Science and Engineering Research Council, U.K.

Registry No. **3**, 130031-79-7; **4a**, 130031-80-0; **4b**, 130143-25-8; **6a**, 130143-23-6; **6b**, 130031-78-6; **7**, 130031-84-4; **8**, 130031-81-1; **9a**, 130031-82-2; **9b**, 130143-24-7; **10**, 130031-83-3; **11**, 100701-98-2; $Cp^*_2TaH_3$, 100701-94-8; C_3H_5MgBr, 1730-25-2; *trans*-$CH_3CH{=}CHCH_2MgBr$, 36306-56-6; $Cp^*_2TaCl_2$, 100701-93-7; $CH_2{=}C{=}CH_2$, 463-49-0; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $CH_3C{\equiv}CCH_3$, 503-17-3; $CH_3C{\equiv}CH$, 74-99-7; $Cp^*_2Ta(H)({=}C{=}CH_2)$, 103619-53-0; $CH_2{=}PMe_3$, 14580-91-7.

Preparation of Tricarbonyl(η^4-vinylketene)iron(0) Complexes from Tricarbonyl(η^4-vinyl ketone)iron(0) Complexes and Their Subsequent Conversion to Tricarbonyl(η^4-vinylketenimine)iron(0) Complexes

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Reaction of tricarbonyl(η^4-vinyl ketone)iron(0) complexes $(CO)_3(PhCH{=}CHC(R){=}O)Fe(0)$ (R = Me, **1**; Bu^n, **3**; Bu^t, **5**; Ph, **7**) with organolithium reagents under an atmosphere of carbon monoxide gave products that were identified as tricarbonyl"(η^4-vinylketene)"iron(0) complexes $(CO)_3(PhCH{=}CHC(R){=}C{=}O)Fe(0)$ (R = Me, **2**; Bu^n, **4**; Bu^t, **6**; Ph, **8**) based on a crystal structure analysis of **2**. Complex **2** crystallizes in space group $P2_1/c$ with a = 13.998 (6) Å, b = 7.955 (5) Å, c = 12.935 (5) Å, β = 113.04 (3)°, and Z = 4. A reaction pathway that postulates the intermediacy of a tricarbonyl(η^3-vinylcarbene)iron(0) complex, **20**, is discussed. Heating the tricarbonyl(η^4-vinylketene)iron(0) complexes **6** and **2** with either *tert*-butyl, cyclohexyl, or 2,6-xylyl isocyanide at 80 °C gave tricarbonyl"(η^4-vinylketenimine)"iron(0) complexes $(CO)_3(PhCH{=}CHC(R^1){=}C{=}NR^2)Fe(0)$ (R^1 = R^2 = Bu^t, **23**; R^1 = Me, R^2 = Bu^t, **24**; R^1 = Me, R^2 = C_6H_{11}, **25**; R^1 = Me, R^2 = $(2,6\text{-}Me_2)C_6H_3$, **26**) via intermediate dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complexes. The intermediacy of tricarbonyl(isocyanide)(η^1-vinylcarbene)iron(0) complexes in this reaction is proposed.

Introduction

Investigations into the reactivity of vinyl ketones complexed to the tricarbonyliron(0) moiety have been neglected in the past in favor of investigations into the reactivity of 1,3-dienes complexed to the tricarbonyliron(0) unit.[1] This is somewhat surprising in view of the central role played by carbonyl compounds in organic synthesis and the potential that these complexes hold for exerting high stereochemical control over reactions of the vinyl ketone ligand. The major application of tricarbonyl(η^4-vinyl ketone)iron(0) complexes to date has been their use as a source of the tricarbonyliron(0) unit, which may be transferred from the vinyl ketone ligand to 1,3-dienes under relatively mild conditions.[2] Other investigations have revealed that they may be protonated[3] or acylated[4] on the ligand oxygen atom and that on heating they cyclodimerize to generate cyclopentene derivatives.[5]

Some time ago we reported the first examples of nucleophilic attack on tricarbonyl(η^4-vinyl ketone)iron(0) complexes.[6] We demonstrated that reactions of Grignard and organolithium reagents with a range of complexes under a nitrogen atmosphere produced 1,4-diketones in good yield, presumably via nucleophilic attack on a metal carbonyl ligand. This chemistry has been subsequently applied to the synthesis of dihydrojasmone and the formal synthesis of cuparene.[7] Recently it has been reported that addition of $LiCMe_2CN$ to an iron(0) complex of a vinyl ketone resulted in a Michael-type addition; i.e., direct attack on the organic ligand occurred.[8] This observation is consistent with the results obtained from studies on tricarbonyl(η^4-1,3-diene)iron(0),[9] tetracarbonyl(η^2-vinyl ester)iron(0),[10] and tetracarbonyl(η^2-vinylamide)iron(0)[11] complexes, which show that in these systems alkyllithium and Grignard reagents add to a carbonyl ligand while

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Table I. Positional Parameters (×10⁴) and Their Estimated Standard Deviations for Complex 2

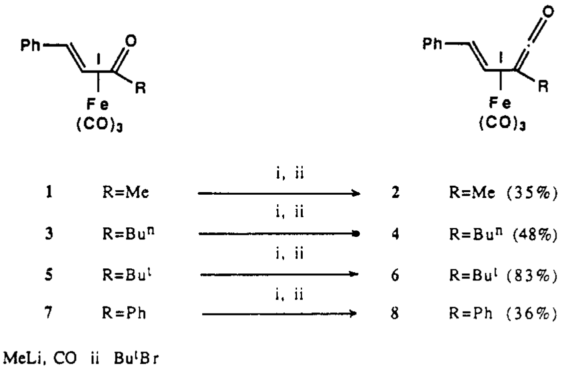
atom	x	y	z
Fe	2059.3 (3)	6405.2 (5)	7265.8 (3)
O(1)	1334 (2)	2935 (3)	6932 (3)
O(2)	3973 (2)	6074 (4)	9273 (2)
O(3)	2868 (2)	6173 (4)	5472 (2)
O(4)	908 (2)	6354 (3)	8777 (2)
C(1)	1641 (3)	4268 (4)	7054 (3)
C(2)	3234 (3)	6168 (4)	8471 (3)
C(3)	2556 (3)	6315 (4)	6147 (3)
C(4)	1104 (2)	6730 (4)	7989 (3)
C(5)	591 (2)	7488 (4)	6895 (2)
C(6)	−442 (3)	6904 (5)	6062 (3)
C(7)	1229 (3)	8621 (4)	6640 (3)
C(8)	2178 (3)	9123 (4)	7506 (3)
C(9)	2967 (2)	10164 (4)	7338 (3)
C(10)	2986 (3)	10494 (4)	6294 (3)
C(11)	3706 (4)	11590 (5)	6188 (4)
C(12)	4415 (3)	12371 (5)	7118 (4)
C(13)	4420 (3)	12039 (5)	8152 (4)
C(14)	3711 (3)	10942 (4)	8268 (3)

stabilized carbanions add to the organic ligand.

