Intramolecular Ene-type Reaction between a Diene–Fe(CO)$_3$ Complex and Alkene Units

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Heating of allylic amide or allylic ester substituted diene–Fe(CO)$_3$ complexes such as (**7**) and (**10**) (140 °C) results in an intramolecular coupling of the pendant double bond with the diene moiety to give spirolactam and spirolactone derivatives; the stereochemical course of this reaction was established by an *X*-ray crystal structure determination of the lactone derivative (**11**).

Carbon–carbon bond formation by addition of nucleophiles to a variety of organotransition metal complexes has resulted in wide-ranging synthetic application.[1] Cationic dienyl–Fe(CO)$_3$ complexes are very reactive toward nucleophiles and show considerable promise as synthetic intermediates,[2] but there are nevertheless many problems associated with their use. For example, the traditional hydride abstraction [*e.g.*, (**1**) to (**2**)] either fails or is non-regioselective in many cases,[3] and a number of dienyl complexes do not undergo nucleophile addition with the most desirable regiochemistry [*e.g.*, (**3**) gives exclusively (**4**)].[4] We are currently examining methods to overcome these shortcomings.

Some years ago, a number of reactions between diene–Fe(CO)$_3$ complexes and electron deficient alkenes were

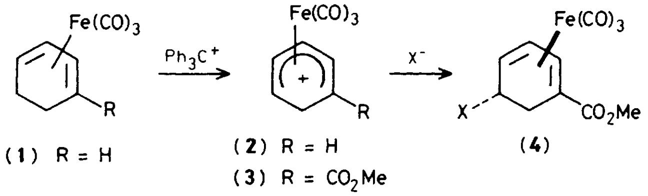
Table 1. Intramolecular coupling of unsaturated groups with a diene–Fe(CO)$_3$ moiety.

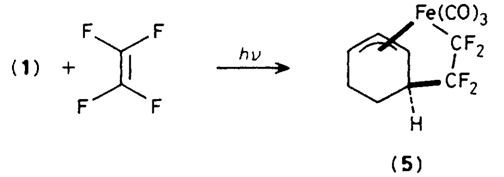
Entry	Substrate complex	Conditions	Product	% Yield
1	**(7)**	Bu$^n{}_2$O, reflux, 16 h	**(8a)** + **(9a)**	29
2	**(7)**	Bu$^n{}_2$O, 1 atm CO, reflux, 6 h	**(8a)** + **(9a)**	80
3	**(7)**	Bu$^n{}_2$O, PPh$_3$, reflux, 6—8 h	**(8b)** + **(9b)**	60
4	**(10)**	Bu$^n{}_2$O, 1 atm CO, reflux, 11 h	**(11)**	88
5	**(12a)**	Bu$^n{}_2$O, 1 atm CO, reflux, 5 h	**(13a)**	84
6	**(12b)**	Bu$^n{}_2$O, 1 atm CO, reflux, 11 h	**(13b)**	88
7	**(12c)**	Bu$^n{}_2$O, 1 atm CO, reflux	No reaction	
8	**(12c)**	C$_6$H$_6$, irradiate (sun lamp), CO, reflux	**(13c)**	40[a]
9	**(12d)**	Bu$^n{}_2$O, 1 atm CO, reflux, 6 h	**(13d)**	92
10	**(12e)**	Bu$^n{}_2$O, 1 atm CO, reflux, 12 h	**(13e)**	15
11	**(12e)**	C$_6$H$_6$, irradiate (sun lamp), CO, reflux	No reaction	

[a] Yield based on starting material consumed at 71% conversion.

described.[5] One example is the photochemical combination of complex (**1**) with tetrafluoroethylene,[5a] which gives the η^3-allyl complex (**5**). In a formal sense, this reaction can be regarded as an incomplete (non-concerted) ene-type reaction between the diene–Fe(CO)$_3$ unit and the alkene; all that is required is hydrogen migration, *via* the metal, with cleavage of the Fe–CF$_2$ σ-bond by reductive elimination. However, complexes such as (**5**) are stable and do not react further. We felt (somewhat intuitively) that an intermediate σ-complex not having strong electron-withdrawing groups would stand a greater chance of exhibiting such behaviour, and in order to force the initial C–C bond-forming reaction to proceed, we reasoned that an *intramolecular* process should be investigated.

The diallylamide (**7**) was readily prepared from the carboxylic acid (**6**) (Scheme 1).[4]† When this complex was heated under N$_2$ atmosphere (reflux, di-n-butyl ether, 16 h) a low yield (26%) of a mixture of spiro-lactams was isolated. The yield of the cyclization process was much improved by conducting the reaction under carbon monoxide atmosphere (reflux, di-n-butyl ether, reaction is complete after 6 h), when a mixture of spiro-lactams was obtained in 77% yield. Chromatographic separation allowed complexes (**8a**) and (**9a**) (ratio *ca.* 1:2) to be isolated, both obtained as equimolar mixtures of epimers at the lactam CHMe group.† Complex (**9a**), a product of allyl group isomerization, was further separated to give *E*- and *Z*-isomers† (ratio *E*:*Z ca.* 2:1). Apparently, addition of a suitable ligand to the reaction mixture is necessary for efficient conversion; addition of triphenylphosphine leads to similar mixtures of lactams (**8b**) and (**9b**) but in slightly lower yield than when CO is used.





