

with retention is the boron analogue of the well-known Wagner-Meerwein rearrangement.

Acknowledgment. We thank Professors K. G. Hancock and R. Huisgen for helpful discussions, and we gratefully acknowledge support of the work by the National Science Foundation (CH76-03738).

References and Notes

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- (3) The NMR data do not permit an unequivocal structural assignment for the boracyclopent-3-ene intermediate **3**. It should be noted that the multiplet observed in the NMR spectrum of the photolysis mixture is a characteristic feature of 1,3-dialkylcyclopentenes: J. D. White and D. N. Gupta, *J. Am. Chem. Soc.*, **90**, 6171 (1968).
- (4) The allylic rearrangement observed on acetolysis of **3** is characteristic of allylic boranes,⁵ and the fact that double-bond protonation and C-B bond cleavage proceeded in only one of the two possible directions is to be expected.
- (5) B. M. Mikhailov, *Organomet. Chem. Rev. A*, **8**, 1 (1972).
- (6) The alcohol **5** was hydrogenated, oxidized to the ketone, and then subjected to the Baeyer-Villiger degradation. Reduction of the resultant ester afforded exclusively *trans*-2-methylcyclohexanol and 3-methyl-1-butanol, thus establishing the configuration of the 2-methylcyclohexyl moiety.
- (7) Since we have not established that *cis*-2-methylcyclohexyl migrates with retention, it is conceivable that the migration with retention observed for *trans*-2-methylcyclohexyl merely reflects stereoselective formation of the more stable product.
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- (11) Alternatively, lithium triethylborohydride may be used to effect cyclization. However, in this case the yields of homoallylic alcohols obtained are slightly lower.

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Synthesis, Structure, and Synthetic Utility of Thallium(I) Tricyanovinylcyclopentadienide

Sir:

Owing to its highly electrophilic nature, tetracyanoethylene (TCNE) has been shown to undergo a wide range of reactions, including insertion, substitution, and addition, as well as the formation of charge-transfer complexes, with a variety of organometallic complexes.¹ Recent work in this laboratory has demonstrated that the reaction of TCNE with cyclopentadienylthallium (TlCp) results in the formation of thallium(I)

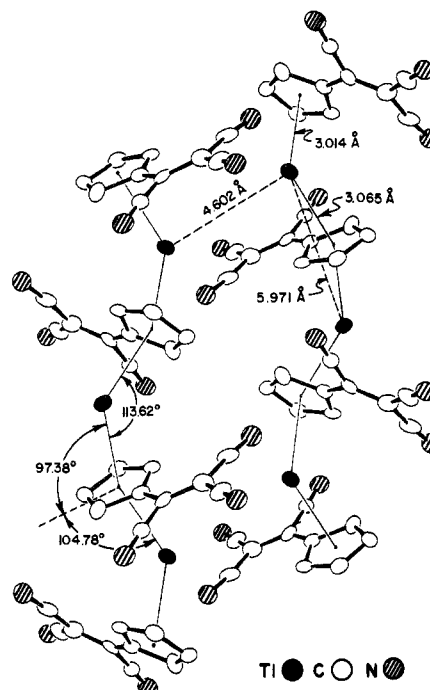


Figure 1. The crystal structure of thallium(I) tricyanovinylcyclopentadienide.

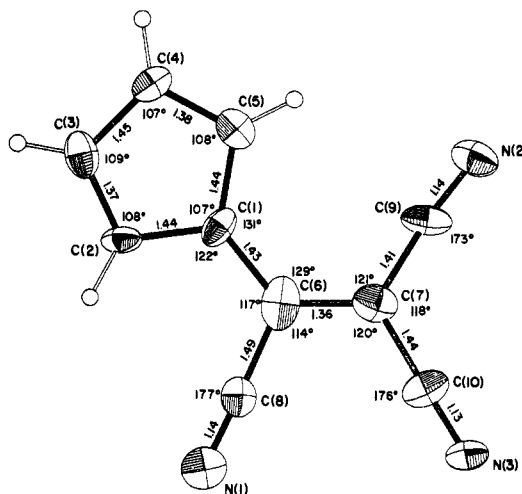
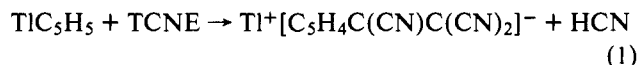


Figure 2. The structure of the tricyanovinylcyclopentadienide anion and bonded distances and angles. All distances are ± 0.02 Å and angles are $\pm 1^\circ$.

tricyanovinylcyclopentadienide (I) and that I has found use as a general reagent for the synthesis of tricyanovinyl-substituted metallocenes.

