Iron-Promoted Allylic Alkylation: Regiochemical, Stereochemical, and Mechanistic Aspects

G. S. Silverman, S. Strickland, and K. M. Nicholas*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

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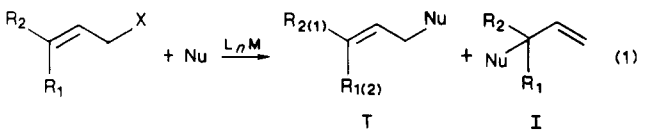
The coupling of several nucleophiles ($NaCH(CO_2Me)_2$, $NaCMe(CO_2Et)_2$, $NaCH(SO_2Ph)CN$, and morpholine) with (η^3-crotyl)$Fe(CO)_4BF_4$ (1), (η^2-crotyl X)$Fe(CO)_4$ (2; X = $-OCOCH_3$, $-OCOCF_3$), and crotyl X catalyzed by $Fe_2(CO)_9$ has been examined, and their regio- and stereoselectivities have been compared. The η^3-complexes 1 undergo preferential attack at the less substituted allyl terminus with a strongly nucleophile-dependent selectivitiy and completely stereospecifically, retaining the allyl fragment's geometry. The η^2-complexes 2 exhibit a lesser regiopreference for attack at the primary carbon but also react stereospecifically. Coupling of allylic acetates with nucleophiles catalyzed by $Fe_2(CO)_9$ also proceeds with high stereospecificty but generally lower regioselectivity than the stoichiometric counterparts. The corresponding crotyl trifluoroacetates show regioselectivities similar to the parallel η^3-complex reactions. Spectroscopic and chemical studies of the interaction of $NaCH(CO_2Me)_2$ (NaDMM) with $Fe_2(CO)_9$ have provided evidence for the formation of nucleophile–coordinated species $NaFe_x(CO)_y(DMM)^-$ ($x = 2, y = 8$; $x = 1, y = 4$). The probable role of such species in the catalytic reactions is discussed.

Introduction

Among the various carbon–carbon bond-forming reactions promoted by transition metals, allylic alkylation has been one of the most aggressively sought after. Accordingly, numerous largely unsystematic studies have appeared dealing with the chemo-, regio-, and stereoselectivity of metal-promoted coupling of electrophilic allyl substrates with various nucleophiles[1a–f] and, especially in the case of palladium,[2] the extensive applications of these reactions in organic synthesis. Beyond the wealth of information compiled on the Pd-catalyzed reactions, much less is known about the selectivity, mechanisms, and synthetic applicability of the known allylic alkylations catalyzed by other metals.

The most fundamental selectivity issue for this reaction is the question of the site of nucleophilic attack on the allylic fragment, i.e., regioselectivity (eq 1). Examination



(1)

of the existing literature regarding this point reveals a significant and often dramatic dependence of regioselectivity on virtually every conceivable reaction parameter including the metal and its auxiliary ligands, the nucleophile, substrate substituents R, and solvent. Despite the voluminous literature, rarely have these various factors been investigated systematically, making comparisons and extrapolations rather tenuous. However, existing data for cross-metal comparisons suggest that Pd and Fe catalysts favor terminal attack, product T, W and Ni catalysts favor internal attack, product I, Mo catalysts are intermediate in behavior showing a strong dependence on the nucleophile, and the Cu catalysts promote allylic transposition. The regioselectivities of these reactions with simple acyclic substrates generally are not very high (e.g., 1:1 → 3:1, vide infra) leaving considerable room for practical improvements. Furthermore, the observed effects of the various reaction parameters on regioselectivity are not well-understood.

Two potential sites of stereoselectivity are presented in allylic alkylation: (a) the carbon undergoing attack by nucleophile and (b) the carbon–carbon double bond (see eq 1). In a few cases (namely, the Pd-, Mo-, and W-catalyzed processes) point a has been examined and found to proceed with either net retention, inversion, or racemization depending upon the particular nucleophile involved. Aside from the Pd- and Cu-promoted reactions, almost no data are available regarding the double-bond stereoselectivity. From the few examples available for Pd, substrates with trisubstituted double bonds react with retention of double bond geometry whereas both *Z*- and *E*-disubstituted substrates give *E* products predominantly.[2] Copper-catalyzed allylic coupling with Grignard reagents has been found to proceed stereospecifically (i.e., $Z \rightarrow Z$, $E \rightarrow E$) in a number of cases.[1a]

This paucity of stereochemical information, especially with respect to point b, combined with desirability of general, regioselective and stereoselective methods for allyl/nucleophile coupling, has stimulated us to seek new catalyst systems for effecting allylic alkylation. Encouraged by the early reports of Whitesides[3] and Pearson[4] and our own unpublished observations[5] on the regio- and stereoselective attack of several nucleophiles on (η^3-allyl)$Fe(CO)_4BF_4$, we have explored the prospects for effecting iron-promoted allylic alkylation using commercially available, inexpensive iron carbonyls as catalysts. The successful realization of this goal was reported recently wherein $Fe_2(CO)_9$ was found to promote the reaction between allylic acetates and malonate ion.[6] Surprisingly, our preliminary observations on the regioselectivity of these reactions argued against the intermediacy of the expected (η^3-allyl)$Fe(CO)_4^+$ complexes. In this report we provide (a) additional data regarding this latter issue including evidence for the operation of a novel mechanism

(1) (a) Cu: Suzuki, S.; Shiano, M.; Fugita, Y. *Synthesis* **1983**, 804; (b) Ni: B. L. Buckwalter, I. V. Burfitt, H. Felkin, M. Joly-Goudket, K. Naemura, M. F. Salomon, E. Wenkert and P. M. Wovkulick, *J. Am. Chem. Soc.* **1978**, *100*, 6445. (c) Co and Fe: Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.*, **1978**, 3721. (d) Mo: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. (e) W: Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1983**, *105*, 7757. (f) Rh: Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 5157.

(2) Reviews: Trost, B. M. *Acc. Chem. Res.* **1980**, *12*, 198. Trost, B. M.; Vorhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8, pp 799–938.

(3) Whitesides, T. H.; Arhardt, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5793.

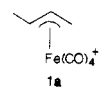
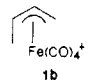
(4) Pearson, A. J. *Tetrahedron Lett.* **1975**, 3617.

(5) Dieter, J.; Nicholas, K. M., unpublished results, 1981.

(6) Ladoulis, S. J.; Nicholas, K. M. *J. Organomet. Chem.* **1985**, *285*, C13.

0276-7333/86/2305-2117$01.50/0

Table I. Regio-/Stereoselectivity of Nucleophilic Addition to (η^3-Crotyl)Fe(CO)$_4^+$

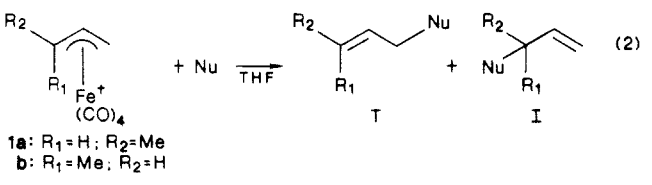
entry	complex	Nu	regiosel % T	regiosel % I	stereochem
1	 1a	NaDMM	57	43	*E*
2	1a	NaMDEM	58	42	*E*
3	1a	NaCH(SO$_2$Ph)CN	79	21	*E*
4	1a	morpholine	88	12	*E*
5	 1b	NaDMM	74	26	*Z*
6	1b	NaMDEM	90	10	*Z*
7	1b	NaCH(SO$_2$Ph)CN	85	15	*Z*
8	1b	morpholine	94	6	*Z*

for allylic alkylation in these reactions, (b) a more complete survey of the regio- and stereochemical features, (c) the parallel stoichiometric reactions of nucleophiles with (η^3-allyl)Fe(CO)$_4^+$ and (η^2-allyl OAc)Fe(CO)$_4$, and (d) examples of a dramatic effect on regioselectivity upon changing the substrate's leaving group from $-OCOCH_3$ to $-OCOCF_3$.