The allyl ester complex (**10**) was similarly prepared from (**6**) and subjected to thermal ring closure conditions (Bu$^n{}_2$O, reflux, 1 atm CO, 11 h), when a 90% yield of spiro-lactone (**11**) was obtained† as an equimolar mixture of epimers. This reaction requires a longer time for completion than the above amide cyclization, but does not suffer from the problem of double bond isomerization.

In order to test the generality of this new coupling reaction, a series of allylic amide and allylic ester complexes (**12a**—**e**) was prepared. The problem of double bond isomerization encountered with the diallyl amide (**7**) was nicely overcome by using the *N*-phenyl derivatives shown. The results of thermal (and in two cases, photochemical) cyclization are summarized in Table 1. Of particular interest is the observation that cyclization of the amide derivatives occurs much more readily than that of the corresponding esters, a striking example being the comparison of the 2-methylprop-2-enyl amide (**12d**) and ester (**12e**) (entries 9 and 10).

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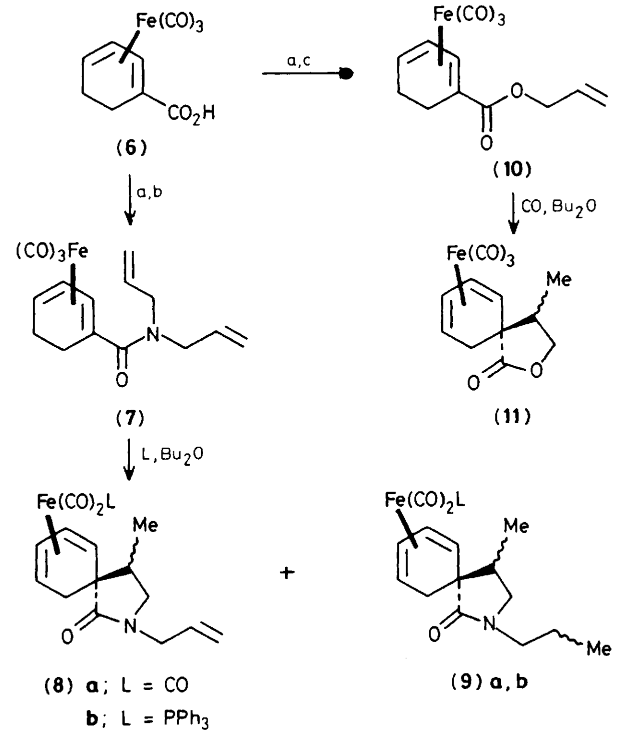
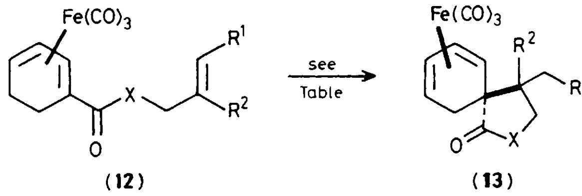
† All new compounds were obtained as racemic mixtures and were fully characterized by i.r., n.m.r., and high resolution mass spectrometry or combustion analysis. Spectral data for representative compounds are as follows. (**8a**): i.r. (CHCl$_3$) $\nu_{max.}$ 2050, 1970, 1692, and 1640 cm^{-1}; n.m.r. (CDCl$_3$; data for one epimer) δ 5.8—5.6 (1H, m, vinyl), 5.55 (2H, m, 'inner' diene), 5.2 (2H, m, vinyl), 3.85 (2H, m, allyl CH$_2$), 3.35 (1H, dd, *J* 10, 7 Hz), 3.23 (1H, m), 2.85 (1H, t, *J* 10 Hz), 2.68 (1H, dd, *J* 6.4, 1.5 Hz), 2.04 (1H, m, C*H*Me), 1.95—1.8 (2H, m, diene ring CH$_2$), and 1.11 (3H, d, *J* 7 Hz, Me); the other epimer shows lactam CH$_2$ peaks at δ 3.7 (dd, *J* 10.4, 6.5 Hz) and 3.03 (d, *J* 10.4 Hz), C*H*Me at δ 2.24 (apparent quintet, *J* 7 Hz), and Me at δ 0.94 (d, *J* 7 Hz). (**9a**) (*E* isomer): i.r. (CHCl$_3$) $\nu_{max.}$ 2050, 1970, 1700, and 1665 cm^{-1}; n.m.r. (CDCl$_3$; data for one epimer, from decoupling experiments): δ 6.8 (1H, dq, *J* 14, 2 Hz, vinyl), 5.5 (2H, m, 'inner' diene), 4.94 (1H, m, vinyl), 3.7 (1H, dd, *J* 10.4, 6.5 Hz), 3.45 (1H, m), 3.03 (1H, d, *J* 10.4 Hz), 2.86 (1H, m), 2.24 (1H, quintet, *J* 7 Hz, C*H*Me), 1.7 (3H, dd, *J* 6.5, 2 Hz, vinyl Me), and 0.94 (3H, d, *J* 7 Hz, Me). (**11**): i.r. (CHCl$_3$) $\nu_{max.}$ 2050, 1970, and 1775 cm^{-1}; n.m.r. (CDCl$_3$; data for one epimer obtained by preparative t.l.c.) δ 5.5 (2H, m), 4.5 (1H, dd, *J* 9.2, 5.6 Hz, lactone), 3.9 (1H, t, *J* 9.2 Hz, lactone), 3.25 (1H, m), 2.74 (1H, dd, *J* 6.4, 1.5 Hz), 2.25 (1H, m) 2.12 (1H, dd, *J* 14, 2.5 Hz), 1.90 (1H, dd, *J* 14, 3.1 Hz), and 1.18 (3H, *J* 7 Hz).



