Fe$_2$(CO)$_9$-mediated [5+1] cycloaddition of vinylcyclopropanes and CO for the synthesis of α, β-cyclohexenones

Cheng-Hang Liu, Zhe Zhuang, Sritama Bose, Zhi-Xiang Yu *

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering, College of Chemistry, Peking University, Beijing 100871, China

A B S T R A C T

A Fe$_2$(CO)$_9$-mediated [5+1] cycloaddition of vinylcyclopropanes (VCPs) and CO to α, β-cyclohexenones has been developed. The reaction can tolerate aryl and aliphatic groups at the α-position of VCPs, while VCP substrates with vinyl or alkynyl substitutions are not suitable ones. In addition, this reaction can also be used to synthesize bicyclic rings if an aryl group is attached to the vinyl moiety of the substrate. Compared to the Fe(CO)$_5$-mediated [5+1] reaction, the use of cheap and safe Fe$_2$(CO)$_9$ and abandoning the photo-irradiation conditions are the two major advantages of the present method.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

During the last 100 years, many reactions and strategies to synthesize the ubiquitously found six-membered carbocycles have been discovered and developed. Among them, the most widely used reaction is the Diels–Alder reaction between dienes and dienophiles.[1] But the Diels–Alder reaction and other existing methods could be inefficient to reach six-membered carbocycles that have substitution patterns and stereochemistries unmatched with the requirements of the known reactions and methods. Consequently, it is significant to develop new reactions and methods to access six-membered carbocycles, which can power the arsenal of synthetic chemists so that the synthesis of the target molecules could have more chances to reach ideal synthesis.[2]

Transition metal-mediated or -catalyzed [5+1] cycloadditions of vinylcyclopropanes/allenylcyclopropanes and CO has emerged recently as alternative approaches to the synthesis of six-membered cyclohexenones.[3] The efficiency of these reactions towards the construction of important skeletons with six-membered carbocycles has been demonstrated by several groups. Typically, high-price noble metals such as Rh[4,5] and Ir[6] play the leading role in the [5+1] cycloadditions (Scheme 1a). Replacing these expensive and potentially toxic metals by inexpensive, earth-abundant, environmentally benign, and less toxic metals like Co and Fe would be more advantageous in terms of costs and sustainability. In 2005, de Meijere's group reported that Co$_2$(CO)$_8$ can mediate stoichiometrically or catalytically (under CO balloon pressure) [5+1] cycloaddition under mild conditions (usually at room temperature).[4a] In their work, the rather special vinylcyclopropanes (VCPs), in which the double bond of VCP is part of a methylenecyclopropane (MCP), show higher reactivity due to the enhanced nucleophilicity of the MCP moiety. Iwasawa's group also reported the Co$_2$(CO)$_8$-mediated [5+1] transformation of allenylcyclopropanols to 1,4-hydroquinones, where formation of the aromatic compounds could be the driving force for the success of this reaction.[7]
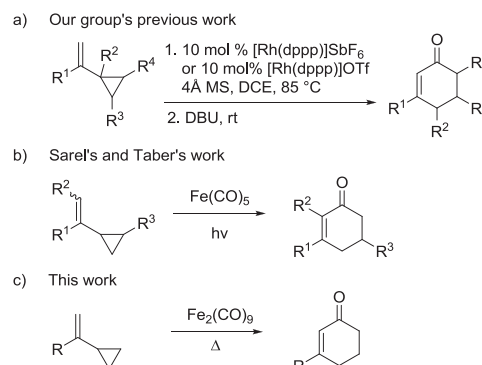
Scheme 1. (a) Our group's Rh-catalyzed [5+1] cycloaddition. (b) Iron-mediated photo-[5+1] cycloaddition. (c) This work.

* Corresponding author. E-mail address: yuzx@pku.edu.cn (Z.-X. Yu).