Results

(η^3-Allyl)Fe(CO)$_4$BF$_4$ + Nucleophiles. Our original hypothesis was that an iron carbonyl catalyzed reaction would possibly proceed through the intermediacy of (η^3-allyl)Fe(CO)$_4^+$ species and, if so, would exhibit the attractive regio- and stereoselectivity features of the stoichiometric counterparts, namely, preferential nucleophilic attack at the less substituted allyl terminus and retention of double-bond geometry.[3,4] In order to have directly comparable data for our catalytic studies, we have examined the reactions of four test nucleophiles—NaCH(CO$_2$Me)$_2$ (DMM$^-$), NaCMe(CO$_2$Et)$_2$ (MDEM$^-$), NaCH(CN)SO$_2$Ph, and morpholine with *syn*- and *anti*-(η^3-1-methylallyl)Fe(CO)$_4$BF$_4$ (**1a,b**). The methallyl (crotyl) substrate is a useful one for such studies since the methyl group exerts modest and reasonably well-defined steric and electronic effects, the requisite *cis*- and *trans*-crotyl alcohol starting materials are commercially available, and the product analysis is straightforward.

The reactions of *syn*- and *anti*-**1** with the above nucleophiles proceeded nearly instantly at 20 °C in THF (monitored by GC, eq 2). Following aqueous workup the

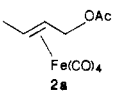
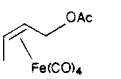


(2)

1a: R$_1$=H; R$_2$=Me
b: R$_1$=Me; R$_2$=H

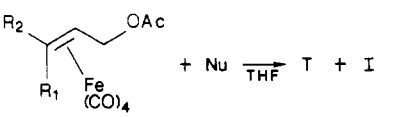
products (T = terminal attack and I = internal attack) were isolated by preparative GC and characterized by IR, ^{1}H and ^{13}C NMR, and mass spectrometry. Results are given in Table I. Qualitatively, the regio- and stereoselectivities observed are comparable to those seen by Whitesides[3] and Pearson[4] —i.e., preferential attack by nucleophile occurs at the less substituted carbon and the reactions are highly stereospecific. In addition, some interesting quantitative features should be noted. First, the regiopreference for C-3 ("terminal") attack is highly nucleophile dependent, with DMM$^-$ the least selective, morpholine the most, and MDEM$^-$ and CH(CN)SO$_2$Ph$^-$ intermediate in behavior. A more subtle and previously unrecognized trend is revealed by comparing the regioselectivities of complex **1a** vs. **1b** with the same nucleophiles

Table II. Regio-/Stereoselectivity of Nucleophilic Substitution on (η^2-Crotyl acetate)Fe(CO)

entry	complex	Nu	regiosel % T	regiosel % I	stereochem
1	 2a	NaDMM	40	60	*E*
2	2a	NaMDEM	60	40	*E*
3	2a	NaCH(SO$_2$Ph)CN	52	45	*E*
4	2a	morpholine	57	43	*E*
5	 2b	NaDMM	71	29	*Z*
6	2b	NaMDEM	90	10	*Z*
7	2b	NaCH(SO$_2$Ph)CN	74	26	*Z*
9	2b	morpholine	52	48	*Z*

(e.g., entries 1/5, 2/6, etc.). Attack by a given nucleophile on the anti complex **1b** is found to be uniformly more terminally (C-3) selective than on the syn complex **1a**.

(η^2-Crotyl acetate)Fe(CO)$_4$ + Nucleophiles. Having shown earlier that a relatively stable (η^2-allyl acetate)Fe(CO)$_4$ complex is formed in the reaction of Fe$_2$(CO)$_9$ with allyl acetate itself,[7] it also seemed plausible that Fe$_2$(CO)$_9$-catalyzed allylic alkylations might proceed via nucleophilic attack on such η^2-intermediates. The viability of this pathway was further supported by the observation that (η^2-allyl acetate)Fe(CO)$_4$ reacts smoothly (20 °C, THF) with NaDEM to give diethyl allylmalonate.[6] Accordingly, we examined the reactions of our test set of nucleophiles with the corresponding *cis*- and *trans*-(η^2-crotyl acetate)Fe(CO)$_4$ complexes **2b** and **2a** (eq 3). The latter were prepared by stirring the respective acetates with Fe$_2$(CO)$_9$ in Et$_2$O. The results of these reactions are provided in Table II.

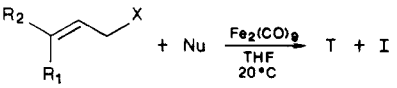


(3)

2a: R$_1$=H; R$_2$=Me
b: R$_1$=Me; R$_2$=H

Key among these results are the following: (1) although terminal attack is generally preferred, quantitatively significant differences exist between the regioselectivities of the corresponding η^2- and η^3-complex reactions; (2) selectivity for terminal attack by a given nucleophile is generally somewhat less for the η^2-complexes; (3) higher terminal attack selectivity is observed for the cis compared to the trans complexes (entries 1/5, 2/6, etc.); and (4) the reactions are stereospecific, $Z \rightarrow Z$, $E \rightarrow E$.

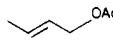
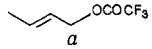
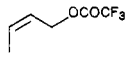
Catalytic Studies—Selectivity. With the selectivity features of the reactions of the respective η^2- and η^3-complexes, possible intermediates in the catalytic reactions, thus delineated, let us examine now the selectivities of the latter. The catalytic reactions were conducted as described in our preliminary report.[6] Typically, a THF solution of the allylic acetate or trifluoroacetate (ca. 0.17 M) and nucleophile (0.34 M)[8] was treated with 0.1 equiv of Fe$_2$(CO)$_9$ at room temperature and monitored periodically by gas chromatography (eq 4). Under these conditions the



(4)

(7) Dieter, J.; Nicholas, K. M. *J. Organomet. Chem.* **1981**, *212*, 107.
(8) Excess nucleophile was employed to suppress dialkylation (<10% observed under these conditions).

Table III. Regio-/Stereoselectivity of Allylic Alkylation Catalyzed by $Fe_2(CO)_9$

entry	substr	Nu	regiosel % T	regiosel % I	stereochem
1		NaDMM	37	63	*E*
2	*a*	NaMDEM	72	28	*E*
3	*a*	$NaCH(SO_2Ph)CN$	50	50	*E*
4	*a*	morpholine	no reaction		
5		NaDMM	52	48	*E*
6	*a*	NaMDEM	77	23	*E*
7	*a*	$NaCH(SO_2Ph)CN$	66	34	*E*
8		NaDMM	52	48	*Z*
9	*a*	NaMDEM	82	18	*Z*
10	*a*	$NaCH(SO_2Ph)CN$	84	16	*Z*
11	*a*	morpholine	no reaction		
12		NaDMM	74	26	*Z*
13	*a*	NaMDEM	91	9	*Z*
14	*a*	$NaCH(SO_2Ph)CN$	90	10	*Z*

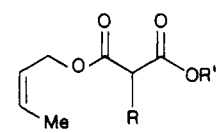
[a] Same as above.

reactions were essentially complete after 3–5 days for X $OCOCH_3$ and 1–2 days for X = $OCOCF_3$. Control experiments indicated that no reaction occurred in the absence of $Fe_2(CO)_9$ and that the products were stable toward isomerization under the reaction conditions. The results of these reactions are collected in Table III.

