 3155, 2977, 2927, 2900, 1958, 1648, 1468, 1382, 1098, 1038 cm^{-1}. ^1H NMR ($CDCl_3$) 7.38–7.05 (m, 10H), 4.66 (s, 5H), 4.12 (d, $J = 6.7$ Hz, 6H), 3.74 (d, $J = 18.0$ Hz, 1H), 3.62 (d, $J = 18.0$ Hz, 1H), 1.92 (s, 3H), 1.18 (q, $J = 8.0$ Hz, 2H), 0.80 (t, $J = 8.0$ Hz, 3H).

4.13. Cycloaddition of iron allyl (42) and tetracyanoethylene

Tetracyanoethylene (0.180 g, 1.40 mmol) was added to iron allyl (0.203 g, 0.576 mmol) (**42**) in 1,2-dichloroethane (30 ml) at −20°C under argon. After stirring for 4 min, the solution was allowed to warm to 25°C. The green solution was filtered through a 3 cm plug of neutral alumina to yield a yellow liquid. Upon removal of the solvent, the remaining red-orange oil was chromatographed on a deactivated silica column eluted with 20% hexane in ether to yield an orange solid which was recrystallized from dichloromethane/petroleum ether to provide the cycloadduct (**44**) as an orange solid (0.177 g, 0.368 mmol, 64%). m.p.: 144–145°C dec. ^1H NMR ($CDCl_3$) 4.58 (s, 5H), 4.28 (d, $J = 5.1$ Hz, 6H), 2.89–2.70 (m, 3H), 2.67–2.50 (m, 2H), 1.22 (q, $J = 7.7$ Hz, 2H), 0.85 (t, $J = 7.7$ Hz, 3H); IR (C_6D_6): 3109, 3028, 2973, 2894, 1951, 1463, 1448, 1154 cm^{-1}. Anal. calc. for $C_{21}H_{21}PO_4FeN_4$: C, 52.52%; H, 4.41%. Found: C, 52.41%; H, 4.42%.

4.14. Reaction of diethylmethylenemalonate with iron allyl (42)

Diethylmethylenemalonate (0.198 g, 1.15 mmol) was added at 0°C to the iron allyl (**42**) (0.200 g, 0.568 mmol) in 1,2-dichloroethane (30 ml). After stirring 3.5 h, the solvent was removed by rotary evaporation and the remaining red-orange oil was then chromatographed on alumina (40% ether in hexane) to yield the cycloadduct (**45**) as an orange solid (0.161 g, 0.31 mmol, 54%) IR ($CDCl_3$): 2978, 2942, 2889, 1937, 1729, 1463, 1446, 1368, 1298, 1255, 1177, 1157, 1095, 1045 cm^{-1}. ^1H NMR ($CDCl_3$) 4.48 (s, 5H), 4.32–3.90 (m, 10H), 2.82–2.41 (m, 2H), 2.30–1.67 (m, 5H), 1.48–1.10 (m, 8H), 1.05 (t, 3H, $J = 7.1$ Hz), 0.81 (t, 3H, $J = 7.8$ Hz). HRMS m/z Calc. for $C_{23}H_{33}FeO_8P$: 524.1262. Found 524.1236.

4.15 Reaction of diethylacetylenedicarboxylate with iron allyl (42)

Diethylacetylenedicarboxylate (0.115 g, 0.676 mmol) was added at 0°C to the iron allyl (**42**) (0.200 g, 0.568 mmol) in 1,2-dichloroethane (30 ml). After warming to 25°C and stirring overnight, the solvent was removed by rotary evaporation. The residue was then chromatographed on alumina (40% ether in hexane) to yield the cycloadduct (**46**) as a yellow-orange solid (0.113 g, 0.22 mmol, 38%). IR ($CDCl_3$) 3690, 2979, 2940, 2892, 1937, 1724, 1636, 1277, 1219, 1097, 1040 cm^{-1}. ^1H NMR ($CDCl_3$) 4.52 (s, 5H), 4.35–4.00 (m, 10H), 3.00–2.72 (m, 2H), 2.58–2.44 (m, 2H), 2.42–2.18 (m, 1H), 1.38–1.20 (m, 8H), 0.82 (t, $J = 7.7$ Hz, 3H); FAB HRMS m/z Calc. for $C_{23}H_{32}FeO_8P$ $(M + H)^+$ 523.1184; $(M + H)^+$ Found: 523.1180.