In contrast, cheap iron-mediated photo-[5+1] reaction of VCPs and CO has a broad reaction scope.[8,9] The iron-mediated [5+1] cyclo-addition was originally developed by Sarel's group,[10] in which they used $Fe(CO)_5$ or $Fe_2(CO)_9$ under ultraviolet irradiation condition.[11,12] After that, Taber's group further advanced photo-irradiated and iron-mediated [5+1] cycloaddition[13a–c] and applied such a methodology to the total synthesis of natural products[13d–f] (Scheme 1b). However, a limitation in both the original and modified iron-mediated [5+1] cycloadditions is that the reaction had to be carried out by photoirradiation, which is difficult for reaction scale-up. Another drawback of the photo-irradiated and iron-mediated [5+1] cycloadditions is the use of toxic and volatile $Fe(CO)_5$. Therefore, we were interested in developing a new iron-mediated [5+1] reaction of VCPs and CO that needs neither difficultly handled $Fe(CO)_5$ nor photoirradiation conditions.

We noticed that $Fe_2(CO)_9$ is a cheap[14] and much easily handled solid. $Fe_2(CO)_9$ is also regarded as precursor of $Fe(CO)_4$,[15a] which is the active species in the $Fe(CO)_5$-mediated photo-[5+1] reaction. We also found that stoichiometrical $Fe_2(CO)_9$ has been used in the carbonylation reactions such as Pauson–Khand reaction[15,16] and [4+1] cycloaddition of allenyl imines and CO[17] under photoirradiation-free conditions. Therefore, we hypothesized that the original photo-irradiated $Fe(CO)_5$-mediated [5+1] reaction of VCPs and CO could be advanced to a $Fe_2(CO)_9$-mediated [5+1] reaction without photoirradiation.[18] We report here our realization of such a $Fe_2(CO)_9$-mediated thermal [5+1] cycloaddition for the construction of α, β-cyclohexenones (Scheme 1c).
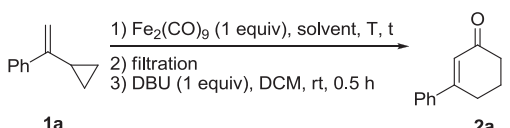
2. Results and discussion

We first screened the reaction conditions using the easily accessible VCP **1a** as the standard substrate and $Fe_2(CO)_9$ as the mediator without using photoirradiation. The [5+1] reaction can give both unconjugated and conjugated cyclohexenones. To obtain α, β-cyclohexenone **2a** exclusively, after the accomplishment of the [5+1] cycloaddition, DBU was added to the reaction solution and stirred at room temperature for 30 min to realize the complete isomerization. Initially, the reaction was performed using ^{i}PrOH as solvent and stirred at 90 °C for 1 h. The desired product **2a** was isolated in a moderate yield and a byproduct **4a** was detected (Table 1, entry 1). Alcohol **4a** is the reductive product of the unconjugated intermediate **3a** and may be formed by the iron-catalyzed hydrogen transfer from ^{i}PrOH.[19] Apart from the reductive byproduct **4a**, some unidentified byproducts with low polarity similar to the substrate **1a**, were also observed from the TLC plate. We proposed that such low-polar byproducts might originate from the heat-induced rearrangement of VCP **1a**.[20] When ^{n}PrOH was used as the solvent, the reaction yield was increased to 62%, together with a byproduct, ketal **5a**, which can be isolated (Table 1, entry 2). To avoid the formation of byproducts **4a** and **5a**, we chose tertiary alcohols such as ^{t}amylOH (tert-amyl alcohol) and ^{t}BuOH as the solvents, finding that the yield could be increased to 65% when the reaction was performed in ^{t}BuOH (Table 1, entry 4). Further prolonging the reaction time led to the increase of the reaction yield of the desired product **2a** to 80%, accompanied by a trace amount of low-polar rearrangement product (Table 1, entry 6). We also screened several other solvents such as HFIP (hexafluoroisopropanol), ethers, toluene, DCE and acetonitrile (Table 1, entries 7–15). HFIP and acetonitrile were found to be inefficient for the present transformation as only a trace amount of target [5+1] product could be isolated in these reaction systems. In ether solvents, the transformation was slow and some other unidentified byproducts were observed. The [5+1] reaction performed in toluene or DCE only gave moderate yields. We also observed that, reducing the equivalent of $Fe_2(CO)_9$ or carrying out such a transformation under the balloon-pressured CO gas had no