We first examine the features of the reactions with *cis*- and *trans*-crotyl acetates. Comparison of the results of the catalytic reactions for *cis*-crotyl acetate with those of the corresponding η^2- and η^3-*anti*-methallyl are most revealing (experiments 7–9, Table III; experiments 5–7, Table II; experiments 5–7, Table I). The selectivity for terminal attack in the catalytic runs is poorer than either of the stoichiometric reactions (except for Nu = $NaCH(SO_2Ph)CN$). The situtation with *trans*-crotyl acetate is less clear-cut with the catalytic reactions exhibiting similar regioselectivities to the reactions of the η^2-complex but still significantly different (less favoring terminal attack) from the η^3-complexes. The catalytic reactions, like their stoichiometric counterparts, are highly stereospecific. Finally, morpholine was not alkylated under catalytic conditions, even upon refluxing for several hours.

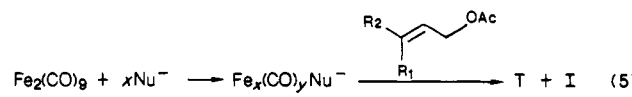
Upon changing the leaving group from acetate to trifluoroacetate, interesting changes in regioselectivity occurred in the catalytic reactions of both cis and trans susbstrates (Table III, experiments 5–7, 12–14). With X = $OCOCF_3$ a uniformly higher selectivity for terminal attack is seen relative to X = $OCOCH_3$ for each nucleophile (experiments 1/5, 2/6, 3/7, 8/13, 9/13, 10.14). In fact with DMM^- and $MDEM^-$ as nucleophiles the regioselectivity of the catalytic reactions of the trifluoroacetates is essentially identical with the η^3-complex reactions (cf. Table III, experiments 5, 6, 12, 13, and Table I). Notable differences between the catalytic process and the η^3-complex reactions, however, turned up with Nu = $NaCH(SO_2Ph)CN$ in regioselectivity (experiments 7, 14 (Table III vs. experiments 3, 7 (Table I)) and Nu = morpholine (no alkylation products in the catalytic run). The catalytic reactions of the crotyl trifluoroacetates also proceeded stereospecifically with retention of double-bond geometry.

Generally, mono-C-alkylated products were formed almost exclusively (>90%) in these reactions along with minor amounts of dialkylation products. However, in the catalytic reactions of Nu = NaMDEM and X = $OCOCH_3$ (experiments 2, 9, Table III) and Nu = NaDMM and NaMDEM and X = $OCOCF_3$ (experiments 5, 12, Table III) byproducts (8–25%) with GC retention times similar to mono-C-alkylation products were also observed. In two cases these byproducts were isolated in impure form by preparative GC and, on the basis of ^1H NMR and MS data, were assigned O-alkylation structures **3** and **4**. Presumably **3** and **4** result from hydrolysis (during workup) of the respective ketene acetals produced by O-allylation. We did not seek to determine the presence of the expected coproduct *cis*-2-butenol (H_2O soluble).



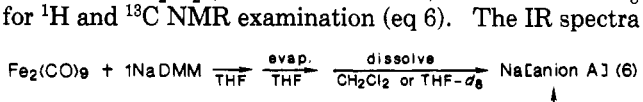
3: R = Me; R' = Et
4: R = H; R' = Me

Catalytic Studies—Role of Coordinated Nucleophile. The differing regioselectivities between the catalytic reactions (especially with the crotyl acetates) and the stoichiometric reactions of the η^2- and η^3-complexes caused us to consider the possibility of catalytic mechanisms involving yet other intermediates. One such possibility is that precoordination of nucleophile occurs generating a species of the type $Fe_x(CO)_yNu^-$ which then reacts with substrate to give product (eq 5). To test this hypothesis,



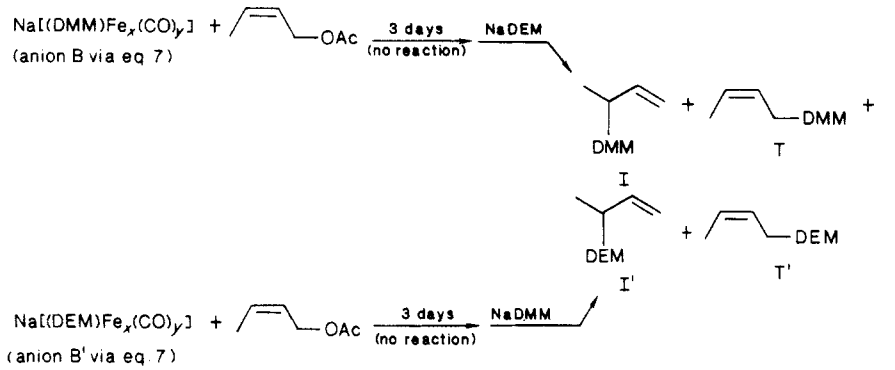
we examined the interaction of NaDMM with $Fe_2(CO)_9$ alone to determine the nature of any species produced and their reactivity toward added allylic acetates.

When a THF solution of NaDMM was treated with 1 molar equiv of $Fe_2(CO)_9$, a deep burgundy color developed over a few minutes, indistinguishable from that of the catalytic reaction mixtures. The dominant species present in such solutions was isolated for spectroscopic study by evaporating the solvent and redissolving the dark red oily residue in CH_2Cl_2 (NaDMM insoluble) for IR or THF-d_8 for ^1H and ^{13}C NMR examination (eq 6). The IR spectra



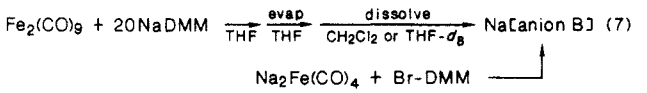
of such solutions exhibited absorptions at 2025 (m), 1985 (m), 1960 (w), 1920 (br, s), 1900 (br, s), and 1705 (m) cm^{-1} (plus bands due to HDMM). The ^1H NMR spectrum of this species displayed singlets at δ 3.55 (6 H) and 3.0 (1 H) from a malonate unit [free NaDMM, δ 3.85 (1 H), 3.35

Scheme I

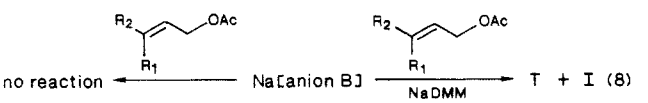


(6 H)]. This conclusion was confirmed from the proton-coupled ^{13}C NMR spectrum which showed singlets at δ 220.1 (M–CO) and 181.7 (CO_2R), a quartet at 50.5 (OMe), and a doublet at 18.5 (X–$CH(CO_2Me)_2$). The same species was produced (judging by IR, color) when $Na_2Fe_2(CO)_8$ was treated with an equimolar amount of $BrCH(CO_2Me)_2$. The sum total of the above data suggested formation of a species of the general type $Fe_x(CO)_y(DMM)_z^{z-}$, anion A. Attempts to obtain a pure, crystalline PPN^+ salt were unsuccessful. Importantly, no reaction was observed between this species and added *cis*- or *trans*-crotyl acetate, even after several days.