We describe herein experiments which demonstrate that treatment of tricarbonyl(η^4-vinyl ketone)iron(0) complexes with organolithium reagents under an atmosphere of *carbon monoxide* leads to tricarbonyl(η^4-vinylketene)iron(0) complexes and that tricarbonyl(η^4-vinylketene)iron(0) complexes can be converted into tricarbonyl(η^4-vinylketenimine)iron(0) complexes simply by heating them with an isocyanide. Experiments that shed light on the reaction pathways of these two novel reactions are also described. Part of this work has been the subject of two preliminary communications.[12,13]

Results and Discussion

Tricarbonyl(η^4-benzylideneacetone)iron(0), **1**, is readily prepared from benzylideneacetone and enneacarbonyldiiron.[14] A solution of complex **1** in tetrahydrofuran (THF)



was cooled to −78 °C under 1 atm of carbon monoxide and treated with 1.1 equiv of methyllithium. After stirring for 2 h and quenching with *tert*-butyl bromide, the reaction mixture was filtered through alumina to remove iron residues and then chromatographed. This led to the isolation of air-stable yellow crystals, which were identified as the novel tricarbonyl(η^4-vinylketene)iron(0) complex **2** on the basis of their spectroscopic and microanalytical data and an X-ray crystal structure analysis (Figure 1; Tables I and II).

Table II. Selected Bond Lengths and Angles in Complex 2

	Bond Lengths, Å		
Fe–C(1)	1.784 (3)	Fe–C(2)	1.778 (3)
Fe–C(3)	1.836 (4)	Fe–C(2)	1.926 (4)
Fe–C(5)	2.103 (3)	Fe–C(7)	2.092 (3)
Fe–C(8)	2.181 (3)	O(1)–C(1)	1.132 (4)
O(2)–C(2)	1.146 (4)	O(3)–C(3)	1.125 (5)
O(4)–C(4)	1.194 (5)	C(4)–C(5)	1.444 (4)
C(5)–C(6)	1.499 (4)	C(5)–C(7)	1.397 (5)
C(7)–C(8)	1.420 (4)	C(8)–C(9)	1.462 (5)
C(9)–C(10)	1.386 (6)	C(9)–C(14)	1.391 (4)
C(10)–C(11)	1.380 (7)	C(11)–C(12)	1.372 (6)
C(12)–C(13)	1.361 (8)	C(13)–C(14)	1.374 (6)
	Bond Angles, deg		
C(1)–Fe–C(2)	99.7 (1)	C(1)–Fe–C(3)	92.6 (2)
C(2)–Fe–C(3)	100.4 (2)	C(1)–Fe–C(4)	87.4 (2)
C(2)–Fe–C(4)	99.7 (2)	C(3)–Fe–C(4)	159.6 (1)
C(1)–Fe–C(5)	97.0 (1)	C(2)–Fe–C(5)	136.8 (2)
C(3)–Fe–C(5)	118.3 (1)	C(4)–Fe–C(5)	41.7 (1)
C(1)–Fe–C(7)	130.1 (1)	C(2)–Fe–C(7)	127.7 (1)
C(3)–Fe–C(7)	93.0 (1)	C(4)–Fe–C(7)	71.9 (1)
C(5)–Fe–C(7)	38.9 (1)	C(1)–Fe–C(8)	165.6 (2)
C(2)–Fe–C(8)	89.3 (1)	C(3)–Fe–C(8)	96.9 (1)
C(4)–Fe–C(8)	80.0 (1)	C(5)–Fe–C(8)	68.9 (1)
C(7)–Fe–C(8)	38.7 (1)	Fe–C(1)–O(1)	176.5 (4)
Fe–C(2)–O(2)	176.6 (4)	Fe–C(3)–O(3)	176.4 (3)
Fe–C(4)–O(4)	144.8 (2)	Fe–C(4)–C(5)	75.7 (2)
O(4)–C(4)–C(5)	138.5 (3)	Fe–C(5)–C(4)	62.5 (2)
Fe–C(5)–C(6)	128.2 (3)	C(4)–C(5)–C(6)	123.0 (3)
Fe–C(5)–C(7)	70.1 (2)	C(4)–C(5)–C(7)	112.5 (3)
C(6)–C(5)–C(7)	123.8 (3)	Fe–C(7)–C(5)	71.0 (2)
Fe–C(7)–C(8)	74.0 (2)	C(5)–C(7)–C(8)	118.8 (3)
Fe–C(8)–C(7)	67.2 (2)	Fe–C(8)–C(9)	124.1 (3)
C(7)–C(8)–C(9)	124.7 (3)	C(8)–C(9)–C(10)	123.7 (3)
C(8)–C(9)–C(14)	118.5 (3)	C(10)–C(9)–C(14)	117.7 (3)
C(9)–C(10)–C(11)	120.7 (3)	C(10)–C(11)–C(12)	120.3 (5)
C(11)–C(12)–C(13)	119.9 (5)	C(12)–C(13)–C(14)	120.3 (4)
C(9)–C(14)–C(13)	121.1 (4)		

Table III. IR Data (cm^{-1})[a] for Vinylketene and Vinylketenimine Complexes

complex	$\nu_{C\equiv O}$	$\nu_{C\equiv N}$	$\nu_{C=O}$	$\nu_{C=N}$
2	2067 vs, 2006 vs, 1995 vs		1791 m	
4	2070 vs, 2009 vs, 1997 vs		1790 m	
6	2065 vs, 2001 vs, 1995 vs		1785 m	
8	2067 vs, 2008 vs, 2003 vs		1789 m	
21	1955 vs	2130 m, 2100 m, 2070 m	1732 m	
22	2014 vs, 1967 vs	2144 m	1753 br m	
23	2045 vs, 1981 vs, 1979 vs			1723 m
24	2040 vs, 1982 vs, 1978 vs			1720 m
25	2055 vs, 1989 vs, 1983 vs			1744 m
26	2067 vs, 2008 vs, 1993 vs			1740 br m
27	2015 vs, 1969 vs	2145 m	1765 br m	
28	2018 vs, 1968 vs	2146 m	1765 br m	

[a] Cyclohexane solution.

The bond lengths and bond angles of **2** correspond closely with those found in other (η^4-vinylketene)iron(0) complexes bearing alkyl or aryl groups on the vinylketene ligand,[15] thus reinforcing the view that the vinylketene–

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(14) Complexes **1**, **3**, **5**, **7**, and **9** were obtained in 81%, 82%, 89%, 79%, and 53% yield, respectively, by heating 2 equiv of $Fe_2(CO)_9$ with the appropriate vinyl carbonyl at 35 °C in diethyl ether for 15–18 h. These conditions were found to be considerably more convenient than conditions used previously,[3,6] which involved heating 1 equiv of $Fe_2(CO)_9$ with the vinyl carbonyl at 60–75 °C in toluene for 3–4 h and gave yields of 30–40%.

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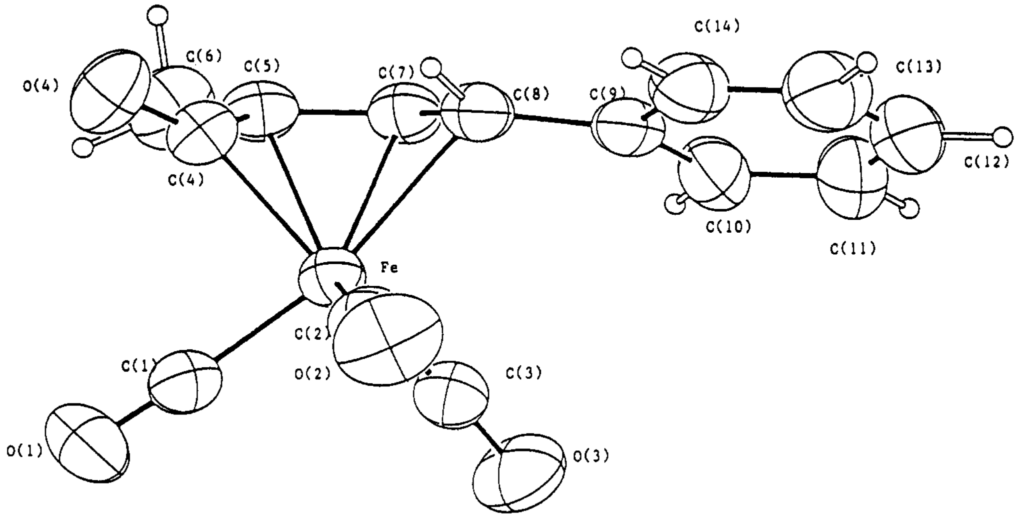


Figure 1. Molecular structure of complex **2**.

