[3 + 2] Cyclopentane Annulation Reactions Using Organoiron Reagents†

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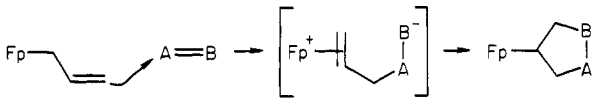
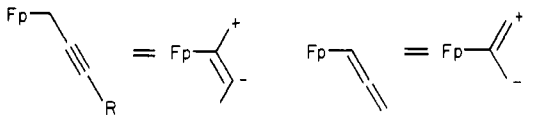
The allyl ligand in the organoiron complex **1**, (η^1-allyl)Fp [Fp = (η^5-C_5H_5)Fe(CO)$_2$], serves as a C_3 dipolar synthon in aluminum bromide catalyzed reactions with cyclohexenone and by itself with 2-carbethoxycycloalkenones, affording cyclopentane annulation products. The structural limitations of these reactions with respect to substitution of the enone and the organometallic reagent have been examined. The acetylenic ligand in (η^1-2-butynyl)Fp similarly underdoes aluminum bromide catalyzed [3 + 2] cycloaddition reaction with cyclohexenone, but (η^1-1-propynyl)Fp yields instead the product of [2 + 2] cycloaddition.

While [4 + 2] cycloadditions serve widely for the construction of carbocyclic and heterocyclic[1] 6-membered ring systems and a number of related hetero dipolar reagents are available for the synthesis of 5-membered heterocycles by [4 + 1][1] or [3 + 2][2] cycloaddition reactions, analogous synthons for the construction of cyclopentane rings are less accessible.[3] Among the latter reagents, dicarbonyl[η^5-cyclopentadienyl)(η^1-allyl)iron complexes, such as **1** and its congeners, have been shown to behave as 1,3 dipoles

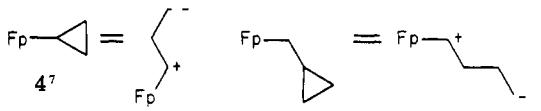


1

in nonconcerted [3 + 2] cycloadditions with a number of electrophiles, affording both carbocyclic and heterocyclic 5-membered rings (Fp = $C_5H_5Fe(CO)_2$). Such cycloadditions are by no means confined to these allyliron complexes but have been shown to occur as well with the related iron complexes **2**–**5**, all of which yield cycloadducts derived from electrophile-initiated attack on the metal-activated unsaturated or cyclic ligand



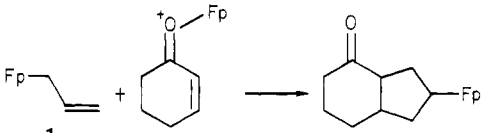
2[5,8] **3**[6]



4[7] **5**[8]

Although these complexes enter into cycloaddition reactions with a number of heteroatomic and carbon-centered electrophilic dipolarophiles, such reactions are confined for the most part to the more reactive members of this class of electrophile. Of the carbon electrophiles, only tetracyanoethylene,[4-8] 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene,[5c] benzylidenemalononitrile,[4] diethyl methylenemalonate,[4] and 1,2-dicyano-4,5-dichloroquinone[4] prove to be sufficiently reactive cycloaddition partners. The research summarized here was undertaken with a view to extending these reactions to the synthetically more useful α,β-unsaturated carbonyl systems.

Cyclohexenone itself fails to react with **1** even at elevated temperatures. However, activation of the enone may be achieved through Lewis acid complexation. We had previously shown that the Fp cation forms relatively stable complexes with a variety of carbonyl groups, including aldehydes, ketones, esters and amides.[9] An X-ray crystallographic structure determination of the cation derived by complexation of Fp^+ to 3-methylcyclohexenone shows the iron to be σ bonded to the oxygen atom.[9] When **1** was allowed to react with Fp(cyclohexenone)$^+BF_4$ (**6**) in refluxing methylene chloride, the hydrindanone **7** was formed in 10% yield.



1 **6** **7**

A number of other Lewis acid reagents were subsequently examined, among them $LiBF_4$, $TiCl_4$, $SbCl_5$, and $AlCl_3$. Of these, only $AlCl_3$ afforded cycloadduct **7** but again in low yield (8%). The stronger Lewis acid $AlBr_3$ was more effective, for when **1** was added at −78 °C to a methylene chloride solution of cyclohexenone containing 5 molar percent of freshly sublimed aluminum bromide, the cycloadduct **7** could be isolated in modest yield (45%).

That the product is a mixture of two stereoisomers is evident from an examination of its proton NMR spectrum,

† Dedicated to the memory of Professor Rowland Pettit.

(1) Hamer, Jan "1-4-Cycloaddition Reactions"; Academic Press: New York, 1967.
(2) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 212. Gompper, *Ibid.* **1969**, *8*, 312.
(3) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. Marino, J. P.; Katterman, L. C. *J. Chem. Soc., Chem. Commun.* **1979**, 946. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429. Turro, N. J. *Acc. Chem. Res.* **1969**, *25*, 2. Dolfini, J. E.; Menick, K.; Corliss, P. *Tetrahedron Lett.* **1966**, 4421. Cooke, F.; Schwindeman, J.; Magnus, P. *Ibid.* **1979**, 1995. Wender, P. A.; Dreyer, G. B. *Tetrahedron* **1981**, *37*, 4445. Paquette, L. A. In "Topics in Current Chemistry"; Verlag Chemie: Berlin, 1979. Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. Takahashi, S.; Suzuku, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1976**, 839.
(4) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495 and references therein.
(5) (a) Thomasson, J. E.; Robinson, P. W.; Ross, D. A.; Wojcicki, A. *Inorg. Chem.* **1971**, *10*, 2130. (b) Lichtenberg, D. W.; Wojcicki, A. *Inorg. Chim. Acta* **1973**, *7*, 311. (c) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 2506. (d) Chen, L. S.; Lichtenberg, D. W.; Robinson, P. W.; Yamamoto, Y.; Wojcicki, A. *Inorg. Chim. Acta* **1977**, *25*, 165.
(6) Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060.
(7) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, J. *J. Am. Chem. Soc.* **1972**, *94*, 4354.
(8) Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1971**, *93*, 5299.
(9) Foxman, B. F.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253.