Since under catalytic conditions the reactants are present in large excess relative to catalyst, we also examined the reaction of $Fe_2(CO)_9$ with 20 molar equiv of NaDMM in THF (eq 7). Once again a burgundy red



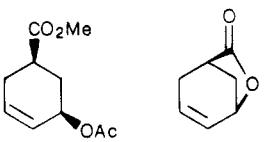
solution was formed with a rather similar IR spectrum (2025, 1995, 1970, 1925, 1895, 1715 cm^{-1}) to the 1:1 reaction. These same absorptions also appeared in the progressing catalytic reaction mixtures. Removal of the THF, trituration with CH_2Cl_2, evaporation of the CH_2Cl_2, and redissolution in THF-d_8 gave an unstable dark red solution whose ^1H NMR spectrum had absorptions at δ 3.65 (s, 6 H) and 3.40 (s, 1 H). We were unable to obtain well-resolved ^{13}C NMR spectra of this species due to its ready decomposition in solution, even at low temperature. The same burgundy red species appears to be produced from the reaction of $Na_2Fe(CO)_4$ with $BrCH(CO_2Me)_2$ in THF (−78 °C). Addition of excess CH_3I to such solutions gave $CH(CH_3)(CO_2Me)_2$ cleanly. The above observations suggest formation of a different $Fe_x(CO)_y(DMM)_z^{z-}$ species, anion B, under these conditions. Interestingly, addition of *cis*- or *trans*-crotyl acetate to a solution of 20NaDMM + $Fe_2(CO)_9$ which had stirred for a few hours gave product mixtures of identical composition to the regularly conducted catalytic reactions. However, addition of crotyl acetate to anion B (isolated by the extraction sequence above) in the absence of excess malonate afforded no alkylation products; only when additional malonate (≥1 equiv) was added, did such solutions yield alkylation product (eq 8). It would appear therefore that two dif-



ferent anionic iron malonate species are formed in the reaction of $Fe_2(CO)_9$ with malonate ion. In the presence of free malonate ion these species catalyze the coupling of allylic acetates with malonate.

In an effort to determine whether it was free or coordinated malonate which actually couples with the allyl unit, the crossover experiments outlined in Scheme I were carried out. When a solution containing anion B derived from NaDMM was treated with *cis*-crotyl acetate followed by NaDEM (ca. 1 equiv), a mixture of all four possible alkylation products were produced ($I/T/I'/T' \simeq 4.7:1.1:1.6:1.0$). Likewise, anion B' derived from NaDEM when treated with *cis*-crotyl acetate and then NaDMM also produced the four alkylation products (1.0:1.3:4.7:3.4).

Catalytic Studies—Attempted Stereochemical Determination at the Carbon Undergoing Substitution. In an effort to shed further light on the mechanism of iron-catalyzed allylic alkylation, we sought to determine the stereochemical course at carbon of the replacement of acetate by malonate. Substrates **5** and **6** effectively used



5 **6**

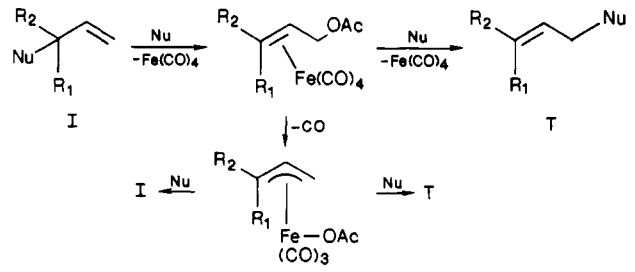
by Trost[9] and Stille[10] in the study of Pd-catalyzed allyl coupling reactions were selected. Unfortunately, neither **5** nor **6** proved reactive toward NaDMM in the presence of $Fe_2(CO)_9$, even at reflux in THF. Attempts to isolate η^2- and η^3-complexes of **5** and **6** also were unsuccessful. It did appear that $Fe_2(CO)_9$ reacts slowly with **5** and **6** in ethyl ether, but attempted isolation of the anticipated η^2-complexes or protonation with $HBF_4 \cdot Me_2O$ (to produce the corresponding η^3-species) only led to decomposition.

Discussion

Let us first examine the features of the stoichiometric reactions of the η^2- and η^3-complexes with nucleophiles, of some interest in their own right and also for comparison with the catalytic reactions. The data from this study for the η^3-complex reactions are generally consistent with earlier reports which show a modest to good regioselectivity for attack at the less substituted carbon of the methallyl fragment and preservation of the allyl unit's geometry. This regioselectivity feature is the same as is typically ascribed to the Pd-catalyzed reactions, generally believed to proceed via nucleophilic attack on a $(\eta^3\text{-allyl})Pd(PR_3)_2^+$ species.[2] A delicate balance of several factors has been considered to account for the regioselectivity observed in nucleophilic attack on unsymmetrical $(\eta^3\text{-allyl})ML_n^+$ species including (a) charge distribution/orbital coefficients

(9) Trost, B. M.; Vorhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.
(10) Sheffy, F. K.; Godshalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833.

Scheme II

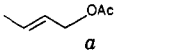
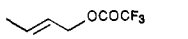
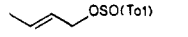
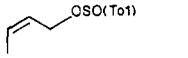
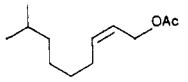


in the allyl fragment,[11,12] (b) unsymmetrical bonding between the metal and the two allyl termini,[13,14] (c) steric interactions between the allyl substituents and the incoming nucleophile,[13] and (d) stability of the resulting η^2-complex.[13] Factors a and d should favor internal (more substituted) C attack for R = Me, whereas factor c favors terminal attack. The assessment of factor b requires a base of crystallographic data which is unavailable. While steric arguments have been used to rationalize the regiopreference for nucleophilic addition to $(\eta^3\text{-allyl})PdL_2^+$ complexes, the correlation of the T/I product ratio with the nucleophile's steric bulk in the reactions of the η^3-iron complexes (Table I) is modest. Especially unexpected is the very high terminal selectivity for Nu = morpholine. It would appear that electronic characteristics of the nucleophile such as HOMO energy, polarizability and/or hardness/softness play a significant and, as yet, undefined role in determining the regiochemical outcome.

Another interesting aspect of allyl–metal reaction chemistry observed in the reactions of the $(\eta^3\text{-allyl})Fe(CO)_4^+$ complexes is the consistently higher terminal attack regioselectivity for the anti species **1b** relative to the *syn*-**1a**. Although high terminal attack regioselectivity has been reported previously for several reactions of nucleophiles with $(anti\text{-}\eta^3\text{-allyl})Fe(CO)_4^+$ complexes,[3,4] reactions of the corresponding syn complexes were previously unknown. Presently we have no convincing explanation for the higher regioselectivity with the anti complexes. A similar effect found in the reactions of $(\eta^5\text{-pentadienyl})Fe(CO)_3^+$ has been rationalized on steric grounds.[15] A careful frontier MO analysis of the reaction profiles for each complex with a representative nucelophile might shed some light on this issue.[16]

Besides the present study apparently no other examples of nucleophilic attack on an $(\eta^2\text{-allyl X})ML_n$ species (X = leaving group) have been reported. Although we have no direct mechanistic information on this process, the distinctly (yet not radically) different regioselectivities found for the η^2-vs. the η^3-complexes rule out the exclusive intermediacy of the latter species in the reactions of the former. Indeed, the regioisomeric products resulting from nucleophilic attack on the η^2-complexes need not be derived from a single, common intermediate. Other reasonable pathways include direct attack by Nu on the η^2-complex (Scheme II) and/or initial isomerization to the covalent $(\eta^3\text{-allyl})Fe(CO)_3X$ followed by nucleophilic attack. The first possibility draws analogy from the known addition of nucleophiles to $Fe(CO)_4$-coordinated α,β-unsaturated carbonyl compounds.[17] The $\eta^2\text{-} \rightarrow \eta^3$-isomerization involved in the second pathway occurs at 40 °C (1–2 h) in the reactions of allyl halides (X = Cl, Br, I) with $Fe_2(CO)_9$.[18] Reactions of the $(\eta^3\text{-allyl})Fe(CO)_3X$ (X = Cl, Br, I) species with nucleophiles have not been reported. Although direct experimental evidence is lacking, presently we favor the former pathway (Nu attack on the η^2-complex) since we have seen no tendency of the η^2-species to undergo $\eta^2 \rightarrow \eta^3$-isomerization in the absence of nucleophiles at the reaction temperatures (20 °C) and, considering the poorer leaving group ability of OAc^- relative to Cl^-, Br^-, and I^-, we would expect its departure to be slower than the actually observed reaction rate. Clearly, additional studies of the reactions of the η^2-allyl X complexes are required to resolve these mechanistic questions and to assess their potential synthetic utility.