benefit for the [5+1] reaction (Table 1, entries 16–18). Very similar result was obtained when $Fe_3(CO)_{12}$ (instead of $Fe_2(CO)_9$) was used under the same reaction conditions (Table 1, entry 19). Therefore, we chose the reaction conditions in entry 6 of Table 1 as the optimal conditions for Fe-mediated [5+1] reaction.

The reaction scope of the iron-mediated [5+1] cycloaddition

Table 1
Optimization of the reaction conditions

Entry[a]	Solvent	T (°C)	t (h)	Yield (%)[b]
1	^{i}PrOH	90	1	53[c]
2	^{n}PrOH	90	4	62[d]
3	^{t}amylOH	90	4	49
4	^{t}BuOH	90	4	65
5	^{t}BuOH	90	7	70
6	**^{t}BuOH**	**90**	**12**	**80**
7	HFIP	60	3	3
8	THF	60	4	58
9	DME	90	4	32
10	Dioxane	90	8	58
11	CPME	90	5	41
12	Toluene	90	6	44
13	DCE	90	7	59
14	MeCN	Reflux	3	13[e]
15	DMF	90	6	—[f]
16[g]	^{t}BuOH	90	12	76
17[h]	^{t}BuOH	90	12	64
18[h,i]	^{t}BuOH	90	12	34
19[j]	^{t}BuOH	90	12	79

[a] The reaction was performed in 0.3 mmol scale and 2 mL solvent was used.
[b] Isolated yields.
[c] Byproduct **4a** can be detected by ^{1}H NMR.
[d] Byproduct **5a** can be detected by ^{1}H NMR.
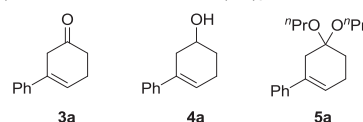[e] Large amount of the substrate **1a** remained.
[f] Complex mixture.
[g] 0.5 equiv $Fe_2(CO)_9$ was used.
[h] 0.2 equiv $Fe_2(CO)_9$ was used.
[i] The reaction was performed under the CO atmosphere (1 atm).
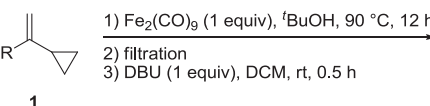[j] 1 equiv $Fe_3(CO)_{12}$ was used instead of $Fe_2(CO)_9$.

under the optimal reaction conditions was studied (Table 2 and Fig. 1). It was found that the electronic properties of the substitutions in the benzene rings of aryl-substituted VCPs had little effect on the yields of the [5+1] reactions (Table 2, **2b–g**). Besides the phenyl group, both electron-withdrawing and -donating groups gave good yields. The position of the substitutions on the aryl ring of the substrate had limited effect on the outcome of the reaction. We found that para-, meta- and ortho-methoxy substituted substrates gave similar yields (Table 2, **2g–i**). We also tried the naphthyl-substituted substrates **1j** and **1k**, finding that the corresponding products **2j** and **2k** were obtained in moderate yields. In addition, heterocyclic aryl substituted substrate **1l** could also give the cyclohexenone product in a good yield when it was subjected to the iron-mediated [5+1] reaction.

