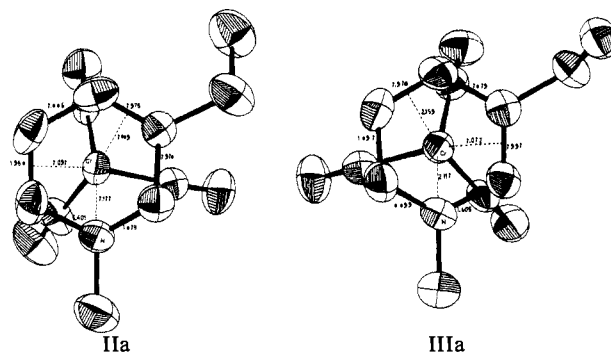


Table I. Atomic Positional Parameters ($\times 10^4$)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
(A) <i>N</i> -Methyl-3-ethyl-1,2-dihydropyridinetricarbonylchromium			
Cr	1267 (1)	1215 (1)	2523 (1)
O(10)	3114 (3)	979 (4)	1632 (4)
O(11)	1487 (4)	3458 (4)	2295 (5)
O(12)	472 (4)	1275 (5)	279 (5)
N(1)	948 (3)	-291 (4)	3004 (4)
C(2)	1619 (4)	-388 (4)	3889 (5)
C(3)	1867 (4)	687 (5)	4174 (5)
C(4)	1179 (5)	1359 (5)	4323 (5)
C(5)	305 (4)	1128 (5)	3890 (6)
C(6)	200 (4)	309 (6)	3224 (6)
C(7)	813 (5)	-1207 (6)	2347 (6)
C(8)	2820 (5)	860 (5)	4578 (6)
C(9)	3104 (5)	1963 (6)	4645 (7)
C(10)	2393 (5)	1062 (5)	1960 (5)
C(11)	1392 (4)	2589 (5)	2399 (6)
C(12)	770 (5)	1227 (6)	1141 (6)
H(2a)	2135	-763	3566
H(2b)	1385	-737	4569
H(4)	1243	1960	4654
H(5)	-181	1543	4009
H(6)	-282	167	2919
H(7a)	484	-987	1736
H(7b)	1221	-1284	2068
H(7c)	634	-1737	2648
H(8a)	3199	513	4043
H(8b)	2825	452	5251
H(9a)	2728	2175	5113
H(9b)	3747	1891	4926
H(9c)	3057	2382	3823
(B) <i>N</i> -Methyl-3-ethyl-1,6-dihydropyridinetricarbonylchromium			
Cr	1612 (1)	2502 (1)	1992 (2)
O(10)	1134 (7)	2010 (6)	-1712 (9)
O(11)	-148 (8)	913 (6)	2357 (10)
O(12)	3876 (7)	1245 (5)	2628 (10)
N(1)	2475 (6)	3828 (5)	1841 (9)
C(2)	1165 (8)	3954 (6)	1444 (12)
C(3)	411 (9)	3671 (6)	2658 (12)
C(4)	1008 (9)	3244 (6)	4184 (12)
C(5)	2303 (9)	3245 (7)	4543 (12)
C(6)	3031 (9)	3929 (8)	3628 (12)
C(7)	3257 (9)	4156 (8)	571 (14)
C(8)	-1007 (9)	3797 (7)	2311 (13)
C(9)	-1424 (8)	4670 (7)	3274 (12)
C(10)	1338 (8)	2202 (7)	-293 (12)
C(11)	535 (10)	1525 (8)	2266 (13)
C(12)	3013 (9)	1721 (7)	2368 (11)
H(2)	785	4260	383
H(4)	500	2987	4764
H(5)	2692	3027	5510
H(6a)	2986	4598	3770
H(6b)	3839	3865	3365
H(7a)	2878	3939	-349
H(7b)	3333	4828	625
H(7c)	4153	3746	1194
H(8a)	-1296	3347	2760
H(8b)	-1199	3806	1020
H(9a)	-1162	5024	2415
H(9b)	-2299	4678	2972
H(9c)	-1291	4549	4643

being 0.067 for the 907 observed reflections. Table I lists the atomic positional parameters.

The bond lengths as shown in IIa and IIIa are intermediate between those normally expected for simple alkene and aromatic systems. In each compound the chromium atom interacts with the double bonds and the lone-pair electrons of the nitrogen to give a distorted octahedral coordination. In both compounds the tetrahedral carbon atom and the carbon atom next to it deviate significantly from the plane of the other



four ring atoms. Intermolecular contacts correspond to van der Waals interactions.