Table IV. ^{1}H NMR Data (δ)[a] for Vinylketene and Vinylketenimine Complexes

complex	C(7)-*H*[b]	C(8)-*H*	C(8)-*Ph*	C(5) substituent	RN≡C or RN=C
2	6.43 (1 H, d, *J* = 9[c])	3.22 (1 H, d, *J* = 9)	7.31–7.47 (5 H, m)	1.94 (3 H, s)	
4	6.36 (1 H, d, *J* = 9)	3.22 (1 H, d, *J* = 9)	7.29–7.47 (5 H, m)	2.30–2.17 (1 H, m), 2.12–1.98 (1 H, m), 1.76–1.37 (4 H, m), 0.97 (3 H, t, *J* = 8)	
6	6.34 (1 H, d, *J* = 9)	3.14 (1 H, d, *J* = 9)	7.31–7.48 (5 H, m)	1.29 (9 H, s)	
8	6.90 (1 H, d, *J* = 9)	3.52 (1 H, d, *J* = 9)	*d*	*d*	
21	6.10 (1 H, d, *J* = 9)	2.56 (1 H, d, *J* = 9)	7.14–7.44 (5 H, m)	1.25 (9 H, s)	1.37 (9 H, s) 1.40 (9 H, s)
22	6.20 (1 H, d, *J* = 9)	2.90 (1 H, d, *J* = 9)	7.20–7.44 (5 H, m)	1.26 (9 H, s)	1.37 (9 H, s)
23	6.10 (1 H, d, *J* = 9)	2.80 (1 H, d, *J* = 9)	7.20–7.36 (5 H, m)	1.33 (9 H, s)	1.40 (9 H, s)
24	6.14 (1 H, d, *J* = 9)	2.88 (1 H, d, *J* = 9)	7.40–7.20 (5 H, m)	2.04 (3 H, s)	1.41 (9 H, s)
25	6.15 (1 H, d, *J* = 9)	2.78 (1 H, d, *J* = 9)	7.20–7.38 (5 H, m)	2.06 (3 H, s)	3.14 (1 H, m), 1.17–1.98 (10 H, m)
26	6.22 (1 H, d, *J* = 9)	2.95 (1 H, d, *J* = 9)	*e*	*e*	*e*
27	6.26 (1 H, d, *J* = 9)	2.97 (1 H, d, *J* = 9)	7.19–7.45 (5 H, m)	1.85 (3 H, s)	1.36 (9 H, s)
28	6.26 (1 H, d, *J* = 9)	2.97 (1 H, d, *J* = 9)	7.17–7.42 (5 H, m)	1.85 (3 H, s)	3.67 (1 H, m), 1.27–1.85 (10 H, m)

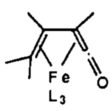
[a] $CDCl_3$. [b] See Figure 1 for numbering. [c] *J* given in Hz. [d] 7.30–7.67 (10 H, m). [e] 7.01–7.35 (8 H, m), 2.20 (9 H, s).

Table V. $^{13}C\{^1H\}$ NMR (δ)[a] Data for Vinylketene and Vinylketenimine Complexes

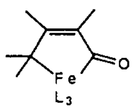
complex	C(4)[b]	C(5)	C(7)	C(8)	C(9)	C(10)–C(14)	C(5) substituent	C≡O	*R*N≡C or *R*N=C
2	234.6	46.0	95.9	58.9	138.0	126.3, 127.3, 128.9	13.9	207.5	
4	234.2	50.2	94.8	59.4	138.2	126.5, 127.4, 129.0	13.6, 22.2, 28.0, 31.4	207.9	
6	232.4	60.5	91.8	60.0	138.1	126.5, 127.5, 129.0	29.2, 30.0	208.3	
8	232.8	49.7	91.4	60.8	137.9	126.6, 127.7, 129.2	127.4, 128.7 129.2, 131.1	207.3	
21	219.7	62.1	93.6	51.9	143.0	124.4, 126.2, 127.4	29.6, 30.2	218.5	30.7, 164.5[c]
22	228.3	61.7	93.4	56.2	140.6	125.9, 126.5, 128.4	29.4, 30.1	213.3	30.4, 57.1, 156.1
23	179.4	70.2	88.7	60.0	138.8	126.3, 126.9, 128.8	29.1, 31.9	205.5 211.8	29.5, 56.5
24	183.6	57.7	93.0	59.0	138.8	126.2, 126.9, 128.8	17.3	205.5, 210.0	29.5, 56.4
25	188.5	59.9	92.4	58.6	138.9	126.2, 126.8, 128.7	17.1	209 br	24.5, 24.7, 25.5, 33.1, 34.2, 70.1
26	196.2	61.6	92.4	59.2	138.8	126.2, 127.0, 128.9	16.7	208.5	18.0, 123.7, 128.0, 149.1[d]
27	225.1	47.6	97.3	55.0	140.7	125.8, 126.4, 128.4	14.0	212.7	30.4, 57.2, 155.6
28	244.1	47.5	97.2	54.9	140.6	125.8, 126.3, 128.4	14.0	209 br	22.6, 24.7, 32.5, 54.5, 157.0

[a] $CDCl_3$, 300 K. [b] See Figure 1 for numbering. [c] CMe_3 not assigned. [d] $C_{2,6}$ not assigned.

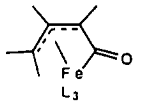
metal linkage cannot be adequately described by a single structure and that structures A, B, and C all make contributions to the ligand–metal bonding.[16] The IR spectrum of **2** in cyclohexane contained three very strong $\nu_{C≡O}$ absorptions at 2067, 2006, and 1995 cm^{-1} and a medium absorption at 1791 cm^{-1} assigned to the $\nu_{C=O}$ of the η^1-acyl carbonyl (Table III). Resonances at δ 6.43 (1 H, d, *J* = 9 Hz) and 3.22 (1 H, d, *J* = 9 Hz) in the ^{1}H NMR spectrum