Apart from the aryl substituted substrates, alkyl substituted VCP substrates were also synthesized and tested for the present [5+1] cycloaddition reaction (Table 2, **2m–p**). Moderate yields could be achieved and more byproducts could be observed from the TLC

Table 2
Scope of the [5+1] reaction

[a] All the yields shown here were the average of two runs on a 0.3 mmol scale. [b] 24 h. [c] 2 equiv. TsOH · H2O was used instead of DBU and stirred for 2 h at rt.
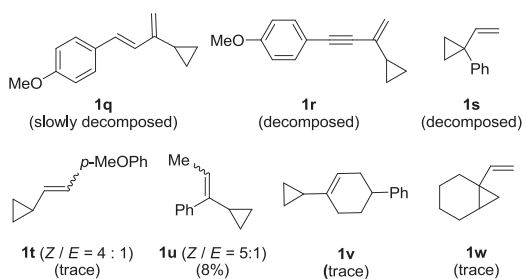
Fig. 1. Some unsuccessful substrates.

plate compared to those from the reactions of the aryl substituted substrates. For substrate **1p** with a TSNH substituent, we had to use *para*-toluenesulfonic acid monohydrate instead of DBU to get the final isomerization cyclohexenone product **2p** after finishing the [5+1] cycloaddition (when DBU was used, **2p** decomposed).[4b] The desired product **2p** was isolated in 42% yield under the acidic conditions.

Furthermore, we synthesized the vinyl and alkynyl substituted VCP substrates **1q** and **1r**, which had never been applied in previously reported [5+1] cycloadditions. To our disappointment, both compounds **1q** and **1r** were not suitable substrates for the present iron-mediated [5+1] reaction: complex mixtures were obtained under the standard reaction conditions, which might have originated from the side-reactions of tricarbonyl iron coordinated substrates (via the diene or ene-yne moieties as the ligands). Compound **1s** was not a suitable substrate either. For VCP substrates **1t** and **1u** with internal alkenes, only trace products could be obtained after heating the reactions for 24 h in ^{t}BuOH solution. The corresponding cyclohexenone product **2u** (from **1u**'s [5+1] reaction) could be isolated in 8% yield.[21,22] Both substrates **1v** and **1w** failed to give the desired [5+1] cycloadducts with a bicyclic skeleton, because these two substrates slowly decomposed under the optimized reaction conditions.[23]

Considering the importance of the substitutions at the α-position of VCPs for the [5+1] reactions, we synthesized bicyclic compound **1x** with a 4-methoxylphenyl group attached to the vinyl moiety and subjected it to the [5+1] reaction. To our delight, the

corresponding bicyclic product **2x** could be isolated in 60% yield (Scheme 2). This result implied that the Fe2(CO)9-mediated [5+1] reaction could be used to synthesize some structurally complicated skeletons.
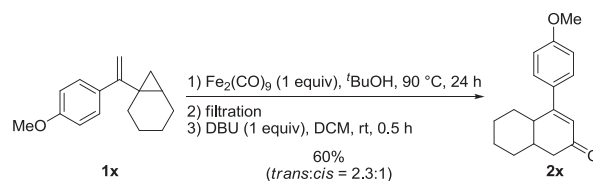
Scheme 2. [5+1] reaction of bicyclic compound **1x**.

3. Conclusion

In conclusion, we have developed an efficient photoirradiation-free Fe2(CO)9-mediated [5+1] cycloaddition to synthesize conjugated cyclohexenones from vinylcyclopropanes and CO. The reaction tolerates aryl and aliphatic groups at the α-position of VCPs, while VCP substrates with vinyl or alkynyl substitutions are not suitable substrates. Bicyclic ring can also be synthesized for VCP with an aryl substitution in the vinyl moiety (see **1x**). Although the substrate scope of Fe2(CO)9-mediated [5+1] cycloaddition, compared to the photo-irradiated Fe(CO)5-mediated [5+1] reaction, is not satisfactory, the use of cheap and safe Fe2(CO)9 and abandoning the photo-irradiation conditions are the two major advantages of the present method.

4. Experimental section

4.1. General information

Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification unless otherwise indicated. Analytical pure ^{t}BuOH was used directly. Fe2(CO)9 was stored in glove box at −20 °C and weighted in the glovebox. NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) nuclear magnetic resonance spectrometers. ^{1}H NMR spectra are reported relative to Me4Si (0.00 ppm). Data for ^{13}C NMR are reported relative to residual solvent peak (CDCl3: 77.0 ppm). Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectrometer (FTIR) and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI) and Micromass U.K. GCT GC–MS mass spectrometer (EI).