In summary, the above complexes provide stable representatives of the isomeric 1,2- and 1,6-dihydropyridine series, and we hope that they will be useful as convenient sources of these reactive dienamine systems. Further results in this direction will form the subject of forthcoming publications.

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C. A. Bear, W. R. Cullen, J. P. Kutney*
V. E. Ridaura, J. Trotter, A. Zananottj

Department of Chemistry, University of British Columbia
Vancouver 8, British Columbia, Canada

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Metal Assisted Cycloaddition Reactions of Dicarbonyl(*pentahaptocyclopentadienyl*)(allenyl)iron. Mechanism and Synthetic Applications. Stereospecificity of Protonation of Dicarbonyl(*pentahaptocyclopentadienyl*)(propargyl)iron

Sir:

A number of cycloaddition reactions of *monohapto*-allyl,¹ *monohapto*cyclopropyl,² *monohapto*cyclopropylmethyl,^{1a} and *monohapto*propargyl^{1c,d,3} metal complexes with a variety of electrophiles have been reported. We now wish to report the extension of these processes to the *monohapto*allenyl complex (1) and to provide evidence for the intermediacy of a cationic iron-acetylene complex in these reactions.

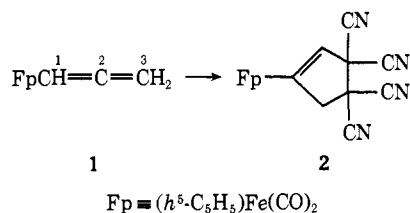
The allenyl complex is readily prepared in 52% yield by the metallation of propargyl benzenesulfonate with

(1) (a) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971); (b) S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **31**, C34 (1971); (c) A. Cutler, D. Ehntholt, R. W. Fish, W. P. Giering, S. Raghu, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 8251 (1972); (d) Y. Yamamoto and A. Wojcicki, *Inorg. Nucl. Chem. Lett.*, **8**, 833 (1972).

(2) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 4354 (1972).

(3) (a) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971); (b) P. W. Robinson and A. Wojcicki, *Chem. Commun.*, 951 (1970); (c) D. W. Lichtenberg and A. Wojcicki, *J. Organometal. Chem.*, **33**, C77 (1971); (d) W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc. A*, 930 (1971).

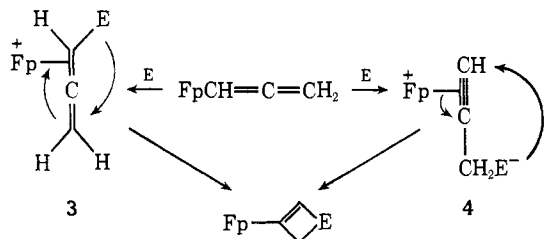
sodium cyclopentadienyldicarbonylferrate.⁴ Treatment of **1** with tetracyanoethylene at room temperature for 15 min gave the adduct **2**⁵ in 42% yield as yellow



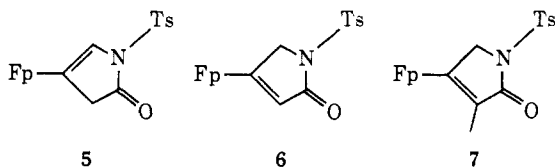
crystals, mp 172–173°. Ir (KBr) 2040, 1980 (C≡O), 2190 cm⁻¹ (CN); nmr (CD₃NO₂) τ 4.40 (1, t, $J = 2$ Hz, =CH), 4.87 (s, 5, Cp), 6.35 (d, 2, $J = 2$ Hz, CH₂).

In principle this reaction may proceed through formation of either an allene or acetylene dipolar ion complex (**3** or **4**), generated by electrophilic attack at C₁ or C₃, which for the general process involving an uncharged electrophile E, may be depicted as shown in Scheme I.

Scheme I



Evidence that it is the second path is provided by the reaction of **1** with unsymmetrical electrophiles. Thus **1** reacts rapidly at room temperature with toluenesulfonyl isocyanate to give only the butenolactam **5** as a



yellow crystalline material, mp 156–158° dec, in 46% yield.⁵ Ir (KBr) 2010, 1950 (C≡O), 1710 cm⁻¹ (C=O); nmr (CDCl₃) τ 2.06, 2.66 (two d, 4, $J = 8.5$ Hz, ArH), 3.71 (t, 1, $J = 2$ Hz, =CH), 5.11 (s, 5, Cp), 7.06 (d, 2, $J = 2$ Hz, CH₂), 7.59 (s, 3, ArCH₃).