A



B



C

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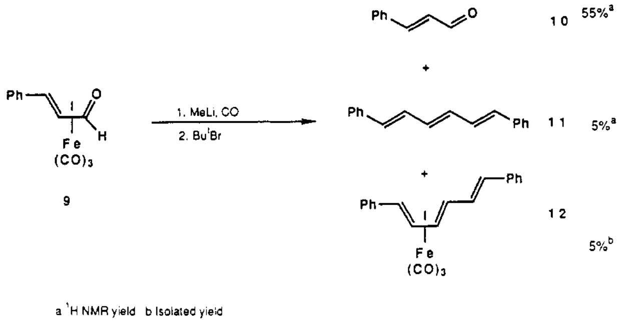
Table VI. MS Data for Vinylketene and Vinylketenimine Complexes

complex	mass spectra[a]
2	299, 43% $(MH)^+$; 270, 40% $(M - CO)^+$; 242, 48%, $(M - 2CO)^+$; 214, 100%, $(M - 3CO)^+$; 186, 49% $(M - 4CO)^+$
4	341, 30%, $(MH)^+$; 313, 11%, $(MH - CO)^+$; 285, 24%, $(MH - 2CO)^+$; 256, 84%, $(M - 3CO)^+$; 228, 100%, $(M - 4CO)^+$
6	341, 33%, $(MH)^+$; 313, 16%, $(MH - CO)^+$; 284, 24%, $(M - 2CO)^+$; 256, 88%, $(M - 3CO)^+$; 228, 100%, $(M - 4CO)^+$
8	361, 22%, $(MH)^+$; 332, 29%, $(M - CO)^+$; 304, 14%, $(M - 2CO)^+$; 276, 91%, $(M - 3CO)^+$; 248, 100%, $(M - 4CO)^+$
21	450, 22%, $(M)^+$; 422, 58%, $(M - CO)^+$; 394, 100%, $(M - 2CO)^+$; 367, 13%, $(M - CN^tBu)^+$; 311, 99%, $(M - 2CO - CN^tBu)^+$; 311, 99%, $(M - 2CO - CN^tBu)^+$; 284, 29%, $(M - 2CN^tBu)^+$; 228, 27%, $(M - 2CO - 2CN^tBu)^+$
22	396, 28%, $(MH)^+$; 367, 25%, $(M - CO)^+$; 340, 17%, $(MH - 2CO)^+$; 311, 100%, $(M - 3CO)^+$; 228, 21%, $(M - 3CO - CN^tBu)^+$
23	396, 16%, $(MH)^+$; 367, 10%, $(M - CO)^+$; 340, 4%, $(MH - 2CO)^+$; 311, 100%, $(M - 3CO)^+$
24	354, 66%, $(MH)^+$; 326, 31%, $(MH - CO)^+$; 297, 18%, $(M - 2CO)^+$; 269, 100%, $(M - 3CO)^+$
25	380, 17%, $(MH)^+$; 352, 12%, $(MH - CO)^+$; 324, 6%, $(MH - 2CO)^+$; 295, 100%, $(M - 3CO)^+$
26	402, 25%, $(MH)^+$; 374, 10%, $(MH - CO)^+$; 346, 5%, $(MH - 2CO)^+$; 317, 100%, $(M - 3CO)^+$
27	354, 17%, $(MH)^+$; 325, 12%, $(M - CO)^+$; 298, 21%, $(MH - 2CO)^+$; 269, 100%, $(M - 3CO)^+$
28	380, 14%, $(MH)^+$; 351, 37%, $(M - CO)^+$; 324, 30%, $(MH - 2CO)^+$; 295, 100%, $(M - 3CO)^+$; 186, 51%, $(M - 3CO - CNCy)^+$

[a] Data presented as m/e, relative abundance, (assignment).

were assigned to the hydrogens attached to C(7) and C(8), respectively, while the Ph and Me substituents on the vinylketene ligand gave rise to signals at δ 7.31–7.47 (5 H, m) and 1.94 (3 H, s) (Table IV). The ^{13}C NMR spectrum of **2** contained resonances at δ 234.6, 46.0, 95.9, and 58.9 assigned to C(4), C(5), C(7), and C(8) of the vinylketene ligand, respectively, in addition to resonances due to the Ph, Me, and carbonyl groups (Table V). The mass spectrum of **2** contained a clear $(MH)^+$ peak and a fragmentation pattern corresponding to the loss of four CO units (Table VI).

The tolerance of the ketone–ketene conversion to variation of the C(5) substituent was investigated. Tricarbonyl(η^4-vinyl ketone)iron(0) complexes **3**,[6] **5**,[6] and **7**[3] were each treated with 1.1 equiv of methyllithium under 1 atm of carbon monoxide followed by a *tert*-butyl bromide quench. The yellow crystalline products isolated gave IR, ^1H NMR, ^{13}C NMR, MS, and microanalytical data fully consistent with the novel tricarbonyl(η^4-vinylketene)iron(0) complexes **4**, **6**, and **8**, respectively (Tables III–VII). In contrast, the vinylaldehyde complex **9**[17] failed to undergo an analogous reaction. Reaction of **9** with methyllithium under 1 atm of carbon monoxide and workup gave a crude product mixture that ^1H NMR analysis revealed to be mainly decomplexed vinylaldehyde **10** together with small amounts of 1,6-diphenylhexatriene (**11**) and its tricarbonyliron(0) complex **12** (**10**:**11**:**12** = 11:1:1). Compounds **10** and **11** were identified by comparison of their ^1H NMR spectra with those obtained from commercially available material, and complex **12** was identified by isolation and comparison of its ^1H NMR, IR, and MS data with corresponding data from authentic **12**[18] synthesized by reacting triene **11** with $Fe_2(CO)_9$.



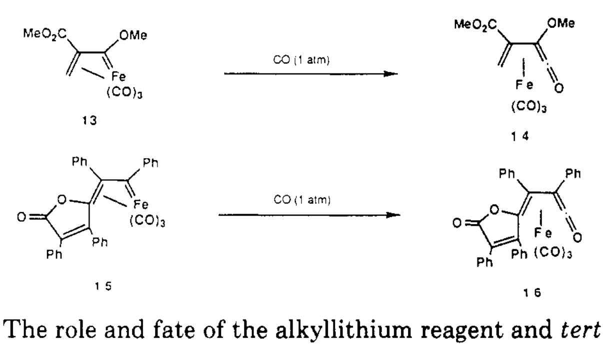
Conversion of complex **9** to triene **11** and its tricarbonyliron(0) complex **12** under the reaction conditions used to transform vinyl ketone complexes **1**, **3**, **5**, and **7** into

Table VII. Microanalysis Data for Vinylketene and Vinylketenimine Complexes[a]

complex	C	H	N
2	56.65 (56.41)	3.37 (3.38)	
4	60.07 (60.03)	4.71 (4.74)	
6	59.95 (60.03)	4.70 (4.74)	
8	63.01 (63.37)	3.20 (3.36)	
21	66.37 (66.67)	7.58 (7.61)	6.16 (6.22)
22	63.58 (63.81)	6.45 (6.37)	3.51 (3.54)
23	63.96 (63.81)	6.52 (6.37)	3.53 (3.54)
24	61.49 (61.21)	5.41 (5.42)	4.05 (3.97)
25	63.72 (63.34)	5.15 (5.58)	3.59 (3.69)
26	65.85 (65.86)	4.74 (4.77)	3.57 (3.49)
27	60.91 (61.21)	5.27 (5.42)	4.06 (3.97)
28	63.48 (63.34)	5.72 (5.58)	3.77 (3.69)

[a] Calculated figures in parentheses.

"vinylketene" complexes **2**, **4**, **6**, and **8** suggests that a vinylcarbene species may be an important intermediate in these reactions, i.e., that **11** and **12** are formed by head-to-head coupling of two vinylcarbene units and that more hindered vinylcarbene intermediates derived from complexes **1**, **3**, **5**, and **7** combine with carbon monoxide to generate vinylketene complexes **2**, **4**, **6**, and **8**. Evidence to support the postulated intermediacy of vinylcarbenes is provided by the observations that the (η^3-vinylcarbene)iron(0) complexes **13** and **15** can be converted into the (η^4-vinylketene)iron(0) complexes **14** and **16**, respectively, by stirring under 1 atm of carbon monoxide at room temperature.[16a,19]



The role and fate of the alkyllithium reagent and *tert*-butyl bromide in the reaction were investigated in order to obtain more insight into how the vinyl ketone ligands of complexes **1**, **3**, **5**, and **7** may be converted into vinylcarbene intermediates. The proton source *tert*-butyl bromides proved to be unnecessary for η^4-vinylketene formation as transformation of **1** into **2** and **7** into **8** proceeded smoothly and in higher yield (48% and 65% yield, respectively) when the *tert*-butyl bromide quench was

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(17) Stark, K.; Lancaster, J. E.; Murdock, H. D.; Weiss, E. *Z. Naturforsch, Teil B.* **1963**, *19*, 284.