4.2. Typical procedure for the [5+1] cycloaddition of (1-cyclopropylvinyl)benzene (1a) to 3-phenyl-cyclohex-2-enone (2a)

A solution of **1a** (44.5 mg, 0.30 mmol) and Fe2(CO)9 (109 mg, 0.30 mmol) in ^{t}BuOH (2 mL) was stirred under an argon atmosphere at 90 °C for 12 h. After the accomplishment of the [5+1] cycloaddition reaction, the reaction mixture was cooled to room temperature and then filtered through a short silica gel eluting with DCM. The filtrate was concentrated and a DCM solution of DBU (45 mg, 0.3 mmol in 2 mL DCM) was added. The mixture was stirred at room temperature for 30 min and then concentrated. The crude mixture was submitted to flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford the corresponding product **2a** as a white solid (42.6 mg, 80% reaction yield).

The second run of this reaction using 44.0 mg **1a** gave 40.7 mg **2a**, with a reaction yield of 78%. Therefore, the average yield of two runs for this substrate was 79%, which is given in Table 2.

2a: White solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56−7.50 (m, 2H), 7.43−7.38 (m, 3H), 6.42 (t, J=1.3 Hz, 1H), 2.79−2.74 (m, 2H), 2.51−2.45 (m, 2H), 2.19−2.11 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature.[4b]

The similar procedure was used for the [5+1] cycloaddition reactions of **1b**−**1p** and **1x**. For substrates **1j** and **1x**, the reaction system was stirred at 90 °C for 24 h. For substrate **1j**, after filtration, *para*-toluenesulfonic acid monohydrate was added instead of DBU and the mixture was stirred at room temperature for 2 h.

4.3. 4-(4-Methoxylphenyl)-4a,5,6,7,8,8a-hexahydronaphthalen-2(1*H*)-one (2x)

First run: 69.3 mg **1x** was converted to 47.1 mg **2x**, with a yield of 60%. Second run: 67.5 mg **1x** was converted to 46.2 mg **2x**, with a yield of 61%. Therefore, the average yield of two runs for this substrate was 60%.

The ratio of two isomers (2.3:1, see Scheme 2) was determined by the integral of ^{1}H NMR of vinyl hydrogen. Pure products ***trans*-2x** and ***cis*-2x** could be obtained by preparative thin layer chromatography. The relative configuration was assigned on comparison by analogy with the chemical shifts of similar compound.[23]

***trans*-2x**: Colorless oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (d, J=8.7 Hz, 2H), 6.91 (d, J=8.7 Hz, 2H), 6.03 (d, J=2.1 Hz, 1H), 3.83 (s, 3H), 2.56−2.47 (m, 1H), 2.42 (dd, J=16.1, 3.6 Hz, 1H), 2.29 (dd, J=16.1, 14.1 Hz, 1H), 2.03−1.95 (m, 1H), 1.92−1.74 (m, 4H), 1.45−1.24 (m, 3H), 0.90−0.79 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.5, 165.2, 159.9, 131.3, 128.0, 127.6, 113.7, 55.3, 44.8, 43.8, 41.6, 33.2, 30.7, 26.9, 25.7. IR (KBr): υ 2925, 2855, 2247, 1659, 1606, 1511, 1446, 1332, 1244, 1179, 1034, 832 cm^{-1}. HRMS (ESI) calcd for C$_{17}$H$_{21}$O$_2$ (M+H$^+$): 257.1536. Found: 257.1541.

***cis*-2x**: Colorless oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, J=8.8 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H), 6.30 (s, 3H), 3.85 (s, 1H), 2.93−2.85 (m, 1H), 2.70 (dd, J=16.6, 14.7 Hz, 1H), 2.55−2.44 (m, 1H), 2.23 (dd, J=16.9, 4.1 Hz, 1H), 1.80−1.57 (m, 5H), 1.52−1.30 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 200.8, 164.4, 161.2, 129.8, 128.1, 123.0, 114.2, 55.4, 39.3, 37.5, 33.6, 30.4, 27.2, 25.9, 20.4. IR (KBr): υ 2930, 2853, 2247, 1656, 1600, 1512, 1256, 1231, 1182, 1033, 836 cm^{-1}. HRMS (ESI) calcd for C$_{17}$H$_{21}$O$_2$ (M+H$^+$): 257.1536. Found: 257.1539.