Reaction of an equimolar acetonitrile solution of TlCp and TCNE at room temperature for 1 h results in the formation of a 90% yield of I, according to eq 1.



The reaction mixture turns initially bright blue, but gradually turns a dark red color characteristic of I. This suggests that the reaction may involve the initial formation of a π complex, followed by nucleophilic attack of TlCp at the TCNE double bond and finally elimination of HCN to form the corresponding carbanion. Similar mechanisms have been proposed for the tricyanovinylation of aromatic compounds² and more recently for the reactions of Grignard reagents with TCNE.³

The NMR spectra and other physical data for all new cy-

Table I.

Compd	Yield, %	Mp, °C	$\nu_{\text{C}\equiv\text{N}}$, cm^{-1} ^a	¹ H NMR, τ	Anal., %
I	85–90	175 dec	2200, 2180 (sh)	3.1 (1), ^b 3.8 (2), ^b 3.9 (1) ^b	Calcd: C, 32.43; H, 1.08; N, 11.35 Found: C, 32.25; H, 1.11; N, 11.36
II	6.2	89.5–90	2220, 2240 (sh)	4.88 (2), ^c 4.20 (2) ^c	Calcd: C, 51.15; H, 1.31; N, 13.77; Mn, 18.03 Found: C, 51.54; H, 1.87; N, 12.89; Mn, 16.55
III		140–141 dec	2195, 2160 (sh)	2.63 (15), ^b 3.80 (2), ^c 3.88 (2) ^c	^e
V	15.7	270 dec	2204, 2199 (sh)	4.87 (4), ^c 5.31 (4), ^c 5.68 (10) ^d	Calcd: C, 64.57; H, 4.04; N, 6.28; Fe, 25.11 Found: C, 64.66; H, 3.89; N, 6.12; Fe, 24.97

^a KBr pellets. ^b Unresolved multiplets. ^c Poorly resolved triplets. ^d Singlet. ^e Satisfactory analysis could not be obtained.

anocarbon compounds are presented in Table I. In contrast to TICp, which shows properties characteristic of both ionic and covalent bonding,⁴ I appears to be largely ionic in behavior, since solution conductivity studies in dimethylformamide give a molar conductivity of $6.5 \times 10^{-2} \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ compared to a value of 5.1×10^{-4} for TICp. Also, unlike TICp, I has a reasonable solubility in several solvents. The insolubility and stability of TICp has often been linked to its polymeric crystal structure⁵ which consists of zig-zag chains of alternating cyclopentadienide ions and thallium atoms. A low-temperature single crystal x-ray investigation confirmed a similar structure for I, as shown in Figure 1.

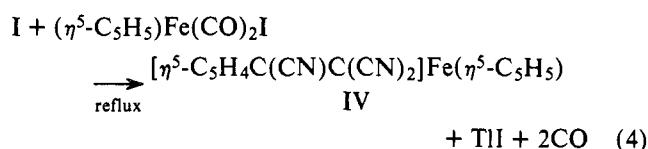
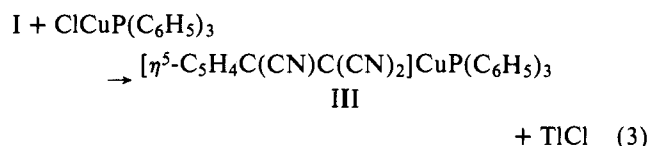
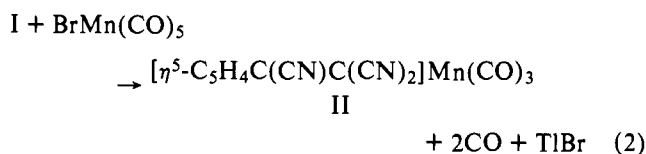
Dark red crystals of various morphological shapes were obtained by crystallization from acetonitrile and occurred as monoclinic, $P2_1/c$ (#14, C_{2n}^5), with $a = 7.852$ (2), $b = 9.937$ (4), $c = 12.961$ (5) Å, $\beta = 111.50$ (1)° and $D_{\text{cal}} = 2.616 \text{ g/cm}^3$ for $z = 4$ at -160 ± 5 °C. A total of 2382 reflections were collected using θ - 2θ scan techniques on a Picker FACS-1 diffractometer equipped with a highly oriented graphite monochromator, and molybdenum radiation ($\lambda = 0.71069$ Å). The data were converted to F_s in the usual manner and corrected for absorption ($\mu = 172.9 \text{ cm}^{-1}$). In all there were 1779 unique intensities, of which 1589 were nonzero and used in the refinement.