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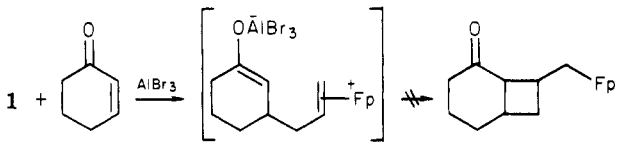
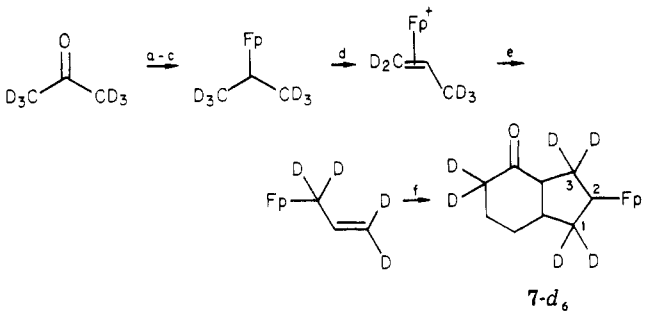
for while this shows only a single resonance, two such resonances of equal intensity are apparent in the presence of Eu(fod)$_3$. A ^{13}C NMR spectrum of the product confirmed this conclusion and furthermore served to exclude the presence of isomeric bicyclo[4.2.0]octanone adducts, which could in principle derive from closure of the intermediate dipolar intermediate to give a cyclobutane ring. The ^{13}C NMR spectrum of the product mixture failed to show any resonance between 0 and 10 ppm, characteristic of the $FpCH_2$ methylene group.[10]

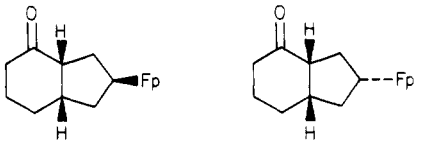


Of the four possible hydrindanone structures **7a–d**, the *trans*-hydrindanone structures **7c,d** may be excluded on the basis of the following observations. The hexadeuterated cyclization product **7-d_6** specifically deuterated at C-1, C-3, and C-5 was prepared from [6,6-$^2H_2$]cyclohexenone[11] and [1,1,3,3-$^2H_4$](η^1-allyl)Fp as shown in the sequence

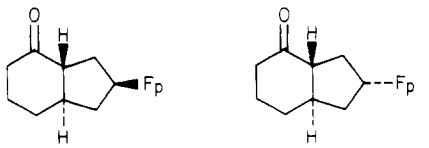


7-d_6

a, $NaBH_4$, diglyme; b, TsCl, pyridine, c, NaFp, THF; d, Ph_3CBF_4; e, Et_3N, CH_2Cl_2; f, [6,6-$^2H_2$]cyclohexenone, CH_2Cl_2, $AlBr_3$



7a **7b**

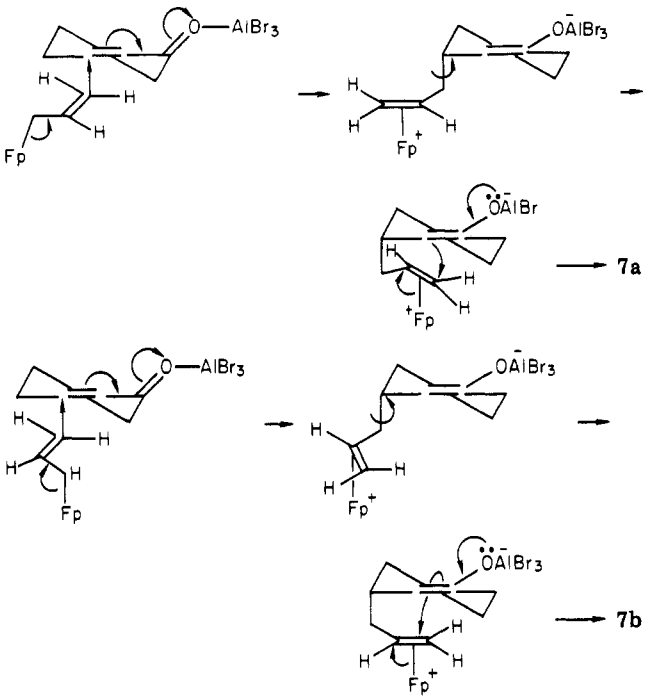


7c **7d**

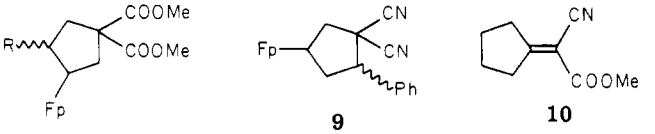
Examination of the proton NMR spectrum of the hexadeuterio complex in the presence of Eu(fod)$_3$ shows the low-field signal at δ 3.35, assignable to H-3a, as a doublet with $J_{3a,7a}$ = 8 Hz, consistent with the assignment of a *cis*-hydrindane structure **7a,b**.[12] A ^{13}C NMR spectrum of **7**, shows carbonyl resonance δ 214 further supporting this assignment.[12]

We have previously provided evidence that [3 + 2] cycloaddition reaction of (η^3-allyl)Fp complexes with electrophiles takes place by suprafacial addition of the electrophile to the C_3-allyl framework.[4] The present results show that closure of the dipolar intermediate, derived from the reaction of **1** and cyclohexenone, also occurs in a suprafacial manner with respect to the enone, affording the thermodynamically preferred *cis*-hydrindanone product. The formation of two diastereomers derives from the orientation of reacting components, which fixes the stereochemical outcome at C-2 in the product, as shown in Scheme I.

Scheme I



It should be possible to promote cycloaddition of (η^1-allyl)Fp complexes with enones, in the absence of Lewis acid catalysts, by further substitution of the acceptor olefin with electron-withdrawing groups. We had previously reported that electron-deficient olefins such as dimethyl methylenemalonate and benzylidenemalononitrile readily react with (η^1-allyl)Fp to give the cycloadducts **8a** and **9**.[4] Even the more sterically demanding (η^1-2-butenyl)Fp, as a mixture of cis and trans isomers, reacts with the methylenemalonate to give **8b** (64%), although **1** fails to react with the β,β-disubstituted cyanoacrylic ester **10**.