Acknowledgments

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.01.046.

References and notes

1. (a) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668; (b) Funel, J.-A.; Abele, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3822.

2. (a) Hendrickson, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 5784; (b) Gaich, T.; Baran, P. S. *J. Org. Chem.* **2010**, *75*, 4657; (c) Wender, P. A.; Verma, V. A.; Paxton, T. J.; Pillow, T. S. *Acc. Chem. Res.* **2008**, *41*, 40; (d) Yu, Z.-X.; Liang, Y. In *Organic Chemistry-breakthroughs and Perspectives*; Ding, K., Dai, L., Eds.; Wiley-VCH: Weinheim, Germany, 2012; pp 561−601.

3. For a review of transition metal-catalyzed or -mediated [5+1] cycloadditions, see: (a) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *471*, 1; (b) Fu, X.-F.; Yu, Z.-X. In *Methods and Applications of Cycloaddition Reactions in Organic Syntheses*; Nishiwaki, N., Ed.; Wiley-VCH: Weinheim, Germany, 2014; pp 551−564; (c) Gao, Y.; Fu, X.-F.; Yu, Z.-X. *Top. Curr. Chem.* **2014**, *346*, 195.

4. For Rh-catalyzed [5+1] reactions of vinylcyclopropanes and CO, see: (a) Kurahashi, T.; de Meijere, A. *Synlett* **2005**, 2619; (b) Jiang, G.-J.; Fu, X.-F.; Li, Q.; Yu, Z.-X. *Org. Lett.* **2012**, *14*, 692.

5. For Rh-catalyzed [5+1] reaction of allenylcyclopropanes and CO, see: (a) Shu, D.; Li, X.; Zhang, M.; Robichaux, P. J.; Tang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 1346; (b) Shu, D.; Li, X.; Zhang, M.; Robichaux, P. J.; Guzei, I. A.; Tang, W. *J. Org. Chem.* **2012**, *77*, 6463; (c) Zhang, M.; Tang, W. *Org. Lett.* **2012**, *50*, 3756.

6. For Ir-catalyzed [5+1] reaction of allenylcyclopropanes and CO, see: Murakami, M.; Itami, K.; Ubukat, M.; Tsuji, I.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 4.

7. (a) Iwasawa, N.; Owada, Y.; Matsuo, T. *Chem. Lett.* **1995**, *115*; (b) Owada, Y.; Matsuo, T.; Iwasawa, N. *Tetrahedron* **1997**, *53*, 11069.

8. For a review of iron-catalyzed organic reactions, see: (a) Bauer, E. B. *Curr. Org. Chem.* **2008**, *12*, 1341; (b) Bolm, C.; Legros, J.; Paih, L.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217; (c) Bauer, I.; Knolker, H.-J. *Chem. Rev.* **2015**, *115*, 3170; (d) Klein, J. E. M. N.; Plietker, B. *Org. Biomol. Chem.* **2013**, *11*, 1271.

9. For selected examples of iron-catalyzed C−C bond activations of VCPs, see: (a) Sherry, B. D.; Fürstner, A. *Chem. Commun.* **2009**, 7116; (b) Dieskau, A. P.; Holzwarth, M. S.; Plietker, B. *J. Am. Chem. Soc.* **2012**, *134*, 5048.

10. (a) Ben-Shoshan, R.; Sarel, S. *Chem. Commun.* **1969**, 883; (b) Victor, R.; Ben-Shoshan, R.; Sarel, S. *Tetrahedron Lett.* **1970**, *49*, 4253; (c) Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204; (d) Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631 Also see Ref. 3a.