Table IV. Regioselectivity of Catalytic Alkylations of 1,2-Disubstituted Allylic Substrates with NaDMM

substr	cat.	T/I	ref
	$W(CO)_3(CH_3CN)$/bpy	24:76	1e
a	$Fe(CO)_3NO^-$	91:9	1c
a	$Fe_2(CO)_9$	37:63	this work
	*a*	52:48	*a*
	$(PPh_3)_4Pd$	50:50	27
	*a*	*a*	27
	$(Ph_3P)_4Pd$	35:65	2

[a] Same as above.

To put the results of the $Fe_2(CO)_9$-catalyzed reactions in proper perspective, it is useful to compare these with other metal-catalyzed alkylations. In Table IV we have collected together regioselectivity data from the literature for crotyl and 1,2-disubstituted olefinic substrates with malonate as nucleophile. Although the data for other metals with these basic reactants are rather limited, it appears that this substrate/nucleophile pairing generally leads to only poor to fair regioselectivity. In fact the W- and Pd-catalyzed reactions, which previously have been characterized as giving predominantly terminal and internal attack respectively, both show a modest *internal* attack selectivity or none at all with the present substrate/nucleophile combination. The $Fe_2(CO)_9$-catalyzed reactions fare no better (nor worse). The reaction catalyzed by $NaFe(CO)_3NO$[1c] stands alone in promoting high terminal attack selectivity. This latter catalyst certainly warrants further study for its general efficacy and selectivity in allylic alkylation.

Although the regioselectivity exhibited by the $Fe_2(CO)_9$-catalyzed reactions is unexceptional when compared to the other catalysts, the unique feature of these reactions emerges when their selectivities are compared to those of the corresponding $(\eta^2\text{-allyl X})Fe(CO)_4$ and $(\eta^3\text{-allyl})Fe(CO)_4^+$ complexes. Comparison of the results for the allylic acetates given in Table III with those of Tables I and II leads one to the conclusion that the major product-forming step(s) in these catalytic reactions is not attack by nucleophile on either the $(\eta^3\text{-crotyl})Fe(CO)_4^+$ or the $(\eta^2\text{-crotyl OAc})Fe(CO)_4$ complexes. This conclusion is most clearly evidenced in the catalytic reactions of *cis*-crotyl acetate in which the observed regioselectivities cannot be obtained by any combination of pathways involving only the η^2- and η^3-complexes. The quantitative differences with the

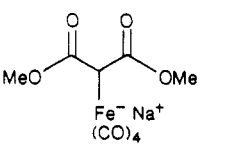
(11) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1984**, *106*, 6837.
(12) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.
(13) Trost, B. M.; Weber, L.; Stege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.
(14) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769.
(15) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954.
(16) Discussions of this question with Prof. O. Eisenstein (University of Paris, Sud) are underway.
(17) Roberts, B. W.; Wong, J. *J. Chem. Soc., Chem. Commun.* **1977**, 20.
(18) Murdoch, H. O.; Weiss, E. *Helv. Chim. Acta* **1962**, *45*, 1927.

trans-crotyl substrate for the three sets of reactions are less substantial but significant nonetheless, especially when the nonreactivity of morpholine in the catalytic reaction is noted. We believe, therefore, that the same conclusion is warranted for the *trans*-crotyl acetate reactions.

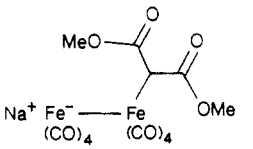
The significance of the above conclusion lies in the fact that (η^3-allyl)ML_n species are almost universally considered to be important intermediates in allylic alkylation reactions. In reality, however, rather little mechanistic information is available for these reactions. A few strictly comparable examples of a metal-catalyzed process and its stoichiometric counterpart for Pd can be extracted from the literature,[9,13,19] and these show similar or identical regioselectivities. Certainly, reports of allylic alkylation occurring with net retention of configuration at the substituted carbon (for Pd, Mo, and W) support a scheme wherein an (η^3-allyl)ML_n species is formed (with inversion at C) followed by external attack by Nu (also with inversion). On the other hand, alternate pathways involving two stereochemically retentive steps generally cannot be ruled out. Suffice it to say that much remains to be done before the mechanisms of catalytic allylic alkylation are well-understood.

The effect of varying the leaving group in the iron-catalyzed reactions is most interesting. Not only does the reaction rate increase significantly in going from X = $OCOCH_3$ to X = $OCOCF_3$ (suggesting that leaving group departure is involved in the rate-determining step), but also there is a substantial change in regioselectivity. With most of the nucleophiles examined the crotyl trifluoroacetates (promoted by $Fe_2(CO)_9$) gave essentially the same product distribution as the corresponding (η^3-crotyl)$Fe(CO)_4^+$ reactions, suggesting the intermediacy of the latter in these catalytic reactions. The exceptions to this generalization, however, require either a different pathway or may indicate that the similar selectivity found in several cases is merely fortuitous. More concrete conclusions must await additional experiments which are underway. In any event, we note that systematic studies of leaving group variation on the course of other metal-catalyzed allylic alkylations are nonexistent. Synthetically speaking, iron-catalyzed couplings using allylic trifluoroacetates as substrates look most promising since their regio- and stereoselectivities are good to excellent, favoring attack at the less substituted allylic carbon and preserving of the substrate's double-bond geometry. Studies to further explore the scope and synthetic utility of these reactions are in progress.

Examination of the reactions of malonate ion with $Fe_2(CO)_9$ in THF has provided some evidence for the involvement of coordinated malonate species in the catalytic reactions. It appears that two different $Fe_x(CO)_y(DMM)_z^{z-}$ species, designated A and B, may be produced depending on the $DMM^-/Fe_2(CO)_9$ stoichiometry employed. The species anion A formed in the 1:1 reaction has been better characterized because of its somewhat greater solution stability. It apparently contains an σ-C-bonded malonate ligand based on the rather shielded methine ^1H and ^{13}C NMR resonances (3.0 and 18.5 ppm, respectively) and IR carboxyl C=O stretch (1704 cm^{-1}). These data may be compared to those for neutral C-bonded $L_2Pd(CH(CO_2R)_2)_2$ (^1H methine, 3.6–3.8 ppm; ^{13}C methine, 50–52 ppm; ν(C=O) 1690–1710 cm^{-1}; ref 20) and (η^3-allyl)$Pd(PMe_3)(CHCNCO_2Me)$ (^{13}C methine, 11 ppm; ref 21) and O-bonded $NaCH(CO_2Me)_2$ (^1H methine, 3.85; ^{13}C methine, 100 ppm; ν(C=O), 1670 cm^{-1}). The terminal metal carbonyl IR absorptions in the 1900–2000 cm^{-1} region and the absence of bridging carbonyl absorptions are consistent with either an anionic mononuclear complex, e.g., $NaFe(CO)_4(DMM)$ (7), or a polynuclear complex lacking bridging carbonyls, e.g., $NaFe_2(CO)_8(DMM)$ (8). The



7



8

available data do not allow us to differentiate these two possibilities, but we favor the latter option 8 for species A as it more readily accommodates the reactivity of A toward additional malonate ion to form species B (vide infra) and the fact that A can also be produced from the reaction of $BrCH(CO_2Me)_2$ with $Na_2Fe_2(CO)_8$. Known species related to the proposed A include $Fe_2(CO)_8H^-$ and $Fe_2(CO)_8CN^-$ which have similar IR spectra to species A.[21,22] Importantly, anion A itself does not react directly with crotyl acetates under ambient conditions in THF, ruling it out as the actual catalyst species.