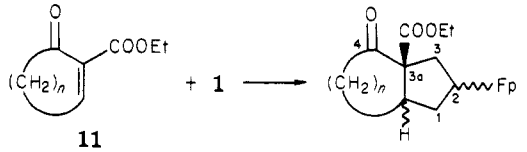
8a, R = H
b, R = Me

9 **10**

The 2-carbethoxycycloalkenones **11a–c**, readily available from the saturated ketoesters by the method of Reich,[13] were found to serve as useful models in these cycloaddition reactions. The 5- and 6-membered keto esters gave moderate yields of cycloadducts **12a,b** on reaction with **1** for 24 h in refluxing methylene chloride, but 2-carbethoxycycloheptenone **11c** gave only a low yield of cycloadduct **12c** under these conditions, and 60% of **1** was recovered unchanged. A proton NMR spectrum of **12b**, even in the presence of Eu(fod)$_3$, failed to give evidence for the presence of more than one isomer, but a ^{13}C spectrum of this

(10) Lennon, P.; Rosenblum, M. *J. Am. Chem. Soc.*, in press.
(11) Following the procefure employed for selective deuteration of cyclopentenone. Chao, T. H.; Laane, J. *J. Mol. Spectrosc.* **1973**, *48*, 266.
(12) Cicero, G. L.; Weisbuck, F.; Dana, G. *J. Org. Chem.* **1981**, *46*, 914. *cis*-4-Hydrindanones: $J_{3a,7a}$ = 9 Hz, δ(CO) 214. *trans*-4-Hydrindanones: $J_{3a,7a}$ = 11 Hz, δ(CO) 211.
(13) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

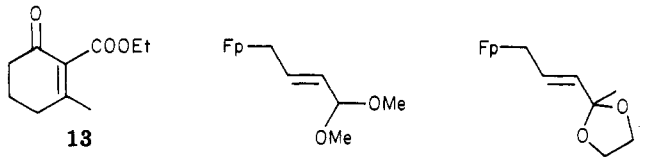
substance clearly shows that it is a mixture of two diastereomers. These show ^{13}C carbonyl resonance at δ 208 and are assigned *trans*-hydrindanone structures. By contrast, the proton and ^{13}C spectra of **12a** show that it is a single cis diasteromer.



11 **12**

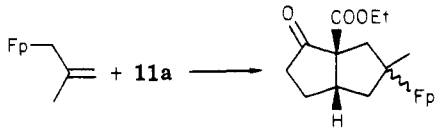
a, n = 2; b, n = 3; c, n = 4

These reactions are very sensitive to steric effects. Thus **1** failed to give any cycloadduct with the keto ester **13** under conditions which led to product with **11a–c**. Both reactants were recovered in high yield from this reaction. When the reaction was carried out at higher temperatures in refluxing 1,2-dichloroethane for 19 h, considerable decomposition of **1** occurred, the keto ester was recovered in moderate yield and no adduct could be isolated. Similarly, starting material was recovered unchanged from the attempted reaction of **11a** with the 3-substituted (η^1-allyl)Fp complexes **14** and **15**.



13 **14** **15**

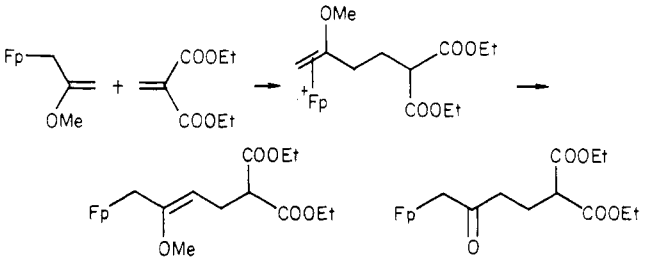
Although these results illustrate the sensitivity of the reaction to steric retardation at the initial site of carbon–carbon bond formation, the moderate yields of cyclized product **12a,b** suggest that closure of the intermediate zwitterion intermediate (Scheme I) may not be as sensitive to these effects. Furthermore, the formation of cycloadduct **16** from the reaction of (η^1-2-methallyl)Fp and **11a**



16

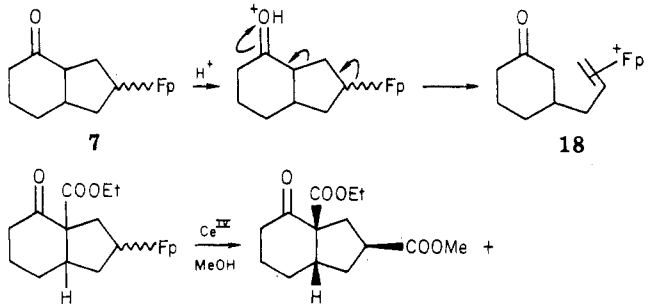
in moderate yield under standard reaction conditions suggests that alkyl substituents may also be tolerated in the donor complex at C-2. However (η^1-2-methoxyallyl)-Fp,[14] which would be expected to be a considerably better nucleophile than either (η^1-allyl)Fp or (η^1-2-methallyl)Fp, failed to give any cycloadduct with cyclohexenone either by itself or in the presence of aluminum bromide or with **12b**. It seems likely that, for these reactions, closure of the zwitterion intermediate may be impeded by the methoxy group, which would be expected to direct cyclization to a thermodynamically disfavored cyclobutane ring, while at the same time stabilizing the cationic center in the zwitterion.[15]

The effect of the methoxy group in retarding the ring closure step is evident from a comparison of the reaction of diethyl methylenemalonate with (η^1-allyl)Fp, (η^1-2-butenyl)Fp, and (η^1-2-methoxyallyl)Fp. As noted earlier the first two give cycloadducts **8a,b**, but the latter affords only the acylic keto ester **17**. This substance is most plausibly derived from the zwitterion intermediate by proton transfer and subsequently hydrolysis of the highly sensitive enol ether during workup of the reaction. Very similar observations have recently been reported by Abram, Baker, and Exon.[16]



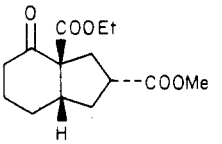
17

A clear demonstration of the reversibility of the cycloaddition reaction or more particularly of the ability of the Fp group to promote carbon–carbon bond cleavage is provided by the reaction of **7** with hydrogen chloride in methylene chloride, which gave the ring opened complex **18** rather than the anticipated demetalated product.[17] Demetalation can however be accomplished without ring opening by oxidative degradation. Treatment of **12b** with ceric ammonium nitrate in methanol solution gave the keto-diesters **19a,b** in 62% yield.