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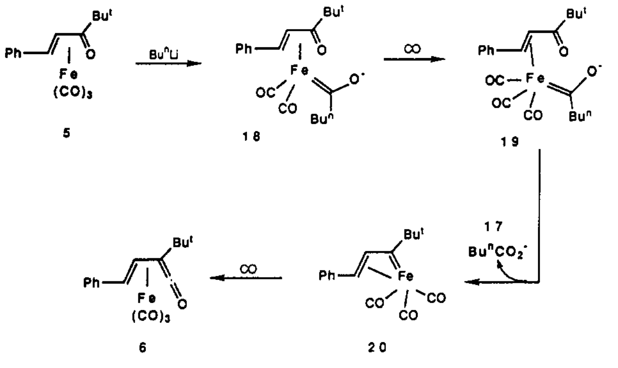
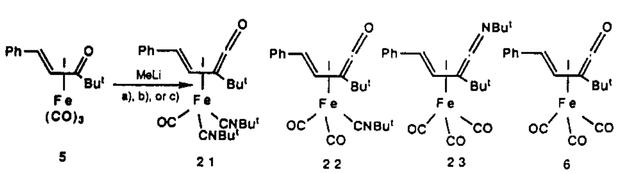
omitted from the reaction sequence. In contrast, the alkyllithium reagent is required for the reaction to occur, and stoichiometric amounts are needed for the reaction to go to completion. Complex **1** was unchanged after stirring under 1 atm of carbon monoxide in the absence of an alkyllithium reagent, and when 0.2 equiv of methyllithium was added to complex **5** and the reaction run under otherwise standard conditions, the crude product contained mainly the starting material **5** together with some η^4-vinylketene complex **6** and uncomplexed vinyl ketone (5:6:vinyl ketone = 3:1:1) as determined by ^{1}H NMR spectroscopy. Investigations into the fate of the alkyllithium reagent revealed that it is efficiently carboxylated. A solution of complex **5** in tetrahydrofuran was cooled to −78 °C under 1 atm of carbon monoxide and treated with 1.1 equiv of *n*-butyllithium. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and filtered to leave a white solid that was identified as lithium pentanoate (**17**) by comparison of its ^{1}H NMR and IR data with those obtained from an authentic sample; chromatography of the filtrate led to the isolation of η^4-vinylketene complex **6**. The isolated yields of **17** (56% based on **5**) and η^4-vinylketene complex **6** (58% based on **5**) suggest that the conversion of *n*-butyllithium to **17** and the transformation of complex **5** to complex **6** are coupled. Thus, a feasible reaction pathway for the alkyllithium-mediated conversion of η^4-vinyl ketone ligands into η^4-vinylketene ligands may be outlined as follows: addition of an alkyllithium reagent to the metal carbonyl ligand of an η^4-vinyl ketone complex, e.g., **5**, results in the formation of a metal acyl/carbene anion **18**, which after carbonylation to give **19** undergoes a metathesis-type reaction between the iron–carbon and carbon–oxygen double bonds of **19** to give lithium alkanoate (**17**) and vinylcarbene **20**; carbonylation then occurs to generate the product η^4-vinylketene complex **6**.



Thus, it appeared that during the conversion of η^4-vinyl ketone ligands to η^4-vinylketene ligands intermediate vinylcarbenes had been generated and coupled with carbon monoxide, so it was of interest to determine whether the postulated vinylcarbenes could also be coupled with isocyanides to generate products containing η^4-vinylketenimine ligands. Thus, a solution of η^4-vinyl ketone complex **5** in tetrahydrofuran was cooled to −78 °C under 1 atm of carbon monoxide, treated with 1.1 equiv of methyllithium stirred for 1 h, and then treated with 5 equiv of *tert*-butyl isocyanide. The resulting mixture was allowed to warm to room temperature, filtered through alumina, and chromatographed. This led to the isolation of the carbonyl(diisocyanide)(η^4-vinylketene)iron(0) complex **21**, the dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complex **22**, and the tricarbonyl(η^4-vinylketenimine)iron(0) complex **23** in 46%, 9%, and 2% yield, respectively (conditions a, Scheme I). Changing to a nitrogen atmosphere had little affect on the yields of products isolated, and reducing the number of equivalents of *tert*-butyl isocyanide added essentially reversed the ratio of **21** to **22** produced (conditions b and c, Scheme I). The novel complexes **21** and **22** were identified on the basis of their IR, ^{1}H NMR, ^{13}C NMR, MS, and microanalytical data (Tables III–VII), and the novel complex **23** was tentatively identified on the basis of its IR, ^{1}H NMR, and MS data. The identification was later confirmed by comparison of this data with data obtained from a fully characterized sample (see below). Thus, it appears that under the conditions employed in these reactions, the postulated vinylcarbene intermediate preferentially couples with a carbon monoxide molecule to give an η^4-vinylketene ligand and does not couple with an isocyanide molecule to give an η^4-vinylketenimine ligand to any significant extent.

Scheme I



5	21	22	23	6
a) 5eq.CNBu^t, 1 atm CO	46%^{a}	9%	2%	-
b) 5eq CNBu^t, 1 atm N$_2$	38%	3%	-	-
c) 1 eq CNBu^t, 1 atm CO	13%	47%	-	4%

a All yields are isolated yields

During the purification of complex **22**, an observation was made that led to the development of a facile method for converting tricarbonyl(η^4-vinylketene)iron(0) complexes into tricarbonyl(η^4-vinylketenimine)iron(0) complexes. It was noted that heating the dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complex **22** produced the tricarbonyl(η^4-vinylketenimine)iron(0) complex **23**. Given that thermal carbonyl–isocyanide exchange should occur readily in tricarbonyl(η^4-vinylketene)iron(0) complexes,[20] it was reasoned that simply hearing these complexes with an isocyanide should lead directly to tricarbonyl(η^4-vinylketenimine)iron(0) complexes. This hypothesis proved to be correct. Heating tricarbonyl(η^4-vinylketene)iron(0) complex **6** with *tert*-butyl isocyanide for 24 h in toluene at 80 °C followed by filtration through alumina and chromatography led to the isolation of a yellow air-stable crystalline complex that was identified as the novel tricarbonyl(η^4-vinylketenimine)iron(0) complex **23** on the basis of its spectroscopic and microanalytical data.