4.16. Reaction of iron allyl (42) with diphenylketene

Iron allyl complex (**42**) (0.203 g, 0.576 mmol) and diphenyl ketene (0.226 g, 1.17 mmol) were dissolved in

THF (10 ml) at 0°C and then the solution was allowed to warm to 25°C and stir overnight. The solvent was removed by rotary evaporation and the remaining oil was chromatographed on a chromatotron (silica, Et_2O) to yield **47** as a yellow solid (0.132 g, 0.242 mmol, 42%). IR ($CDCl_3$) 3064, 3028, 2975, 2892, 1942, 1715, 1626, 1580, 1557, 1495, 1464, 1457, 1318, 1188, 1156, 1032 cm^{-1}. ^1H NMR ($CDCl_3$) 7.60–7.12 (m, 11H), 5.78 (d, $J = 15.3$ Hz, 1H), 5.37 (s, 1H), 4.22 (s, 5H), 4.16 (d, $J = 5.3$ Hz, 6H), 1.70 (m, 1H), 1.54 (m, 1H), 1.20 (m, 2H), 0.81 (t, $J = 8.0$ Hz, 3H).

4.17. Reaction of iron allyl (42) and 1-acetylimidazole (48) in the presence of $AlCl_3$

Under an atmosphere of argon, iron allyl (**42**) (0.200 g, 0.568 mmol) was dissolved in CH_2Cl_2 (30 ml). Imidazole (**48**) (0.71 g, 0.64 mmol) was added at −78°C followed by $AlCl_3$ (0.86 g, 0.64 mmol). The reaction was stirred at −78°C for 1.5 h before it was quenched with triethylamine (0.16 ml, 1.14 mmol). Satd. sodium bicarbonate solution (20 ml) was added and the solution was extracted (CH_2Cl_2, 3 × 20 ml). The extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product ^1H NMR showed that the residue was a 2:1 mixture of **49** and unreacted **42**. The residue was purified using an alumina prep plate (0.015 g, 0.038 mmol, 20% based on unreacted **42**). ^1H NMR ($CDCl_3$) 7.30 (m, 1H), 5.71 (d, $J = 15.6$ Hz, 1H), 4.39 (d, $J = 1.0$ Hz, 5H), 4.20 (d, $J = 6.0$ Hz, 6H), 2.17 (s, 3H), 1.75 (m, 1H), 1.59 (m, 1H), 1.20 (m, 2H) 0.82 (t, $J = 8.0$ Hz, 3H). IR ($CDCl_3$) 3155, 2977, 2897, 1947, 1793, 1647, 1619, 1591, 1466, 1381 cm^{-1}. FAB HRMS m/z Calc. for $C_{17}H_{24}FeO_5P$ $(M + H)^+ = 395.0710$; Found: 395.0719.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Wake Forest University Research and Creative Activities Fund for their support of this work. The Midwest Center for Mass Spectrometry, a National Science Foundation regional instrumentation facility (CHE 8211164), performed mass spectral analyses.

References and notes

[1] For recent reviews of transition-metal mediated 3+2 cycloadditions see: (a) M.E. Welker, *Chem. Rev., 92* (1992) 97; (b) D.M.T. Chan, in B.M. Trost (ed.), *Comprehensive Organic Syntheses*, Pergamon, New York, 1991, p. 271; (c) A. Wojcicki, *Coord. Chem. Rev., 105* (1990) 35; (d) M. Rosenblum, *J. Organomet. Chem., 300* (1986) 191.

[2] L.S. Chen, D.W. Lichtenberg, P.W. Robinson, Y. Yamamoto and A. Wojcicki, *Inorg. Chim Acta, 25* (1977) 165.

[3] L. Ni, J.A. Belot and M.E. Welker, *Tetrahedron Lett., 33* (1992) 177.

[4] See for example: (a) J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, *Inorg. Chem., 10* (1971) 2130; (b) J.L. Roustan and P. Cadiot, *C.R. Acad. Sci., 268* (1969) 734.