7 **18**

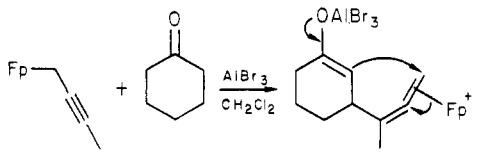
12b **19a**



19b

In order to complete this survey of cycloaddition reactions, the reaction of cyclohexenone with the organoiron complexes **2** (R = Me) and with **3** were examined. In the presence of catalytic amounts of aluminum bromide, cyclohexenone and **2** (R = Me) yield the anticipated cycloadduct **21** (20%). Both proton and ^{13}C NMR spectra show the product to be a single stereoisomer, and this is assigned a *cis*-hydrindenone structure (δ_{CO} 215).[12] This reaction may be depicted as proceeding stepwise by way of the cationic allene complex **20**.[5,8] The alternative closure of **20** at C-2 of the cationic allene center, to give the isomeric cycloadduct **22**, is without precedent and can in the present circumstance be excluded, since the product fails to exhibit high-field ^{13}C resonance characteristic of the $FpCH_2$ methylene group.[10]

(14) Preister, W.; Rosenblum, M.; Samuels, S. B. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 525. Abram, T. S.; Baker, R. *Ibid.* **1979**, *9*, 471.
(15) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930. Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4103.
(16) Abram, T. S.; Baker, R.; Exon, C. M. *Tetrahedron Lett.* **1979**, 4103.
(17) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Waterman, P. *J. Am. Chem. Soc.* **1980**, *102*, 7033.



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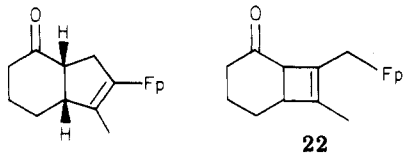
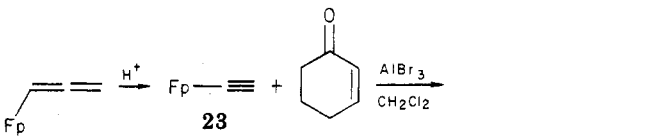


21 22

The reaction of the allenyl complex **3** with cyclohexenone, in the presence of aluminum bromide, takes an entirely unanticipated course and gives the cycloadduct **25**. The same product is obtained in considerably better yield when (η^1-1-propynyl)Fp (**23**) is used instead of **3**. Consequently it seems likely that **3** is initially isomerized by traces of acid to **23**,[18] and this latter complex is the effective reactant in both reactions. The formation of **25** may be accounted for in terms of the intermediacy of a metal stabilized vinylidene carbene[19] **24**, and the structure of the product is supported by the following spectral data. A proton NMR spectrum of the adduct exhibits vinyl methyl resonance at δ 1.72 (d, J = 1 Hz), while broad-band and off-resonance ^{13}C NMR spectra clearly show the presence of two fully substituted vinyl carbons, two tertiary carbon centers, three methylene groups, and a single methyl carbon center. The IR spectrum of **25** shows carbonyl absorption at unusually low frequency (1673 cm^{-1}),[20] but its UV is very similar to that of **7** from 230 to 300 nm and is virtually indistinguishable from that of **21** in this region.



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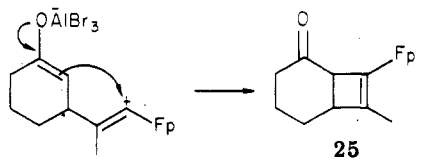
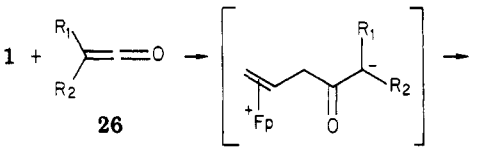
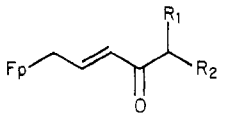


24 25

Finally, it was of interest to examine the question of [2 + 2] vs. [3 + 2] cycloaddition in the reactions of **1** with ketenes. There is ample evidence for concertedness in the reactions of ketenes and olefins,[21] although two-step processes involving dipolar intermediates for these reactions are not unknown.[22] The reaction of **1** with ketenes **26a–c**, at room temperature, gave condensation products **28a–c** in low yields. These substances are evidently derived by proton transfer within the dipolar intermediate **27**, which competes with ring closure. Such proton transfer has been observed in the reactions of (η^1-allyl)Fp complexes with some isocyanates,[4] and as noted earlier, in the reaction of (η^1-2-methoxyallyl)Fp with methylene malonate and other highly electrophilic olefins.[16]



26 27



28

a, R_1 = Me, R_2 = Ph; b, R_1 = Et, R_2 = Ph; c, R_1 = R_2 = Ph

In summary, (η^1-allyl)Fp complexes function as moderately reactive 1,3-dipoles in [3 + 2] cycloaddition reactions with Lewis acid activated cyclohexenone or with 2-carbethoxycycloalkenones. The related propargyl complex **2** behaves similarly with cyclohexenone, although its chemistry has been less extensively examined, while complex **23** engages in [2 + 2] cycloaddition with cyclohexenone. The cycloaddition reactions of (η^1-allyl)Fp complexes are sensitive to steric retardation, particularly at the primary site of C–C bond formation, but the second step, involving ring closure, is less so. Finally alkyl substitution at C-2 of the allyl ligand appears to be tolerated, but groups with strong resonance donor properties, such as methoxy, which promote initial condensation, tend to retard ring closure. Some further applications of this chemistry especially in related intramolecular processes may provide a unique entry to the isocomene[23] type terpenes and to analogous fused tricyclic systems.

Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen.

All organometallic reactions and subsequent manipulations including reagent additions, filtrations, extractions, recrystallizations, and chromatographic purification as well as the preparation of NMR samples and solution IR samples were conducted under a nitrogen atmosphere.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 137 and 457. ^1H nuclear magnetic resonance spectra were recorded on the following spectrometers: Varian A-60 (NIH GM-13183), Perkin-Elmer R-32 (NSF GU 3852), Bruker WH-90 (NSF GU 3852, GP 37156). ^{13}C nuclear magnetic resonance spectra were determined at 22.62 MHz on the latter instrument. Both ^1H and ^{13}C chemical shifts are reported relative to internal tetramethylsilane (Me_4Si) at δ 0.

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage and are uncorrected.

Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction of (η^1-allyl)Fp with Cyclohexenone. Preparation of 7a,b. Freshly sublimed aluminum tribromide (0.20 g, 0.8 mmol) was dissolved in 40 mL of methylene chloride and cooled to −78 °C. Cyclohexenone (0.67 g, 12 mmol) was added. The reaction

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turned cloudy, and after 10 min (η^1-allyl)Fp (0.87 g, 4.0 mmol) was added by syringe. The reaction was stirred for another 10 min at −78 °C. The dry ice–acetone bath was then replaced with an ice bath, and the reaction was stirred for an additional hour and was then quenched with 10 mL of ice cold water. Methylene chloride was separated, the mixture was dried over $MgSO_4$, and solvent was removed under reduced pressure. The residue was taken up in a minimum of ether and chromatographed on 50 g of neutral activity III alumina. The product eluted with 40–60% ether–petroleum ether and was isolated as an orange oil (0.57 g, 45%): IR (CH_2Cl_2) 1995, 1935, 1700 cm^{-1}; NMR ($CDCl_3$) δ 4.78 (s, 5, Cp), 1.3–3.0 (m, 13, CH_2CH). The addition of Eu(fod)$_3$ (0.5 equiv) revealed two cyclopentadienyl proton resonances, one at δ 5.15 and the other at δ 5.10, of equal intensity: ^{13}C NMR ($CDCl_3$) δ 217.23 (MCO) 214.37, 214.11 (CO) 85.29 (Cp) 53.46, 47.36, 46.38, 43.00, 42.87, 42.61, 41.77, 39.63, 39.24, 29.17, 27.41, 23.52, 23.00, 20.53, 17.86.

Anal. Calcd for $C_{16}H_{18}FeO_3$: C, 61.17; H, 5.77. Found: C, 61.24; H, 5.86.

4,4-Dideuteriocyclohexen-3-one. This was prepared following the procedure of Chao and Laane[11] employed for the deuteration of cyclopentenone. Cyclohexenone (3.0 g, 31 mmol) and D_2O (99.8% D, 10 g, 500 mmol) was stirred at 55 °C for 24 h. The product was extracted with methylene chloride and dried over $MgSO_4$. Solvent was removed in vacuo, and the product was distilled at 54–55 °C (8 mm) to give 1.93 g (64%) of recovered deuterated material. Proton NMR analysis in the presence of Eu(fod)$_3$ showed the material to be 90% deuterated at C-4 and 50% deuterated at C-2.

Fp(η^1-1,1,3,3-tetradeuterioallyl). Hexadeuterioacetone (99.5% D) was reduced with $NaBH_4$ in diglyme, and the alcohol was converted to the tosylate by treatment with tosyl chloride in pyridine (0 °C, 4.5 h). The tosylate (13.0 g, 57.5 mmol) in THF solution was metalated with NaFp[24] (−78 °C, 15 min; 25 °C, 0.5 h) to give (hexadeuterioisopropyl)Fp (11.5 g, 88%): NMR (CS_2) δ 4.63 (s, Cp), 2.58 (b s, 1, CH). This material (49 mmol) was taken up in methylene chloride (150 mL), cooled to 0 °C, and treated with trityl tetrafluoroborate. After 1 h, ether was added and the yellow precipitate was collected. Reprecipitation of the product from acetone–ether gave 13.4 g (88%) of Fp(η^2-1,1,3,3,3-pentadeuteriopropene)BF_4 as yellow crystals: IR (acetone) 2082, 2042 cm^{-1}; NMR (CD_3NO_2) δ 5.68 (s, 5), 5.19 (b s, 1, CH=). A portion of this material (4.0 g, 12.8 mmol) was suspended in methylene chloride and cooled to 0 °C. Triethylamine (1.3 g, 12.9 mmol) was added, and the solution was stirred at 0 °C for 0.5 h and then at 25 °C for 0.5 h. Solvent was removed in vacuo, and the residue was taken up in ether–petroleum ether and filtered through a bed of a celite–alumina (activity III) mixture. Removal of solvent left 2.4 g (83%) of product: IR (CH_2Cl_2) 2000, 1947 (cm^{-1}; NMR ($CDCl_3$) δ 4.71 (s, 5), 6.07 (b s, 1).

Diethyl Methylenemalonate.[25] A solution of phenylselenium bromide was prepared by dissolving diphenyl diselenide (4.8 g, 15 mmol) in 30 mL of THF under N_2 and adding 2.4 g (15 mmol) of bromine with vigorous stirring.

A suspension of sodium hydride (1.44 g 50% oil dispersion, 30 mmol) was prepared by washing it three times with skelly B and then charging the flask with 125 mL of THF. The suspension was then cooled in an ice bath. Methyl malonic acid diethyl ester (5.1 g, 29 mmol) was added dropwise to the sodium hydride suspension. When hydrogen evolution had ceased, the phenylselenium bromide solution was added as rapidly as possible by syringe. This mixture was added to 125 mL of ether and 125 mL of saturated $NaHCO_3$ solution. The aqueous layer was removed. The organic layer was washed twice with 100 mL of 10% $NaHSO_3$ solution and three times with 100 mL of water. The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The product was a yellow oil: NMR ($CDCl_3$) δ 7.5 (m, 5, Ph), 4.13 (q, 4, J = 7 Hz, OCH_2), 1.68 (s, 3, CH_3), 1.22 (t, 6, J = 7 Hz, CH_3).