With excess malonate (10–20:1), $Fe_2(CO)_9$ or species A is largely converted to a different species whose IR and ^1H NMR spectra again point to a C-bonded iron malonate derivative. The instability of species B has prevented its isolation and more complete characterization. However, considering the requirement of excess malonate, the available spectroscopic data, and the apparent production of B from $Na_2Fe(CO)_4/BrCH(CO_2Me)_2$ a reasonable interpretation of these results would involve conversion of $NaFe_2(CO)_8DMM$ (8, species A) to $NaFe(CO)_4(DMM)$ (7, species B) according to eq 9.

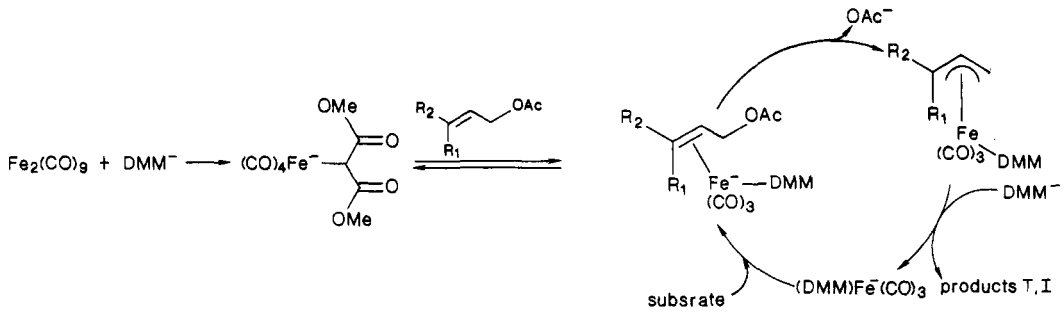
$$Fe_2(CO)_9 + NaDMM \rightarrow NaFe_2(CO)_8(DMM) \xrightleftharpoons{NaDMM} 2NaFe(CO)_4(DMM) \quad (9)$$

The IR spectral features of B (as the Na salt) are comparable to other $RFe(CO)_4^-$ species (as PPN^+ salts)—R = CH_2CN, 2010, 1892, 1863 cm^{-1}, R = CH_2CO_2Et, 2000, 1902, 1878 cm^{-1},[24] and R = CN, 2034, 1946, 1927 cm^{-1} [23]—but surprisingly little different from species A.[25] Until the solution state structures of anions A and B are completely elucidated, it is dangerous to offer an explanation for this observation, but we point out that a similar effect has been seen for the homologs $Fe(CO)_4CN^-$ and $Fe_2(CO)_8CN^-$.[23]

The fact that species B reacts with crotyl acetates only in the presence of excess malonate ion indicates that B (like A) also is not the true catalyst but rather a catalyst precursor. The neither free nor coordinated malonate alone react with allylic acetates directly suggests that both malonate and the allyl substrate must be coordinated for coupling to occur. The requirement of excess malonate for successful coupling, however, implies that coordination of a single substrate molecule, and malonate ion is a necessary but not sufficient condition for coupling. Crossover experiments therefore were conducted in an

(19) Godleski, S. A.; Gundlach, K. B.; Ho, H. Y.; Keinan, E.; Frolow, F. *Organometallics* **1984**, *3*, 21.
(20) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R. *Organometallics* **1984**, *3*, 1549.
(21) Jolly, P. W.; Mynott, F.; Raspel, B.; Schick, K.-P. *Organometallics* **1986**, *5*, 473.
(22) Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J. Chem. Soc. a* **1969**, 2339.
(23) Ruff, J. K. *Inorg. Chem.* **1969**, *8*, 86.
(24) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 2516.
(25) The presence of terminal metal carbonyl IR bands in excess of the number expected for an $XFe(CO)_4^-$ species may indicate the presence of more than one ion-pair species or a byproduct which has no protons (hence not detected by ^1H NMR).

Scheme III



effort to determine whether malonate incorporated in the product was precoordinated or derived from external attack. Unfortunately, the results obtained were equivocal. Thus the formation of crossover products could be accommodated by *either* a combination of external and internal (precoordination) nucleophilic attack pathways *or* a preequilibrium between free and coordinated malonates followed by a slower coupling step (either intra- or intermolecular or both). We decline to speculate about the significance of the quantitative product distributions observed in these experiments because of significant uncertainties in the actual concentrations of the somewhat unstable anions B and B′ relative to the added NaDEM or NaDMM. With these observations in mind we suggest Scheme III as a plausible contributing mechanistic pathway in the coupling of allylic acetates with nucleophiles catalyzed by $Fe_2(CO)_9$. More conventional nucleophilic attack on (η^3-allyl)$Fe(CO)_4^+$ or (η^2-allyl OAc)$Fe(CO)_4$ may also play some role.

Although we have not examined directly the interaction of the other nucleophiles in this study with $Fe_2(CO)_9$, the dissimilarity of regioselectivities between the catalytic reactions and the corresponding η^2- and η^3-complex reactions (most obvious with *cis*-crotyl acetate) suggests that they too may proceed via $NuFe_x(CO)_y^-$ intermediates. We believe the failure of $Fe_2(CO)_9$ to catalyze the coupling of morpholine with allylic acetates is due to formation of stable (morpholine)$Fe(CO)_4$[26] which is unreactive toward substrate.

Finally we come back to the relevance of these results to the mechanism of catalytic allylic alkylation involving other metals. Trost and co-workers have suggested the possible involvement of species derived from the reaction of $Mo(CO)_6$ with dimethyl malonate (e.g., $(CO)_xMo(DMM)^-$) in Mo-catalyzed allylic alkylations[1d] though no data supporting this contention has been given. Indeed, the ability of metal carbonyl fragments to accommodate negative charge via the agency of the π-accepting carbonyl ligands renders such $NuML_n^-$ species as highly viable intermediates in allylic alkylations catalyzed by metal carbonyls. While direct comparisons between the Mo- and Fe-catalyzed reactions are difficult because of the differing nucleophiles and substrates employed, there appear to be some qualitative similarities but quantitative differences in the regioselectivities of the two processes. So while both classes of reactions show increasing terminal attack selectivity with increasing steric bulk of the nucleophile, the Fe-promoted reactions appear to be significantly less sensitive to such changes.