6 R^1=Bu^t $\xrightarrow{\text{1.2 eq. Bu}^t\text{NC, 24 h, 80 °C}}$ 23 R^1=Bu^t, R^2=Bu^t (58%)

2 R^1=Me $\xrightarrow{\text{1.3 eq. Bu}^t\text{NC, 10 h, 80 °C}}$ 24 R^1=Me, R^2=Bu^t (64%)

2 R^1=Me $\xrightarrow{\text{1.2 eq. C}_6\text{H}_{11}\text{NC, 16 h, 80 °C}}$ 25 R^1=Me, R^2=cyclohexyl (59%)

2 R^1=Me $\xrightarrow{\text{1 eq. (2,6-Me}_2\text{)C}_6\text{H}_3\text{NC, 24 h, 80 °C}}$ 26 R^1=Me, R^2=2,6-xylyl (60%^{a})

a Accounting for recovered starting material

The IR spectrum of **23** in cyclohexane contained three very strong $\nu_{C{=}O}$ absorptions at 2045, 1981, and 1979 cm^{-1} and a medium absorption at 1723 cm^{-1} assigned to $\nu_{C{=}N}$ (Table III). Resonances at δ 1.33 (9 H, s) and 1.40 (9 H, s) in the ^{1}H NMR spectrum were assigned to the hydrogens of the

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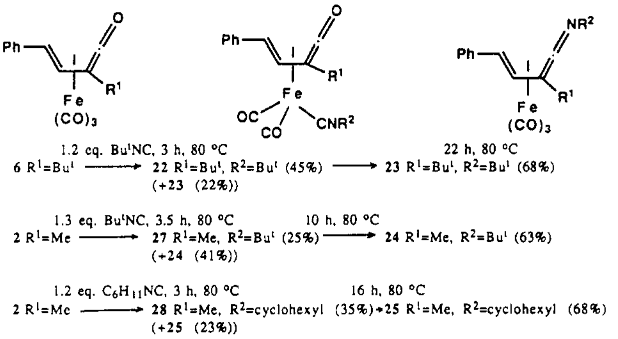
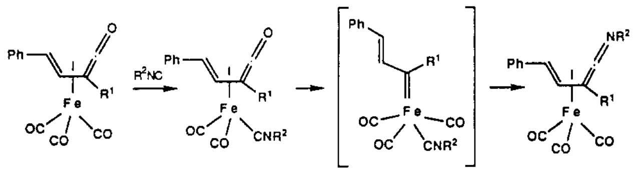
(20) Thermal carbonyl–triphenylphosphine exchange has been shown to proceed efficiently in tricarbonyl(vinylketene)iron(0) complexes.[15c]

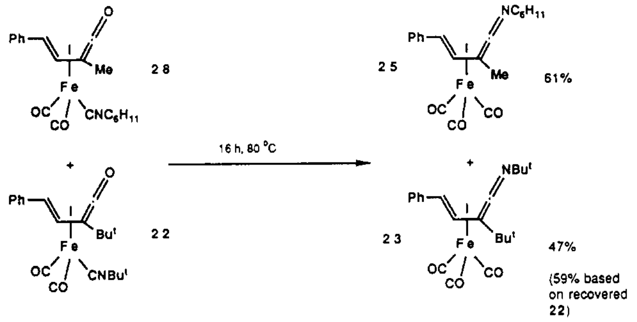
Bu^t groups bound to the C(5) carbon atom and the nitrogen atom of the η^4-vinylketenimine ligand, respectively, while the hydrogens attached to C(7), C(8), and the Ph substituent of the η^4-vinylketenimine ligand gave rise to signals at δ 6.10 (1 H, d, J = 9 Hz), 2.80 (1 H, d, J = 9 Hz), and 7.20–7.36 (5 H, m) (Table IV). The ^{13}C NMR spectrum of **23** contained resonances at δ 179.4, 70.2, 88.7, and 60.0 assigned to C(4), C(5), C(7), and C(8) of the vinylketenimine ligand, respectively, in addition to resonances due to the Ph, Bu^t, and carbonyl groups (Table V). The mass spectrum of **23** contained a (MH)$^+$ peak and a fragmentation pattern corresponding to the loss of three CO units (Table VI). These data are in good agreement with values reported for a related tricarbonyl(η^4-vinylketenimine)iron(0) complex that had been further characterized by an X-ray diffraction study.[21] The tolerance of the η^4-vinylketene to η^4-vinylketenimine conversion toward other isocyanides was examined. Complex **2** was heated in toluene with *tert*-butyl isocyanide and also with cyclohexyl and 2,6-xylyl isocyanide. The yellow crystalline products of these reactions were identified as the tricarbonyl(η^4-vinylketenimine)iron(0) complexes **24–26** on the basis of their IR, ^{1}H NMR, ^{13}C NMR, MS, and microanalytical data (Tables III–VII).

Several experiments were performed that were designed to confirm the course of the reaction pathway from the η^4-vinylketene complexes to the η^4-vinylketenimine complexes. Halting the reaction between η^4-vinylketene complex **6** and *tert*-butyl isocyanide in toluene after 3 h led to the isolation of not only product η^4-vinylketenimine **23** (22%) but also the dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complex **22** (45%). Similarly, interruption of the reactions between complex **2** and *tert*-butyl isocyanide or cyclohexyl isocyanide revealed that the reaction mixtures contained dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complexes **27** and **28** in addition to products **24** and **25**. Heating pure samples of complexes **22**, **27**, and **28** in toluene converted them into tricarbonyl(η^4-vinylketenimine)iron(0) complexes **23**, **24** and **25**, respectively. Thus, it would appear that the first step in the conversion of the η^4-vinylketene complexes to η^4-vinylketenimine complexes is indeed substitution of a carbonyl ligand by an isocyanide molecule. It has been observed that heating the tricarbonyl(η^4-vinylketene)iron(0) complex **16** at 60 °C results in the expulsion of carbon monoxide and the formation of vinylcarbene **15**.[19] Therefore, a feasible pathway for the conversion of dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) intermediates into tricarbonyl(η^4-vinylketenimine)iron(0) products might be initiated by breakdown of the ketene into a carbene ligand and a carbonyl ligand. This process requires the creation of a coordination site, which could be achieved either by expulsion of the isocyanide ligand or by expulsion of the π-bound alkene. To test whether or not decomplexation of the isocyanide ligand occurs during this process, a 1:1 mixture of complexes **28** and **22** were heated in toluene at 80 °C until complex **28** had been consumed. The resulting material contained a mixture of η^4-vinylketenimine complexes **25** and **23** and starting complex **22**, which were isolated in 61%, 47%, and 19% yield, respectively. We were unable to detect any evidence for the generation of crossover products during the experiment. Thus, it is proposed that the tricarbonyl(η^4-vinylketene)iron(0) complexes **6** and **2** are converted into tricarbonyl(vinylketenimine)iron(0) complexes **23–26** by the reaction pathway depicted in Scheme II, i.e., that the reaction proceeds via an η^1-vinylcarbene intermediate and that the final step involves combination of this carbene with the isocyanide ligand to form the ketenimine ligand of the product. Coupling of metal carbenes and isocyanides is a well-established method of generating ketenimines.[21,22] Consistent with our findings that isocyanide–carbonyl exchange in dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complexes is intramolecular in nature are observations made during the course of studies on the ketene complex tricarbonyl(η^4-diphenylketene)iron(0).[23] Stirring this complex under a ^{13}CO atmosphere gave material in which the ketene carbonyl and metal carbonyls were equally enriched, and a double labeling experiment was performed, which demonstrated that the carbonyl-exchange process in this complex was intramolecular in nature.