The oil was dissolved in 20 mL of methylene chloride and cooled to −78 °C. Ozone was bubbled into the solution until it turned blue (ca. 1 h). The reaction mixture was degassed with N_2 to remove excess ozone and then allowed to warm to room temperature. Phenylseleninic acid precipitated and was filtered off. Solvent was removed under reduced pressure, and the product was distilled first under vacuum (bp 55–60 °C (0.3 mm)) and then at atmospheric pressure (bp 200–205 °C) to yield 3.5 g (77%) of product: IR (CH_2Cl_2) 1728 cm^{-1}; NMR (CCl_4) δ 6.35 (s, 2, =CH_2), 4.23 (q, 4, J = 7 Hz, OCH_2), 1.30 (t, 6, J = 7 Hz, CH_3).

4-Fp-1,1-dicarbethoxy-3-methylcyclopentanone (8b). (η^1-2-butenyl)Fp (cis, trans mixture, 0.5 g, 2.2 mmol) and diethyl methylenemalonate (0.37 g, 2.2 mmol) were dissolved in 10 mL of ether. The solution was stirred overnight, worked up, and purified by chromatography on activity III alumina (pentane eluant). The product, a yellow oil, was isolated in 64% yield: IR(CH_2Cl_2) 2000, 1950, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.80 and 4.76 (2s, 5, Cp) 4.20 (q, 4, J = 7 Hz, OCH_2), 1.5–2.8 (m, 6, CH_2,CH), 1.23 (t, 6, J = 7 Hz, CH_3), 1.05 (d, 3, J = 6 Hz, CH_3).

Anal. Calcd for $C_{19}H_{24}O_6Fe$: C, 56.45; H, 5.99. Found: C, 56.48; H, 6.16.

Reaction of (η^1-allyl)Fp with 2-Carbethoxycyclopentenone. Preparation of 12a. (η^1-allyl)Fp (1.0 g, 46 mmol) and 2-carbethoxycyclopentenone (0.71 g, 46 mmol) were dissolved in 20 mL of methylene chloride, and the solution was refluxed for 24 h. Solvent was removed under reduced pressure, and the residue was taken up in a minimum of ether and was chromatographed on 75 g of activity III neutral. Elution with Skelly-B gave 1 (40% recovered) and a small amount of Fp_2. The product was eluted with 30–40% ether–petroleum ether, 0.85 g (50%). This was recrystallized for analysis from ether–petroleum ether, to give yellow crystals: mp 96–98 °C; IR ($CHCl_3$) 2000, 1950, 1740, 1715 cm^{-1}; NMR ($CDCl_3$) δ 4.75 (s, 5, Cp), 4.13 (q, 2, J = 7 Hz, OCH_2), 1.40–3.10 (m, 10, CH_2, CH), 1.12 (t, 3, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.65, 216.78, 216.91 (3s, MCO, CO), 171.76 (s, COOR), 85.36 (d, Cp), 67.36 (s, C-3a), 61.13 (t, OCH_2), 48.79, 48.66 (2t, C-1, C-3), 47.49 (d, C-6a), 39.82 (t, C-5), 26.63 (t, C-6), 18.64 (d, C-2), 14.10 (q, Me).

Anal. Calcd for $C_{18}H_{20}FeO_5$: C, 58.09; H, 5.42. Found: C, 58.04; H, 5.50.

Reaction of (η^1-allyl)Fp with 2-Carbethoxycyclohexenone. Preparation of 12b. (η^1-Allyl)Fp (1.0 g, 46 mmol) and 2-carbethoxycyclohexenone (0.78 g, 46 mmol) were dissolved in 20 mL of methylene chloride. The solution was heated to reflux, was stirred overnight, and was worked up as in the previous procedure. Chromatographic purification gave 28% of recovered **1**, a small amount of Fp_2, and 1.10 g (63%) of product **12b** as yellow crystals: mp 87–89 °C; IR ($CHCl_3$) 2000, 1950, 1720, 1700 cm^{-1}; NMR ($CDCl_3$) δ 4.76 (s, 5, Cp), 4.16 (q, 2, J = 7 Hz, OCH_2), 1.50–3.00 (m, 12, CH_2, CH), 1.20 (t, 3, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.97 (MCO), 208.85, 208.46 (CO), 173.25, 172.21 (COOR), 85.36 (d, Cp), 66.85, 66.13 (2s, C-3a), 61.13 (t, OCH_2), 48.72 (d, C-7a), 47.62, 46.97, 46.45, 44.37, (C-1, C-3), 40.28, 39.28 (2t, C-5) 27.09, 26.83 (2t, C-7), 22.22 (t, C-6), 18.71, 18.25 (2d, C-2), 14.10 (q, CH_3).

Anal. Calcd for $C_{19}H_{22}FeO_5$: C, 59.08; H, 5.74. Found: C, 58.94; H, 5.65.

Reaction of (η^1-allyl)Fp with 2-Carbethoxycycloheptenone. Preparation of 12c. (η^1-allyl)Fp (1.0 g, 46 mmol) and 2-carbethoxycycloheptenone (0.84 g, 46 mmol) were dissolved in 20 mL of methylene chloride. The solution was heated to reflux, stirred overnight, and worked up as in the previous procedure. Chromatography on alumina gave 60% of recovered (η^1-allyl)Fp, 30% of Fp, and 0.16 g (9%) of cycloadduct **12c** as yellow crystals: mp 117–120 °C; IR (KBr) 1995, 1935, 1725, 1700 cm^{-1}; NMR ($CDCl_3$) δ 4.67 (s, 5, Cp), 4.12 (q, 2, J = 7 Hz, OCH_2), 1.00–3.00 (m, 14, CH_2, CH), 1.20 (t, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{20}H_{24}O_5Fe$: C, 60.02; H, 6.04. Found: C, 59.91; H, 6.07.