Scheme 1. *Reagents:* a, $(COCl)_2$, CH_2Cl_2, room temp., 3 h; b, diallylamine, pyridine, benzene, room temp., overnight; c, allyl alcohol, pyridine, benzene, room temp., overnight.



a; X = NPh, $R^1 = R^2 = H$
b; X = NPh, $R^1 = Me$, $R^2 = H$
c; X = O, $R^1 = Me$, $R^2 = H$
d; X = NPh, $R^1 = H$, $R^2 = Me$
e; X = O, $R^1 = H$, $R^2 = Me$

The stereochemical outcome of this new cyclization process was elucidated by a single crystal *X*-ray structure determination on one of the epimers of lactone (**11**) (Figure 1).‡ This is indicative of a mechanism involving co-ordination of the pendant double bond to iron, and the further details will form the basis of future investigations.

In summary, intramolecular coupling between unsaturated groups and a diene–Fe(CO)$_3$ complex provides a novel and efficient method for the construction of quaternary carbon centres. The scope, mechanism, and synthetic application of this reaction are being studied.

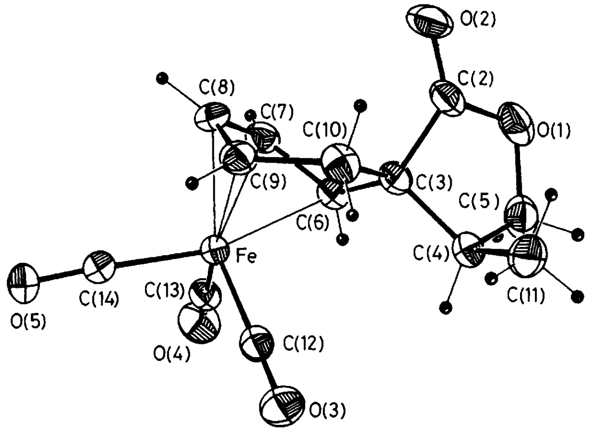


Figure 1. View of complex (**11**) showing the atom labels. Selected distances (Å): Fe–C(6) 2.088(2); Fe–C(7) 2.045(2); Fe–C(8) 2.056(2); Fe–C(9) 2.110(3); Fe–C(12) 1.768(2); Fe–C(13) 1.790(2); Fe–C(14) 1.791(3); C(6)–C(7) 1.426(3); C(7)–C(8) 1.397(4); C(8)–C(9) 1.409(4). Selected angles (°): C(6)–Fe–C(7) 40.36(9); C(7)–Fe–C(8) 39.8(1); C(8)–Fe–C(9) 39.5(1); C(6)–C(7)–C(8) 114.4(2); C(7)–C(8)–C(9) 115.4(2); C(3)–C(6)–C(7) 118.2(2); C(6)–C(3)–C(10) 109.4(2); C(3)–C(10)–C(9) 111.5(2); C(8)–C(9)–C(10) 120.6(2).

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‡ *Crystal data*, complex (**11**): $C_{13}H_{12}FeO_5$; crystal dimensions = 0.34 × 0.30 × 0.22 mm; orthorhombic; space group *Pbca*; $a = 22.450(3)$, $b = 12.489(3)$, $c = 9.240(2)$ Å; $Z = 8$; $M_r = 304.08$ g/mol; $D_c = 1.56$ g/cm^3; $\mu = 11.7$ cm^{-1}; Enraf-Nonius CAD4 diffractometer; graphite monochromatized Mo-K_α radiation; $0 < 2\theta \leq 52°$; 3339 total reflexions, 2913 unique; $R = 0.030$; $R_w = 0.040$ for 1798 reflections with $F_o^2 > 3\sigma F_o^2$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.