Scheme II





Experimental Section

All reactions were performed by using standard Schlenk tube and vacuum line techniques.[24] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Diethyl ether and toluene were dried over sodium wire. Petroleum ether refers to the fraction boiling in the range 40–60 °C. Methyllithium (1.4 M in diethyl ether) and n-butyllithium (2.5 M in hexanes) were purchased from Aldrich and their concentrations checked by a literature procedure.[25] Enneacarbonyldiiron(0) was prepared by a published procedure.[25] All other reagents were used as obtained from commercial sources. Chromatography was performed on SiO_2 (Merck, 40–63 μm). Melting points were determined in

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Table VIII. Melting Points for Vinylketene and Vinylketenimine Complexes

complex	mp, °C	complex	mp, °C
2	111–112[a]	**23**	71–72[b]
4	84–85[a]	**24**	79–79.5[a]
6	127–129[a]	**25**	*e*
8	136–139[a,d]	**26**	153–154[a]
21	109.5–110.5[a]	**27**	64–65[c]
22	113.5–114.5[a]	**28**	81–82[b]

[a] Hexane. [b] *n*-Pentane. [c] Hexane/diethyl ether. [d] With decomposition. [e] Noncrystalline solid.

nitrogen-filled capillaries and are not corrected. Elemental analyses were performed by Butterworth Laboratories Ltd. IR spectra were obtained on a Perkin-Elmer 580B instrument and calibrated with a polystyrene standard. NMR spectra were recorded on Perkin-Elmer R34 (200-MHz ^{1}H) and Bruker WH400 (100.6-MHz ^{13}C) spectrometers. Mass spectra were recorded on a Kratos MS 80 instrument by using FAB (matrix—*m*-nitrobenzyl alcohol[27]) techniques.

Synthesis of Tricarbonyl(η^4-vinylcarbonyl)iron(0) Complexes 1, 3, 5, 7, and 9. The preparation of complex **1** is representative of the procedure used for complexes **1**, **3**, **5**, **7**, and **9**. Enneacarbonyldiiron(0) (4.703 g, 12.9 mmol) and benzylideneacetone (0.945 g, 6.46 mmol) were added to diethyl ether (24 mL), and the resulting mixture was heated at reflux with stirring for 18 h. The dark reaction mixture was cooled and passed through alumina, (Grade IV; diethyl ether) and the solvent removed in vacuo. Chromatography of the resulting red solid (SiO$_2$; ethyl acetate–petroleum ether, 1:9) led to the isolation of red crystals of pure **1**[3] (1.504 g, 81%). Complexes **3**[6] (82%), **5**[6] (89%), **7**[3] (79%), and **9**[16] (53%) were prepared by using the procedure described above. Chromatography conditions: SiO$_2$; ethyl acetate–petroleum ether, **3**, 3:97; **5**, 3:97; **7**, 3:97; **9**, 1:9.

Synthesis of Tricarbonyl(η^4-vinylketene)iron(0) Complexes 2, 4, 6, and 8. The preparation of complex **2** is representative of the procedure used for complexes **2**, **4**, **6**, and **8**. To a solution of **1** (0.264 g, 0.92 mmol) in THF (5 mL) at −78 °C under a carbon monoxide atmosphere (1.1 atm) was added methyllithium (1.02 mmol). After stirring at −78 °C for 2 h, *tert*-butyl bromide (0.21 mL, 1.8 mmol) was added. Stirring was maintained at −78 °C for a further 0.5 h and then the reaction mixture was removed from the cooling bath and stirred for a further 1 h. The dark brown reaction mixture was passed through an alumina column (Grade IV; diethyl ether) and the solvent removed in vacuo. Chromatography (SiO$_2$; ethyl acetate–petroleum ether, 1:19) of the resulting dark orange viscous oil led to the isolation of yellow crystals of **2** (0.096 g, 35%). See Tables III–VIII for IR, ^{1}H NMR, ^{13}C NMR, MS, microanalysis, and mp data, respectively.

Complexes **4** (48%), **6** (83%), and **8** (36%) were prepared by using the procedure described above. Chromatography conditions: SiO$_2$; ethyl acetate–petroleum ether, **4**, 1:49; **6**, 3:97; **8**, 3:97. See Tables III–VIII for IR, ^{1}H NMR, ^{13}C NMR, MS, microanalysis, and mp data, respectively.

Reaction of Complex 9 with Methyllithium under CO. To a solution of **9** (0.306 g, 1.12 mmol) in THF (6 mL) at −78 °C under a carbon monoxide atmosphere (1.1 atm) was added methyllithium (1.23 mmol). The reaction mixture was stirred at −78 °C for 2 h. *tert*-Butyl bromide (0.26 mL, 2.3 mmol) was then added and the procedure described above for the synthesis of complex **2** followed. This led to the formation of a dark viscous oil whose ^{1}H NMR spectrum was examined (see Results and Discussion) and which on chromatography (SiO$_2$; ethyl acetate–diethyl ether, 3:97, followed by dichloromethane–petroleum ether, 1:49) gave yellow crystals of **12**[17] (0.010 g, 5%).

Preparation of Complexes 2 and 8 Omitting *tert*-Butyl Bromide Quench. To a solution of **1** (0.542 g, 1.83 mmol) in THF (9 mL) at −78 °C under a carbon monoxide atmosphere (1.1 atm) was added methyllithium (2.02 mmol). The reaction mixture was stirred at −78 °C for 1 h and then removed from the cooling bath and stirred for a further 1.5 h. Workup as described above for the preparation of **2** gave yellow crystals of **2** (0.261 g, 48%). Similarly, reaction of complex **7** omitting the *tert*-butyl bromide quench gave yellow crystals of complex **8** (65%).

Reaction of Complex 5 with *n*-Butyllithium under CO. To a solution of **5** (0.205 g, 0.62 mmol) in THF (3 mL) at −78 °C under a carbon monoxide atomsphere (1.1 atm) was added *n*-butyllithium (0.67 mmol). The reaction mixture was stirred at −78 °C for 1 h and then removed from the cooling bath and stirred for a further 2 h. Filtration gave **17** as a creamy white solid (0.038 g, 56% based on **5**) and workup of the filtrate as described above for the preparation of **6** led to the isolation of yellow crystals of **6** (0.123 g, 58%).

Reaction of Complex 5 with Methyllithium and *tert*-Butyl Isocyanide. To a solution of **5** (0.311 g, 0.95 mmol) in THF (5 mL) at −78 °C under a carbon monoxide atmosphere (1.1 atm) was added methyllithium (1.00 mmol). After stirring at −78 °C for 1 h, *tert*-butyl isocyanide (0.394 g, 4.74 mmol) in THF (0.5 mL) was added. The reaction mixture was removed from the cooling bath and stirred for a further 1.5 h. The reaction mixture was passed through alumina (Grade IV, diethyl ether) and the solvent removed in vacuo. The resulting dark yellow viscous oil was chromatographed (SiO$_2$; ethyl acetate–petroleum ether, 1:4 and 1:49) to yield **21** (0.198 g, 46%), **22** (0.034 g, 9%), and **23** (0.009 g, 2%) as viscous yellow oils.

Reactions of **5** with (a) 5 equiv of *tert*-butyl isocyanide under a nitrogen atmosphere and (b) 1 equiv of *tert*-butyl isocyanide under a carbon monoxide atmosphere were performed by using the same procedure.

Synthesis of Tricarbonyl(η^4-vinylketenimine)iron(0) Complexes 23, 24, 25, and 26. The preparation of **23** is representative of the method used for complexes **23**, **24**, **25**, and **26**. A mixture of **6** (0.100 g, 0.29 mmol) and *tert*-butyl isocyanide (0.024 g, 0.29 mmol) in toluene (3 mL) was stirred at 80 °C for 24 h. To the reaction mixture were added 0.10-mL portions of a solution of *tert*-butyl isocyanide (0.025 g, 0.30 mmol) in toluene (1.0 mL) after 2 h and 3 h. The reaction mixture was passed through alumina (Grade IV, diethyl ether) and the solvent removed in vacuo. Chromatography (SiO$_2$; ethyl acetate–petroleum ether, 1:19) of the resulting yellow viscous oil yielded **23** (0.067 g, 58%) as a viscous yellow oil. See Tables III–VIII for IR, ^{1}H NMR, ^{13}C NMR, MS, microanalysis, and mp data, respectively.