(η^1-2-methoxyallyl)Fp. A solution of Fp(η^2-2-methoxypropene)BF_4[14] (1.0 g, 3 mmol) in 10 mL of methylene chloride was cooled to −78 °C. Triethylamine (0.3 g, 3 mmol) was added by syringe, and after 10 min, 50 mL of ether was added to precipitate the ammonium salt. The mixture was transferred cold through a 2-mm cannula into a Schlenk tube, for filtration, under

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nitrogen. Removal of solvent from the filtrate left the product as an orange oil: 0.71 g (95%); IR (CH_2Cl_2) 2030, 1955 cm^{-1}; NMR ($CDCl_3$) δ 4.72 (s, 5, Cp), 3.84 (d, 1, J = 2 Hz, CH=), 3.70 (b, s, 1, CH=), 3.52 (s, 3, OCH_3), 2.0 (s, 2, $FpCH_2$).

Reaction of (η^1-methallyl)Fp with 2-Carbethoxycyclopentenone. Preparation of 16. (η-methallyl)Fp (1.10 g, 47 mmol) and 2-carbethoxycyclopentenone (0.68 g, 43 mmol) were dissolved in 20 mL of methylene chloride. The solution was heated to reflux, stirred overnight, and worked up as in the previous procedure to give 0.75 g (45%) of yellow crystals: mp 84–87 °C; IR (KBr) 1995, 1935, 1745, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.76 (s, 5, Cp), 4.15 (q, 2, J = 7 Hz, OCH_2), 1.50–3.50 (m, 9, CH_2, CH), 1.25 (s, 3, CH_3), 1.22 (t, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{19}H_{22}FeO_5$: C, 59.08; H, 5.74. Found: C, 59.44; H, 5.96.

Reaction of (η^1-2-methoxyallyl)Fp with Diethyl Methylenemalonate. Preparation of 17. (2-methoxyallyl)Fp (0.315 g, 1.3 mmol) and diethyl methylenemalonate (0.218 g, 1.3 mmol) were dissolved in 5 mL of ether. After the solution was stirred for 4 h, the solvent was removed under reduced pressure. The residue was taken up in a minimum of ether and was chromatographed on 50 g of activity III alumina. Five bands were observed. The first, which eluted with 100% petroleum ether contained (η^1-methallyl)Fp and ferrocene. The second, which eluted with 10% ether–petroleum ether was (η^1-cyclopentadienyl)Fp. The third, which eluted with 30–40% ether–petroleum ether, was Fp_2 and organic ester. The fourth, which eluted with 50% ether–petroleum ether, was $FpCH_2COOMe$. The fifth, which eluted with 70–100% ether-petroleum ethers, was the product contaminated with some $FpCH_2COCH_3$.

Careful rechromatography of the fifth fraction gave the desired product eluting with 70–80% ether–petroleum ether: yield 0.081 g (16%); IR (CH_2Cl_2) 2010, 1940, 1700, 1645 cm^{-1}; NMR ($CDCl_3$) δ 4.88 (s, 5, Cp), 4.25 (q, 4, J = 7 Hz, OCH_2), 3.46 (t, 1, J = 7 Hz, CH), 2.0–2.6 (m, 4, CH_2CH_2), 1.76 (s, 2, $FpCH_2$), 1.28 (t, 6, J = 7 Hz, CH_3).

Anal. Calcd for $C_{16}H_{22}FeO_7$: C, 53.22; H, 5.46. Found: C, 52.61; H, 5.57.

Oxidation of 3a-Carbethoxy-2-Fp-hydrindan-4-one. Preparation of 19. The keto ester **17b** (0.885 g, 2.29 mmol) was dissolved in 50 mL of methanol, and 5.0 g (9.2 mmol) of $Ce(NH_4)_2(NO_3)_6$, dissolved in 50 mL of methanol, was added to this. The solution was stirred at room temperature for 0.5 h, solvent was then removed in vacuo, and the residue was taken up in ether–water. The combined ether extracts were dried over $MgSO_4$, solvent was removed in vacuo, and the residue was chromatographed on silica gel. The product **19** (0.38 g, 62%) was eluted with ether as an oil: IR (CH_2Cl_2) 1730, 1715 cm^{-1}; NMR ($CDCl_3$) δ 4.17 (q, 2, J = 7 Hz, OCH_2), 3.68, 3.67 (2s, 3, OCH_3), 1.5–3.3 (m, 12, CH, CH_2), 1.23 (t, 3, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 206.8, 175.8, 175.1, 171.9, 171.2, 66.2, 65.6, 61.5, 51.8, 46.6, 46.1, 41.3, 40.3, 40.1, 39.6, 35.2, 34.9, 33.5, 31.7, 26.0, 24.7, 23.1, 22.8, 14.1.

Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.68; H, 7.46. Found: C, 61.95; H, 7.39.

Reaction of (η^1-2-butynyl)Fp with Cyclohexenone. Preparation of 21. Freshly sublimed aluminum bromide (0.046 g, 0.17 mmol) was dissolved in methylene chloride and cooled to −78 °C. Cyclohexenone (0.167 g, 1.74 mmol) was added to this. After 15 min, 1-Fp-2-butyne (0.40 g, 1.74 mmol) was added, and the reaction was allowed to warm to 0 °C over a period of 2.5 h. The reaction was quenched with water, the organic layer was separated and dried over $MgSO_4$, and solvent was removed in vacuo. The crude product, after being pumped on overnight (1 mm), was taken up in a small volume of methylene chloride and chromatographed on silica gel. The product was eluted with 60% either–petroleum ether and was isolated as a yellow oil (0.115 g, 20%): IR (CH_2Cl_2) 2005, 1950, 1690 cm^{-1}; NMR ($CDCl_3$) δ 4.80 (s, 5, Cp), 2.87 (m, 2, CH_2), 2.65 (m, 2, CH_2), 2.31 (m, 2, CH_2), 1.77 (d + m, 7, J = 2 Hz, CH, CH_2, CH_3); ^{13}C NMR ($CDCl_3$) δ 215.74, 215.61, 215.02 (3s, MCO, CO), 144.60, 132.52 (2s, >c=), 85.66 (d, Cp) 52.68, 51.84 (2d, CH), 51.32 (t, CH_2), 40.02 (t, CH_2CO), 27.61, 22.35, (2t, CH_2), 17.21 (q, CH_3).