[5] For a review of ketene synthesis and reaction chemistry see H.R. Seikaly and T.T. Tidwell, *Tetrahedron, 42* (1986) 2587.

[6] For some recent relevant examples and a review (6e) see: (a) D.L. Reger, E. Mintz and L. Lebioda, *J. Am. Chem. Soc., 108* (1986) 1940; (b) A.G.M. Barrett, J. Mortier, M. Sabat and M.A. Sturgess, *Organometallics, 7* (1988) 2553; (c) D.L. Reger, S.A. Klaeren, J.E. Babin and R.D. Adams, *Organometallics, 7* (1988) 181; (d) L.S. Liebeskind, M.E. Welker and R.W. Fengl, *J. Am. Chem. Soc., 108* (1986) 6328; (e) M.D. Johnson, *Acc. Chem. Res. 11*, (1978), 57.

[7] For some examples of this reactivity see (a) M. Shimizu, R. Ando and I. Kuwajima, *J. Org. Chem., 49* (1984) 1230; (b) R.J. Chorvat, J.R. Palmer and R. Pappo, *J. Org. Chem., 43* (1978) 966.

[8] T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem., 3* (1956) 104.

[9] (a) T.A. Shackleton and M.C. Baird, *Organometallics, 8* (1989) 2225; (b) T.H. Whitesides and J. Shelley, *J. Organomet. Chem., 92* (1975) 215.

[10] (a) M. Rosenblum and J.C. Watkins, *J. Am. Chem. Soc., 112* (1990) 6316; (b) M.F. Semmelhack and J.W. Herndon, *Organometallics, 2* (1983) 363; (c) for a related example of Fp removal under basic conditions see A. Rosan and M. Rosenblum, *J. Org. Chem., 40* (1975) 3622.

[11] (a) D. Seebach, R. Amstutz and J.D. Dunitz, *Helv. Chim. Acta, 64* (1981) 2622; (b) D.J. Cram and J.-P. Mazaleyrat, *J. Am. Chem. Soc., 103* (1981) 4585; (c) T. Mukaiyama, K. Soai, T. Sato, H. Shimizu and K. Suzuki, *J. Am. Chem. Soc., 101* (1979) 1455.

[12] R.A. Ruden, *J. Org. Chem., 39* (1974) 3607.

[13] (a) M. Saha and K.M. Nicholas, *J. Org. Chem., 49* (1984) 418 and references cited therein; (b) W.A. Smit, A.A. Schegolev, A.S. Gybin and G.S. Mikaelian, *Synthesis* (1984) 887 and references cited therein.

[14] (a) B. Foxman, D. Marten, A. Rosan, S. Raghu and M. Rosenblum, *J. Am. Chem. Soc., 99* (1977) 2160; (b) D.W. Lichtenberg and A. Wojcicki, *J. Organomet. Chem., 94* (1975) 311; (c) P. Klemarczyk and M. Rosenblum, *J. Org. Chem., 43* (1978) 3488.

[15] A. Hassner and J. Dillon, *Synthesis, 9* (1979) 689.

[16] T.S. Abram, R. Baker, C.M. Exon and V.B. Rao, *J. Chem. Soc. Perkin Trans. 1* (1982) 301.

[17] A. Bucheister, P. Klemarczyk and M. Rosenblum, *Organometallics, 1* (1982) 1679.

[18] M. Rosenblum and P.S. Waterman, *J. Organomet. Chem., 187* (1980) 267.

[19] R. Baker, V.B. Rao and E. Erdik, *J. Organomet. Chem., 243* (1983) 451.

[20] See Ref. [1a] and references cited therein.

[21] (a) H.A. Staab, *Angew. Chem., Int. Ed. Engl. 1* (1962) 351; (b) D.C. Baker and S.R. Putt, *Synthesis* (1978) 478.

[22] (a) R.D. Adams, A. Davison and J.P. Selegue, *J. Am. Chem. Soc., 101* (1979) 7232; (b) G.J. Baird and S.G. Davies, *J. Organomet. Chem., 262* (1984) 215.

[23] E.C. Taylor, A. McKillop and G.H. Hawks, *Org. Syn. Coll. Vol VI* (1988) 549.

[24] M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.*, (1963) 189.