The alternative structural formulation for this product (**6**) may be excluded since the closely related derivative **7**¹⁰ exhibits methylene absorption at τ 5.70.

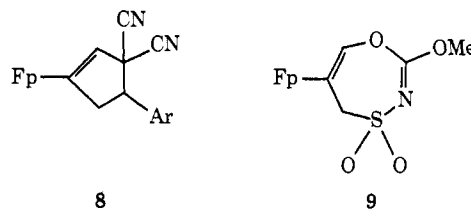
Similarly, cycloaddition of **1** and β,β -dicyano-*o*-chlorostyrene takes place to give **8**, mp 114–115°, as the exclusive product.⁵ Nmr (CDCl₃) τ 3.65 (m, 4, Ph),

(4) This substance has been reported by P. W. Jolly and R. Pettit, *J. Organometal. Chem.*, **12**, 491 (1968), who prepared it by metallation of propargyl bromide, and assigned it the structure $(h^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-CH}_2\text{C}\equiv\text{CH}$. This assignment was subsequently questioned by M. D. Johnson and C. Mayle, *Chem. Commun.*, 192 (1969), on the basis of the nmr spectrum reported for this substance. J. Roustan and P. Cadiot, *C. R. Acad. Sci., Ser. C*, **268**, 734 (1968), have also studied the reaction of sodium cyclopentadienyldicarbonylferrate with several propargyl bromides and have concluded from spectral data that the complex in question is an allenyl and not a propargyl complex. The spectral data for the complex obtained here show it to be identical with that obtained by Jolly and Pettit and by Roustan and Cadiot. Nmr (CS₂) τ 5.02 (t, 1, $J = 6.5$ Hz, =CH), 5.2 (s, 5, Cp), 6.06 (d, 2, $J = 6.5$ Hz, =CH₂); ir (neat) 2020, 1970 (C≡O), 1905 cm⁻¹ (C=C=C).

(5) A satisfactory elemental analysis was obtained for this substance.

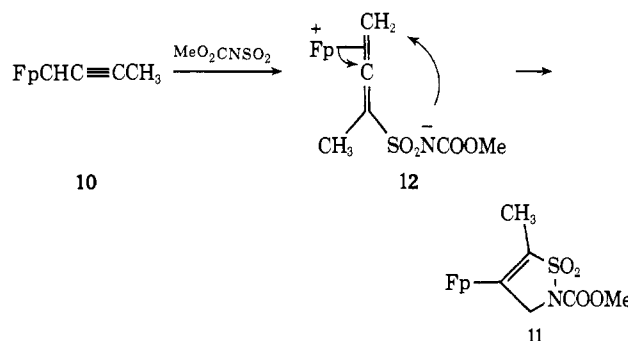
4.60 (t, 1, $J = 1.5$ Hz, =CH), 5.08 (s, 5, Cp), 5.28 (t, 1, $J = 7.5$ Hz, CHPh), 7.00 (two m, $J = 7.5$ Hz, CH₂).

The allenyl complex (**1**) also reacts readily with *N*-carbomethoxysulfonylamine⁶ to give the oxathiazepine derivative **9**, mp 108–109°, in 56% yield.⁵ Ir (KBr)



2040, 1980 (C≡O), 1590 cm⁻¹ (C=N); nmr (CDCl₃) τ 3.33 (s, 1, =CH), 4.85 (s, 5, Cp), 5.83 (s, 2, CH₂), 6.00 (s, 3, OCH₃). This is apparently the first example of this heterocyclic system.

By contrast, the related butynyl complex **10** reacts with the *N*-sulfonylurethane to give the isothiazoline derivative **11**⁵ whose formation, by analogy with the reactions of the corresponding metal-allyl complexes, may be formulated as proceeding through the intermediacy of the dipolar ion **12**.^{3c,d} Ir (KBr) 1960,



2015 (C≡O), 1715 (C=O), 1305, 1150 (SO₂); nmr (CDCl₃) τ 4.98 (s, 5, Cp), 5.66 (m, 2, CH₂), 6.11 (s, 3, OCH₃), 7.85 (m, 3, CH₃C).