Anal. Calcd for $C_{17}H_{18}FeO3$: C, 61.60; H, 5.52. Found: C, 62.26; H, 5.67.

Reaction of (η^1-allenyl)Fp and Cyclohexenone. Preparation of 25. Freshly sublimed aluminum bromide (0.076 g, 0.28 mmol) was dissolved in 6 mL of methylene chloride and cooled to −78 °C. Cyclohexanone (0.27 g, 2.8 mmol) was added, and after 15 min (η^1-allenyl)Fp (0.60 g, 2.8 mmol) was added to this. The reaction was allowed to warm to 0 °C over a 2-h period, was then quenched with water, and was worked up as before. A portion of the residue (20%, 0.172 g) was chromatographed by TLC (1000-μm silica gel) by using 60% ether–petroleum ether. The third band yielded 0.04 g (24%) of product as an amber oil: IR (CH_2Cl_2) 2010, 1955, 1673 cm^{-1}; NMR ($CDCl_3$) δ 4.92 (s, 5, Cp), 3.42 (m, 1, CH), 3.17 (m, 1, CH), 1.3–3.6 (d + m, 9, J = 1.5 Hz, CH_2, CH_3); ^{13}C NMR ($CDCl_3$) δ 214.57, 213.85 (2 s, MCO, CO), 165.72 (s, >C=) 140.12 (s, >C=), 84.84 (d, Cp), 63.92 (d, CH), 46.25 (d, CH), 40.08 (t, CH_2CO, 24.88 (t, CH_2), 17.60 (t, CH_2), 14.55 (q, CH_3).

Reaction of (η^1-propynyl)Fp and Cyclohexene. The reaction of (propynyl)Fp (0.4 g, 1.85 mmol) with cyclohexene (0.18 g, 1.9 mmol) in the presence of 10 molar % of freshly sublimed $AlBr_3$ was carried out as with (η^1-allenyl)Fp and gave 0.31 g (54%) of product identical with that obtained in the above experiment.

Anal. Calcd for $C_{16}H_{16}FeO_3$: C, 61.57; H, 5.13. Found: C, 61.84; H, 5.36.

Reaction of (η^1-allyl)Fp with Diphenylketene. Preparation of 28c. (η^1-allyl)Fp (0.5 g, 2.5 mmol) and diphenylketene (0.6 g, 3.0 mmol) were dissolved in 20 mL of methylene chloride and the mixture stirred overnight at room temperature. Solvent was removed, and the residue was taken up in ether and chromatographed on 50 g of neutral, activity II alumina. The product was eluted with 30% ether–petroleum ether and was obtained as an orange oil (0.25 g, 30%): IR (neat) 2010, 1960, 1650 cm^{-1}; NMR (CS_2) δ 7.15 (s, 11, H, CH), 5.80 (d, 1, J = 15 Hz, CH=), 5.10 (s, 1, CH=), 4.45 (s, 5, Cp), 1.92 (d, 2, J = 10 Hz, CH_2).

Reaction of (η^1-allyl)Fp with Ethylphenylketene. Preparation of 28b. (η^1-allyl)Fp (0.5 g, 2.5 mmol) and 0.44 g of ethylphenylketene (3.0 mmol) were dissolved in 20 mL of methylene chloride and stirred overnight at room temperature. Workup as above gave the product, an orange oil, in 10% yield: IR (neat) 2010, 1960, 1640 cm^{-1}; NMr (CS_2) δ 7.17 (s, 5, Ph), 5.62 (d, 1, J = 15 Hz, CH=), 4.40 (s, 6, Cp, CH=), 3.50 (t, 1, J = 7 Hz, CH), 1.90 (d, 2, J = 9 Hz, $FpCH_2$), 0.5–1.3 (m, 5, CH_2CH_3).

Reaction of (η^1-allyl)Fp with Methylphenylketene. Preparation of 28a. Reaction of these components and workup as above gave the product as an orange oil in 11% yield: IR (CH_2Cl_2) 2010, 1960, 1640 cm^{-1}; NMR (CS_2) δ 7.17 (s, 5, Ph), 5.63 (d, 1, J = 15 Hz, CH=), 4.60 (s, 1, CH=), 4.42 (s, 5, Cp), 3.75 (q, 1, J = 7 Hz, CH), 1.97 (d, 2, J = 10 Hz, $FpCH_2$), 1.30 (d, 3, J = 7 Hz, CH_3).

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Registry No. **1**, 38960-10-0; **3**, 42043-77-6; **7a**, 83350-41-8; **7b**, 83378-20-5; **8b**, 83350-43-0; **11a**, 57020-97-0; **11b**, 57205-09-1; **11c**, 57205-20-6; **12a**, 83350-44-1; **12b**, 83350-45-2; **12c**, 83350-46-3; **16**, 83350-47-4; **17**, 82195-84-4; **19**, 83350-39-4; **21**, 83350-40-7; **23**, 33248-70-3; **25**, 83350-48-5; **26a**, 3156-07-8; **26b**, 20452-67-9; **26c**, 525-06-4; **28a**, 83350-51-0; **28b**, 83350-50-9; **28c**, 83350-49-6; (#^{1}–1,1,3,3–tetradeuterioallyl)Fp, 83350-42-9; (#^{1}–methallyl)Fp, 31781-60-9; (#^{1}–2–butenyl)Fp, 31781-59-6; (#^{1}–2–methoxyallyl)Fp, 71844-55-8; (hexadeuterioisopropyl)Fp, 83363-78-4; Fp(#^{2}–1,1,3,3,3–pentadeuteriopropene)BF_4, 83350-53-2; 4,4–dideuteriocyclohexen–3–one, 83350-38-3; cyclohexenone, 930-68-7; cyclohexene, 110-83-8; diethyl methylenemalonate, 3377-20-6; hexadeuterioacetone, 666-52-4; methyl malonic acid diethyl ester, 609-08-5; aluminum bromide, 7727-15-3.