Complexes **24** (64%), **25** (59%), and **26** (60%) were prepared by using the procedure described above. Chromatography conditions: SiO$_2$; ethyl acetate–dichloromethane–petroleum ether 1:4:15. See Tables III–VIII for IR, ^{1}H NMR, ^{13}C NMR, MS, microanalysis, and mp data, respectively.

Isolation of Dicarbonyl(isocyanide)(η^4-vinylketenimine)iron(0) Complexes 22, 27, and 28. Halting the reactions used to prepare **23**, **24**, and **25** after 3–3.5 h followed by the workup described for complex **23** resulted in the isolation of complexes **22** (45%) and **23** (22%), **27** (25%) and **24** (41%), and **28** (35%) and **25** (23%), respectively. Chromatography conditions: SiO$_2$; **22** and **23**, ethyl acetate–petroleum ether, 1:19; **27** and **24**, **28** and **25**, ethyl acetate–dichloromethane–petroleum ether, 1:4:15. See Tables III–VIII for IR, ^{1}H NMR, ^{13}C NMR, MS, microanalysis, and mp data, respectively.

Conversion of Dicarbonyl(isocyanide)(η^4-vinylketenimine)iron(0) Complexes 22, 27, and 28 into Tricarbonyl(η^4-vinylketenimine)iron(0) Complexes 23, 24, and 25. The conversion of **22** into **23** is representative of the procedure used. A solution of **22** (0.093 g, 0.24 mmol) in toluene (2.5 mL) was heated at 80 °C for 22 h. The reaction mixture was passed through alumina (Grade IV, diethyl ether) and the solvent removed in vacuo. Chromatography (SiO$_2$; ethyl acetate–petroleum ether, 1:19) of the resulting yellow viscous oil yielded **23** (0.063 g, 68%) as a viscous yellow oil.

Complexes **27** and **28** were converted into complexes **24** and **25**, respectively, by using the procedure described above. Chromatography conditions: SiO$_2$; ethyl acetate–dichloromethane–petroleum ether, 1:4:15.

Thermolysis of Complexes 22 and 28. A mixture of **22** (0.099 g, 0.25 mmol) and **28** (0.095 g, 0.25 mmol) in toluene (5 mL) was heated at 80 °C for 16 h. The reaction mixture was passed through alumina (Grade IV, diethyl ether) and the solvent removed in vacuo. The resulting yellow viscous oil was chromatographed (SiO$_2$; ethyl acetate–dichloromethane–petroleum ether, 1:3:16) to yield recovered **22** (0.019 g, 19%), **25** (0.058 g, 61%), and **23**

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[27] Bowen, R. D.; Danks, T. N.; Mitchell, D.; Thomas, S. E. *Org. Mass Spectrom.* **1988**, *23*, 674.

(0.047 g, 47%) as viscous yellow oils.

X-ray Crystal Structure Analysis of 2. $C_{14}H_{10}O_4Fe$, M = 298.1, monoclinic, space group $P2_1/c$, a = 13.998 (6) Å, b = 7.955 (5) Å, c = 12.935 (5) Å, β = 113.04 (3)°, U = 1325 (1) Å^3, Z = 4, D_c = 1.49 g cm^{-1}. Data were collected with a Syntex $P2_1$ four-circle diffractometer, maximum 2θ 50°, using Mo Kα radiation, λ = 0.71069 Å, μ(MoKα) = 11.4 cm^{-1}, T = 293 K, crystal dimensions 0.12 × 0.30 × 0.64 mm. Profile analysis gave 2343 unique reflections (R_{int} = 0.03); 1854 were considered observed [$I/\sigma(I) >$ 2.0] and used in refinement; they were corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method. The Fe atom was located from a Patterson synthesis, and the light atoms were then found on successive syntheses (including H atoms). Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors. Phenyl H atoms were inserted at calculated positions and not refined; the methyl group was treated as a rigid CH_3 unit, with its original orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Other H-atom coordinates were refined. Final refinement was on F by cascaded least-squares methods refining 181 parameters. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0014 was used and shown to be satisfactory by a weight analysis: final R = 0.039, R_w = 0.043; maximum shift/error in final cycle 0.03. Computing was with SHELXTL (Sheldrick, 1983) on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from *International Tables* (1974).

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Supplementary Material Available: Listings of thermal parameters, bond lengths and angles, and H atom coordinates (3 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Rigid Bent Bridges between Cyclopentadienylmetal Fragments. Iron Derivatives of the 4,8-Ethano-2,4,6,8-tetrahydro-*s*-indacene-2,6-diyl Dianion[†]

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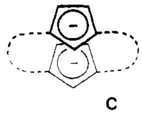
From the reaction of the 4,8-ethano-2,4,6,8-tetrahydro-*s*-indacene-2,6-diyl dianion (L) and cyclopentadienyl (Cp) anion with iron(II) chloride the bridged ferrocenes *syn,syn*-CpFeLFeCp (4), *syn,anti*-CpFeLFeCp (5), and *all-syn*-CpFeLFeLFeCp (6) were obtained. The structures of 4–6, including syn, anti isomerism, were deduced from their ^1H and ^{13}C NMR and mass spectra. X-ray crystal analyses were carried out for 4 and 5 (4, monoclinic, $P2_1/n$, a = 8.665 (1) Å, b = 7.724 (1) Å, c = 26.286 (2) Å, β = 97.82 (1)°, R_w = 0.028 for 235 refined parameters and 3107 observables; 5·0.5C_6H_6, monoclinic, $P2_1/n$, a = 6.087 (1) Å, b = 41.475 (4) Å, c = 7.995 (1) Å, β = 96.58 (1)°, R_w = 0.074 for 262 refined parameters and 2219 observables). They showed that both molecules are rather distorted, leading to Fe–Fe distances which are almost 0.5 Å longer than those expected for an idealized geometry. In the cyclic voltammograms of 4–6 separate waves indicated that the ferrocene units were oxidized at different potentials. These potentials were shown to depend on the number of bridges and $CpFe^+$ fragments next to the ferrocene unit under study. The separation of the potentials reflected the metal–metal interaction.

Introduction

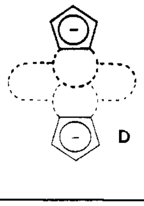
Bridging of ligands is a general strategy for assembling two or more metal fragments in close proximity. The resulting compounds are expected to have properties that differ from those of the mononuclear analogues, owing to extended interactions between the metals. One possibility for tailoring these interactions is precise stereochemical control by the ligand. For the cyclopentadienyl (Cp) anion various linear arrangements of type A have been realized.[1]

A

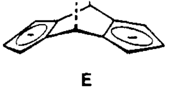
B



C



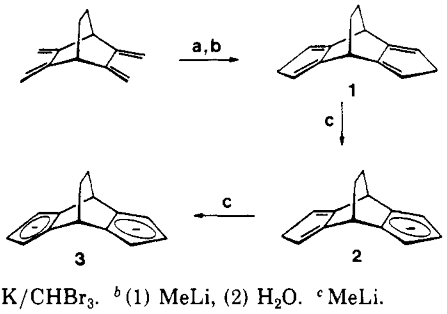
D



E

However, for A the orientation of the π-systems relative to each other is difficult to adjust. A better approach are cofacial and the noncofacial stacks obtainable from type C[2] or type D[3] ligands or the coplanar arrangement B.[4]

Scheme I



[a] *t*-BuOK/$CHBr_3$. [b] (1) MeLi, (2) H_2O. [c] MeLi.

[†] Dedicated to Professor I. Ugi on the occasion of his 60th birthday.

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