Conclusions

Using crotyl acetate as the allyl component, a common set of nucleophiles, and regioselectivity as a measure, allylic alkylation catalyzed by $Fe_2(CO)_9$ occurs by a pathway not requiring the intermediacy of either (η^3-allyl)$Fe(CO)_4^+$ or (η^2-allyl OAc)$Fe(CO)_4$ complexes. Studies of the interaction of NaDMM with $Fe_2(CO)_9$ have provided evidence for the formation of $Fe_x(CO)_yDMM^-$ ions in the catalytic reactions and their involvement as precursors to the actual catalyst species. The regioselectivities observed in the catalytic reactions with crotyl acetates are modest to good depending on, in part, the steric demands of the nucleophile; the reactions are stereospecific, retaining the substrates double-bond geometry. Finally, significantly higher regioselectivity toward attack at the less substituted allylic carbon have been observed with crotyl trifluoroacetates as substrates.

Experimental Section

General Data. All operations were carried out under prepurified nitrogen or argon atmospheres using standard Schlenk line techniques. Glassware was flame-dried prior to use.

^1H and ^{13}C NMR spectra were recorded on a IBM NR80 or on a Varian XL-300 spectrometer. All NMR chemical shifts are reported in parts per million (δ) relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer and are reported in inverse centimeters. Mass spectra were determined on a Hewlett-Packard 5985 GC/mass spectrometer. Analytical and preparative GLPC were carried out on a Hewlett-Packard 5790A using a 5 ft × $^1/_8$ in. OV 101 and a 6 ft × $^3/_8$ in. OV 101 packed columns, respectively.

Reagent grade tetrahydrofuran was distilled from sodium benzophenone ketyl. Reagent grade dichloromethane was distilled under nitrogen from P_2O_5. The NMR solvents THF-d_8 and CD_2Cl_2 were dried for 24 h over molecular sieves and were degassed by the freeze–pump–thaw technique and stored under an inert atmosphere. Diiron nonacarbonyl (Pressure Chemical) was purified by washing with concentrated HCl, followed by distilled water, ethanol, and diethyl ether before use. *trans*-Crotyl acetate (95%; Columbia Organics) was purified by distillation. *cis*-Crotyl acetate (98%) was prepared by acetylation of 98% *cis*-2 buten-1-ol (Wiley Organics). *cis*- and *trans*-crotyl trifluoroacetates were prepared by trifluoroacetylation ($(CF_3CO)_2O$/pyridine) of the commercial alcohols. Anionic nucleophiles were prepared by reacting 1 equiv of 50% sodium hydride (Alfa) with 1 equiv of freshly distilled dimethyl malonate (Sigma Chemical), diethyl methylmalonate (CTC Organics) or (phenylsulfonyl)acetonitrile (CTC organics). Dimethyl bromomalonate was prepared by a published procedure.[27] (η^2-Crotyl acetate)$Fe(CO)_4$ complexes were prepared according to the method reported previously for (η^2-allyl acetate)$Fe(CO)_4$.[7] (η^2-Crotyl)$Fe(CO)_4BF_4$ complexes were also prepared as described earlier.[7]

Reaction of (*syn*- or *anti*-η^3-Crotyl)$Fe(CO)_4BF_4$ with Nucleophiles. To a 1-mL THF solution containing 0.3 mmol of nucleophile was added 0.2 mmol of **1a** or **1b**. The reactions were complete within 1 h (by GC) and worked up by quenching with 1 N HCl, washing with H_2O, solvent extraction, and evaporation on a rotory evaporator. The green oil was flash chromatographed on silica gel eluting with 8% EtOAc/hexane. Separation of the product isomers was carried out by preparative GC and the yields and relative ratios are reported in Table I.

(26) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

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Characterization was accomplished by ^1H and ^{13}C NMR, IR, and mass spectrometry and comparison with literature[3] data.

Reaction of ((*E*)- or (*Z*)-η^2-Crotyl acetate)Fe(CO)$_4$ with Nucleophiles. To 2 mL of THF at 20 °C containing 0.7 mmol of nucleophile was added 0.2 mmol of **2a** or **2b** in 1 mL of THF. The reactions were generally complete (by GC) within 1 h and the product ratios (Table II) determined by GC.

Allylic Alkylation Catalyzed by $Fe_2(CO)_9$. To a 2-mL solution of THF containing 0.5 mmol of allylic substrate and 1 mmol of sodium enolate species was added at ambient temperature 0.05 mmol of $Fe_2(CO)_9$ and an additional 1 mL of THF. The reactions were monitored by GC, and when judged complete (3–5 days for X = OAc, 1–2 days for X = $OCOCF_3$), if desired, they were worked up as described on the reactions of the η^3-complexes.

From the catalytic reactions of $NaCMe(CO_2Et)_2$ with *cis*-crotyl acetate and $NaCH(CO_2Me)_2$ with *cis*-crotyl trifluoroacetate minor products **3** and **4** were isolated by preparative GC (retention times slightly shorter than C-alkylation products).

3: ^1H NMR ($CDCl_3$) δ 5.65 (2 H, m), 4.70 (2 H, m), 4.20 (2 H, q, J = 7 Hz), 3.45 (1 H, q, J = 7 Hz), 1.7 (3 H, b d, J = 6.5 Hz), 1.4 (3 H, d, J = 7 Hz), 1.3 (3 H, t, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 170, 131, 129, 123, 66, 62, 61, 46, 17, 14, 13; MS (12 EV, m/e) 200 (M^+).

4: ^1H NMR ($CDCl_3$) δ 5.5 (2 H, m), 4.70 (2 H, apparent d, J = 7 Hz), 3.7 (3 H, s), 3.4 (2 H, s), 1.7 (3 H, d, J = 7 Hz).

Reaction of $Fe_2(CO)_9$ and $NaCH(CO_2Me)_2$ (1:1) (Anion A). To a 1-mL THF solution containing 0.6 mmol of sodium dimethyl malonate was added 0.6 mmol of $Fe_2(CO)_9$, and the mixture was diluted with another 2 mL of THF. After 2 h of stirring the solution was homogeneous, the solvent was removed by vacuum evaporation, redissolved in dichloromethane, and filtered with a filter stick, and the solvent removed again by vacuum evaporation. The resulting oily solid was taken up in THF-d_8 (for NMR) or CH_2Cl_2 (for IR): ^1H NMR δ 3.54 (s, 6 H, OMe), 2.98 (s, 1 H, CH); ^{13}C NMR δ 220.1 (s, FeCO), 181.7 (CO_2), 50.5 (OMe), 18.5 (FeCH); IR 2025 (m), 1985 (m), 1960 (w), 1920 (s), 1900 (s), 1703 (m) cm^{-1}.

Reaction of $Na_2Fe_2(CO)_8$ with $BrCH(CO_2Me)_2$. According to ref 28 $Na_2Fe_2(CO)_8$ was produced from the reaction of $Na_2Fe(CO)_4$·1.5dioxane (0.50 g, 1.44 mmol) with $Fe(CO)_5$ (0.195 mL, 1.44 mmol) in 10 mL of THF at room temperature. When the resulting mixture containing orange precipitated $Na_2Fe_2(CO)_8$·nTHF was cooled to −78 °C and treated with 0.30 g (1.4 mmol) of $BrCH(CO_2Me)_2$, the solid quickly dissolved and the solution turned deep red with deposition of a white solid (NaBr?). The IR spectrum of this solution was virtually identical with that formed from the 1:1 reaction of $Fe_2(CO)_9$ with $NaCH(CO_2Me)_2$.