11. Thermal [5+1] reactions using Fe(CO)$_5$ were also reported when ceric ammonium nitrate (CAN) and high temperature (150 °C) was used, see: (a) Schulze, M. M.; Gockel, U. *Tetrahedron Lett.* **1996**, *37*, 357; (b) Schulze, M. M.; Gockel, U. *J. Organomet. Chem.* **1996**, *525*, 155.

12. For preliminary mechanistic study of iron-mediated [5+1] reactions of VCPs and CO, see ref. 10d and 11b.

13. (a) Taber, D. F.; Kanai, K.; Jiang, Q.; Bui, G. *J. Am. Chem. Soc.* **2000**, *122*, 6807; (b) Taber, D. F.; Joshi, P. V.; Kanai, K. *J. Org. Chem.* **2004**, *69*, 2268; (c) Taber, D. F.; Guo, P.; Guo, N. *J. Am. Chem. Soc.* **2010**, *132*, 11179; (d) Taber, D. F.; Bui, G.; Chen, B. *J. Org. Chem.* **2001**, *66*, 3423; (e) Taber, D. F.; Sheth, R. B. *J. Org. Chem.* **2008**, *73*, 8030; (f) Taber, D. F.; Sheth, R. B.; Tian, W. *J. Org. Chem.* **2009**, *74*, 2433.

14. Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317.

15. (a) Williams, D. R.; Shah, A. A.; Mazumder, S.; Baik, M.-H. *Chem. Sci.* **2013**, *4*, 238; (b) Williams, D. R.; Shah, A. A. *J. Am. Chem. Soc.* **2014**, *136*, 8829.

16. For Fe$_2$(CO)$_9$ catalyzed hetero-Pauson−Khand-type [2+2+1] cycloaddition, see: (a) Imhof, W.; Göbel, A. *J. Mol. Catal. A: Chem.* **2003**, *197*, 15; (b) Imhof, W.; Anders, E.; Göbel, A.; Görls, H. *Chem.—Eur. J.* **2003**, *9*, 1166; (c) Imhof, W.; Anders, E. *Chem.—Eur. J.* **2004**, *10*, 5717.

17. Sigman, M. S.; Eaton, B. E. *J. Org. Chem.* **1994**, *59*, 7488.

18. Fe$_2$(CO)$_9$-mediated ring-opening process of VCPs has been reported and Fe-carbonyl complexes containing both π-allyl and σ-components could be isolated, see: (a) Aumann, R. *Angew. Chem., Int. Ed.* **1971**, *10*, 188; (b) Moriarty, R. M.; Yeh, C.-L. *J. Am. Chem. Soc.* **1971**, *93*, 6709; (c) Moriarty, R. M.; Yeh, C.-L.; Chen, K.-N. *Tetrahedron Lett.* **1972**, *13*, 5325; (d) Sarel, S.; Ben-Shoshan, R.; Kirson, B. *Isr. J. Chem.* **1972**, *10*, 787.

19. Similar reaction has been reported using Fe$_3$(CO)$_{12}$, see: Yu, S.; Shen, W.; Li, Y.; Dong, Z.; Xu, Y.; Li, Q.; Zhang, J.; Gao, J. *Adv. Synth. Catal.* **2012**, *354*, 818.

20. (a) Sarel, S.; Ben-Shoshan, R.; Kirson, B. *J. Am. Chem. Soc.* **1965**, *87*, 2517 Also see Ref. 11a.

21. The ^{1}H NMR spectroscopy is consistent with the literature: Jin, T.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 5259.

22. Low yield of **1u** compared to **1a** was also reported by Schulze in the Fe(CO)$_5$/CAN-mediated [5+1] reaction, showing that VCP substrates with internal alkene were not good for the [5+1] reaction, see ref. 11a.

23. For substrate **1w**, after stirred for 1 h, 18% [5+1] cycloadduct **2w** product could be detected according to the ^{1}H NMR (1,3,5-trimethoxybenzene as internal standard substance). The ^{1}H NMR spectroscopy of **2w** is consistent with the literature: Kim, W. H.; Lee, J. H.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2009**, *131*, 12576.