Evidence for the intermediacy of the dipolar ions (**4** and **12**) in the reactions of the allenyl and butynyliron complexes may be obtained from protonation studies.

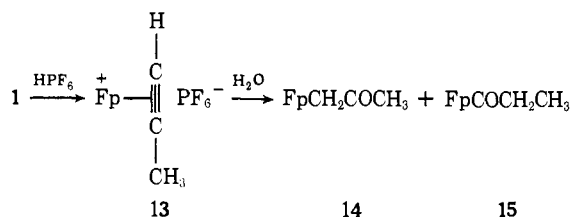
Thus, protonation of **1** with HPF₆ etherate at -20° gives the cationic acetylene-iron complex (**13**)⁷ exclusively, as a very air and water sensitive yellow solid. Ir (Nujol) 3210 cm⁻¹ (≡CH); nmr (CD₃NO₂, -10°) τ 4.28 (s, 5, Cp), 6.00 (q, 1, $J = 2.5$ Hz, ≡CH), 7.35 (d, 3, $J = 2.5$ Hz, -CH₃). While a number of uncharged polynuclear iron-acetylene complexes are known,⁸ the complex **13** represents the first example of a mononuclear cationic iron-acetylene complex. The substance reacts rapidly with water to give a 2:1 mixture of the ketones **14** and **15**.⁹

(6) E. M. Burgess and W. M. Williams, *J. Amer. Chem. Soc.*, **94**, 4386 (1972).

(7) Iron analysis (Perkin-Elmer Model 305 atomic absorption spectrophotometer): calcd, 13.4; found, 13.3.

(8) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965); J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, **88**, 292 (1966); K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).

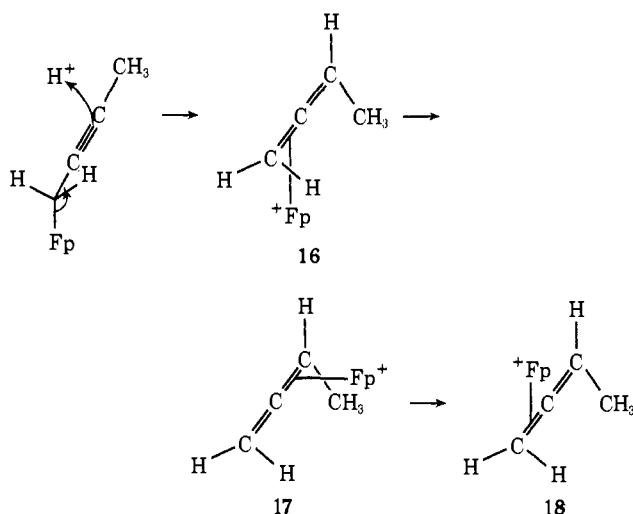
(9) Jolly and Pettit (ref 4) report that treatment of **1** with HCl in ethanol solution gave **14** and some **15**. The isomeric acetylide $\text{FpC}\equiv\text{CCH}_3$ gives only **15** on hydration, and it seems likely that this latter complex is formed in the hydration of **13** through prior isomerization to the acetylide, while the ketone **14** is the product of direct hydration of the acetylene-iron cation.



By contrast protonation of **10** gives a cationic allene-iron complex (A) as a *single stereoisomer*.¹⁰ Ir (KBr) 2000, 2040 cm^{-1} ; nmr (CD_3NO_2) τ 3.0 (m, 1, =CH), 4.20 (s, 5, Cp), 6.8 (m, 2, = $\text{CH}_2(\text{M}^+)$), 7.70 (d, t, 3, $J = 7.0$, $J' = 3$ Hz, = $\text{CCH}_3(\text{M}^+)$).

On heating in nitromethane solution, this substance is smoothly converted to an equilibrium mixture with an isomer (B). Nmr (CD_3NO_2) τ 3.5 (m, 1, =CH), 4.25 (s, 5, Cp), 6.8 (m, 2, = $\text{CH}_2(\text{M}^+)$), 7.85 (d, t, 3, $J = 7.0$, $J' = 2.5$ Hz, = CCH_3). The reaction follows first-order kinetics, $k^{50^\circ} = 2.03 \times 10^{-5} \text{ sec}^{-1}$, $K^{50^\circ}_{\text{eq}} (\text{B}/\text{A}) = 1.95$.