Reaction of $Fe_2(CO)_9$ and $NaCH(CO_2Me)_2$ (1:20) (Anion B). To a 16 mL of THF solution containing 5.4 mmol of $NaCH(CO_2Me)_2$ was added 0.27 mmol of $Fe_2(CO)_9$. After 12 h of stirring the solvent was removed by a rotary evaporator. Isolation as described above gave an unstable solid and only marginal spectra could be obtained: ^1H NMR (THF-d_8) δ 3.64 (s, 6 H, OMe), 3.49 (s, 1 H, CH); IR (THF) 2025, 1995, 1970, 1925, 1885, 1715 cm^{-1}.

Reaction of $Na_2Fe(CO)_4$ with Dimethyl Bromomalonate–CH_3I Trapping. Into a 50-mL side-arm round-bottomed flask was placed 0.35 g (1.0 mmol) of $Na_2Fe(CO)_4$·1.5dioxane (in drybox) and a stir bar, and the flask was fitted with a rubber septum. THF (30 mL) was added via syringe, and the mixture was cooled to −78 °C with stirring. $BrCH(CO_2Me)_2$ (0.21 g, 1.0 mmol) was added dropwise via syringe resulting in an instantaneous color change from pink to deep red and formation of a light precipitate (NaBr?). Withdrawal of a solution aliquot and rapid IR scanning revealed bands at 2010, 1990, 1915, and 1710 cm^{-1} (decomposition apparent upon warming). An excess of CH_3I (ca. 1 mL) was then added and the mixture allowed to warm to room temperature. After 20 h GC analysis of the rust colored mixture showed the presence of a 3:1 mixture of $CH_3CH(CO_2Me)_2$ and $CH_2(CO_2Me)_2$ as the only volatile products.

Allylic Alkylation Catalyzed by $Na_2Fe(CO)_4$/$BrCH(CO_2Me)_2$ with Excess $NaCH(CO_2Me)_2$. The reaction of $Na_2Fe(CO)_4$·1.5dioxane with $BrCH(CO_2Me)_2$ was carried out as above. To this reaction mixture at −78 °C was added 10 mmol of $NaCH(CO_2Me)_2$ dissolved in 10 mL of THF. After 15 min *trans*-crotyl acetate (5 mmol) was added and the mixture allowed to warm with stirring. Periodic GC analysis revealed gradual formation of the expected alkylation products (I/T = 2:1).

Attempted Reaction of 1:1 $NaCH(CO_2Me)_2$/$Fe_2(CO)_9$ with Allylic Substrates in the Presence of Excess Malonate. A 2-mL solution of THF containing 1 mmol of $Fe_2(CO)_9$ and 1 mmol of $NaCH(CO_2Me)_2$ was stirred for 2 h after which 5 mmol of the allylic substrate species was added. No product formation was observed by GC even after 10 days.

Reaction of 20:1 Sodium Malonate/$Fe_2(CO)_9$ with Allylic Substrates. A 2-mL THF solution containing 1 mmol of nucleophile and 0.05 mmol of $Fe_2(CO)_9$ was stirred for 2 h, and then 0.5 mmol of substrate was added. GC Monitoring indicated product distributions essentially identical with those in the catalytic reactions (Table III).

Attempted Reaction of Isolated Anion B (20:1 DMM^-/$Fe_2(CO)_9$) with Crotyl Acetate. Preparation and isolation of anion B (1 mmol of $Fe_2(CO)_9$) as described above was followed by addition of 5 mmol of *cis*- or *trans*-crotyl acetate. No product formation was detected by GC analysis even after 5 days. Subsequent addition of 5 mmol of NaDMM in 5 mL of THF resulted in gradual appearance of alkylation products (detected by GC) over 12–24 h.

Crossover Experiment 1: Reaction of DMM/Anion B with *cis*-Crotyl Acetate and NaDEM. To a solution of $NaCH(CO_2Me)_2$ in 8 mL of THF prepared from 0.32 mL of $CH_2(CO_2Me)_2$ (2.7 mmol) and 0.13 g of 50% NaH/mineral oil (2.7 mmol) was added 0.050 g (0.14 mmol) of $Fe_2(CO)_9$ and the mixture stirred under nitrogen for 11 h. Volatiles were pumped off, the residue was triturated with CH_2Cl_2, the extracts were filtered, the filtrate was concentrated in vacuo, and the residue was redissolved in 5 mL THF. *cis*-Crotyl acetate (0.010 mL) was then added; after 3 days GC analysis showed no product formation. A solution containing 0.14 mmol of $NaCH(CO_2Et)_2$ in 1 mL of THF was then added and the reaction monitored by GC. Graduate appearance over a few days of the products I, T, I′, and T′ (Scheme I) was indicated by GC analysis (~4.7:1.1:1.6:1.0).

Crossover Experiment 2: Reaction of DEM/Anion B with *cis*-Crotyl Acetate and NaDMM. Following the same procedure described above the complex from $NaCH(CO_2Et)_2$ and $Fe_2(CO)_9$ was treated first with *cis*-crotyl acetate (3 days) followed by ca. 1 molar equiv of $NaCH(CO_2Me)_2$. GC analysis revealed the gradual formation (1–5 days) of products I, T, I′, and T′ (Scheme I) in the approximate ratio 1.0:1.3:4.7:3.4.

Attempted Reactions of NaDMM with 5 and 6 Promoted by $Fe_2(CO)_9$. To a THF solution (4 mL) containing 1.0 mmol of NaDMM and 0.25 mmol of **5** or **6** was added 0.2 mmol of $Fe_2(CO)_9$. After the solution stirred for ca. 50 h at 20 °C, no product formation was detected by GC analysis. Subsequent refluxing of the mixture containing for an additional 50–90 h failed to produce any reaction as indicated by GC.

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Registry No. **1a**, 56083-12-6; **1b**, 46135-08-4; **2a**, 104011-71-4; **2b**, 97969-99-8; **3**, 103935-60-0; **4**, 103935-61-1; (*E*)-crotyl/DMM T-couple, 82545-71-9; crotyl/DMM I-couple, 61979-92-8; (*E*)-crotyl/MDEM T-couple, 82545-68-4; crotyl/MDEM I-couple, 78331-64-3; (*E*)-crotyl/CH(SO_2Ph)CN T-couple, 103935-56-4; crotyl/CHnSO_2Ph)CN I-couple, 103935-57-5; (*E*)-crotyl/morpholine T-couple, 35755-83-0; crotyl/morphoiline I-couple, 33591-72-9; (*Z*)-crotyl/DMM T-couple, 99922-88-0; (*Z*)-crotyl/MDEM T-couple, 103935-58-6; (*Z*)-crotyl/CH(SO_2Ph)CN T-couple, 103935-59-7; (*Z*)-crotyl/morpholine T-couple, 59385-94-3; $Fe_2(CO)_9$, 15321-51-4; $Na_iFe_2(CO)_8$, 66016-41-9; NaCH(SO_2Ph)CN, 77081-24-4; NaDMM, 18424-76-5; NaMDEM, 996-82-7; NaCHnSO_2Ph)CN, 77081-24-4; $CH_3CH(CO_2Me)_2$, 609-02-9; $CH_2(CO_2Me)_2$, 108-59-8; (*E*)-CH_3CH=$CHCH_2OAc$, 7204-29-7; (*E*)-CH_3CH=$CHCH_2OCOCF_3$o, 103935-62-2; (*Z*)-CH_oCH=$CHCH_iOAc$, 7204-36-6; (*Z*)-CH_3CH=$CHCH_2OCOCF_3$, 65909-62-8; $BrCH(CO_2Me)_2$, 868-26-8; $Na_2Fe(CO)_4$, 14878-31-0; morpholine, 110-91-8.

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