We interpret the high stereospecificity of the protonation reaction in terms of trans periplanar participation of the organometallic group concerted with protonation. The initial cationic allene complex is accordingly assigned structure **16**. Its conversion to the isomeric cation (**18**) represents a thermodynamically favored change to a less sterically hindered ion. Such an isomerization may take place through intermediacy of the cation (**17**), in a process closely analogous to that proposed to account for the fluxional behavior of tetracarbonyltetramethylalleneiron.^{11,12}



The same mixture of isomeric cations (**16** + **18**) may also be obtained directly from methylallene in an exchange reaction with dicarbonyl cyclopentadienyl-(isobutylene)iron cation. Such a reaction has previously been employed for the preparation of a number

(10) The protonation of **10** and of the related phenylpropargyl complex has very recently been reported by D. W. Lichtenberg and A. Wojcicki, *J. Amer. Chem. Soc.*, **94**, 8271 (1972), and earlier by J. Benaim, J. Merour, and J. Roustan, *C. R. Acad. Sci., Ser. C*, **272**, 789 (1971), but neither of these authors makes reference to the stereospecificity of the reaction or to the stereochemistry of the allene salts obtained.

(11) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 2231 (1967).

(12) The lower thermodynamic stability of **17** compared with **16** or **18** is in accord with our observations that the Fp(ethylene) cation is considerably more stable than the corresponding propenyl cation.

of cationic iron-olefin complexes from the free olefin.¹³

The chemistry of these allenyl-iron and cationic allene-iron complexes is being further examined.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (GP 27991X).

(13) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971)

S. Raghu, M. Rosenblum*

Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154

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Additions of Nucleophiles to Metal-Activated Olefins. Synthesis of Carbon-Carbon Bonds

Sir:

The addition of simple nucleophiles to cyclobutadiene,¹ pentadienyl,² cyclopentadienyl,³ hexadiene,⁴ arene,⁵ and cycloheptatrienyl⁶ ligands coordinated to a variety of transition metals has been extensively examined.⁷ By contrast, relatively few investigations of the corresponding reactions of *dihapto*olefin and acetylene ligands have been carried out and these are largely confined to platinum and palladium complexes.^{1,8}

We wish to report several observations concerning the reactions of a variety of nucleophiles⁹ with the readily accessible $h^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ (olefin) cations¹⁰ and to draw attention to the potential use of these substances as stoichiometric reagents in organic synthesis.

A variety of enolate anions add readily and in moderate to good yield to the parent complex **1** affording the corresponding neutral complex.

(1) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971.

(2) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1970); J. E. Mahler, D. E. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955, 3959 (1963); M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc. A*, 240 (1967); R. J. H. Cowles, B. F. G. Johnson, P. L. Jasty, and J. Lewis, *Chem. Commun.*, 392 (1969); G. Maglio, A. Musco, R. Palumbo, and A. Sirigu, *ibid.*, 100 (1971).

(3) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959), 989 (1960); E. O. Fischer and R. D. Fischer, *Z. Naturforsch. B*, **16**, 556 (1961); E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961); E. O. Fischer, W. Fellmann, and G. E. Herberich, *ibid.*, **95**, 2254 (1962).

(4) F. Haque, J. Miller, P. L. Pauson, and J. B. Pd. Tripathi, *J. Chem. Soc. C*, 743 (1971).

(5) (a) P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, **10**, 404 (1971); (b) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961); (c) I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. C*, 2257 (1967) 116, 2024 (1969); (d) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967); (e) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4485 (1962).

(6) (a) P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc. C*, 1057 (1969); (b) P. L. Pauson and K. H. Todd, *ibid.*, 2638 (1970).

(7) A review of the reactions of electrophiles and nucleophiles with metal-coordinated olefins has been given by D. A. White, *Organometal. Chem. Rev.*, **3**, 497 (1968).

(8) J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969); M. H. Chisholm, H. C. Clark, and L. E. Manzer, *J. Amer. Chem. Soc.*, **94**, 1532 (1972), and references cited therein.

(9) The addition of several oxygen and nitrogen nucleophiles to this cation has recently been reported by: (a) L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometal. Chem.*, **25**, 207 (1970); (b) M. Graziani, L. Busetto, and A. Palazzi, *ibid.*, **26**, 261 (1971).

(10) (a) W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, **94**, 7170 (1972); (b) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971); (c) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963); (d) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963); (e) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961), **95**, 2063 (1962).