The thallium atom was located by direct methods, and its position confirmed by Patterson techniques. Two successive Fourier syntheses were used to locate all remaining nonhydrogen atoms. Full matrix anisotropic refinement with hydrogen atoms placed in calculated positions ($d_{\text{C-H}} = 0.95$ Å, $B_{\text{iso}} = 3.5$) led to final residuals of $R(F) = 0.060$ and $R_w(F) = 0.035$, where $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w(F) = \sum w ||F_o| - |F_c|| / \sum w |F_o|$, with $w = 1/\sigma(F_o)$. The function minimized was $\sum (|F_o| - |F_c|)^2$.

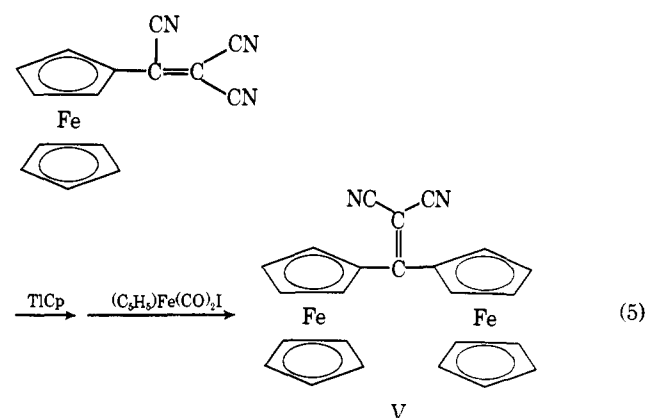
The thallium atoms are located between the cyclopentadienide rings (Figure 1) at distances of 3.014 (12) and 3.065 (19) Å from the centers of the rings, and the closest thallium contact is 3.064 (12) Å to C(1). The anion (Figure 2) is nearly planar, with the cyclopentadienide ring tilted 8.00° with respect to the tricyanovinyl group, and there is no evidence for delocalized bonding.

TICp has found extensive use⁶ as a mild reagent for the synthesis of metallocenes and we explored the possibility of using I as a similar reagent for the production of tricyanovinyl-substituted metallocenes. Only one such substituted metallocene,⁷ $[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{CN})\text{C}(\text{CN})_2]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, had been previously known.

The reaction of I with $\text{BrMn}(\text{CO})_5$, $\text{ClCuP}(\text{C}_6\text{H}_5)_3$, or $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in tetrahydrofuran solution results in the formation of the corresponding tricyanovinylcyclopentadienyl compounds (eq 2–4).



When reaction 4 was carried out in the presence of additional TICp, a second compound, 1,1-dicyano-2,2-diferrocenylethene (V), was formed. Subsequently, an alternate synthesis of V was developed, which involves the reaction of IV followed by addition of $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and reflux (eq 5)



Although a number of bridged ferrocenyl systems are known, compound V is unique, since it appears to be the only example of such a system containing strongly electron-withdrawing groups on the bridging unit. The differential pulsed polarogram of V showed two reversible 1-electron waves at 0.62 and 0.75 vs. SCE. Such polarographic behavior has been shown to be characteristic of two weakly interacting metal centers⁸ and we are currently attempting controlled oxidations of V in order to isolate a mixed valence salt.

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Supplementary Material Available: Crystallographic data including positional and thermal parameters and a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

References and Notes

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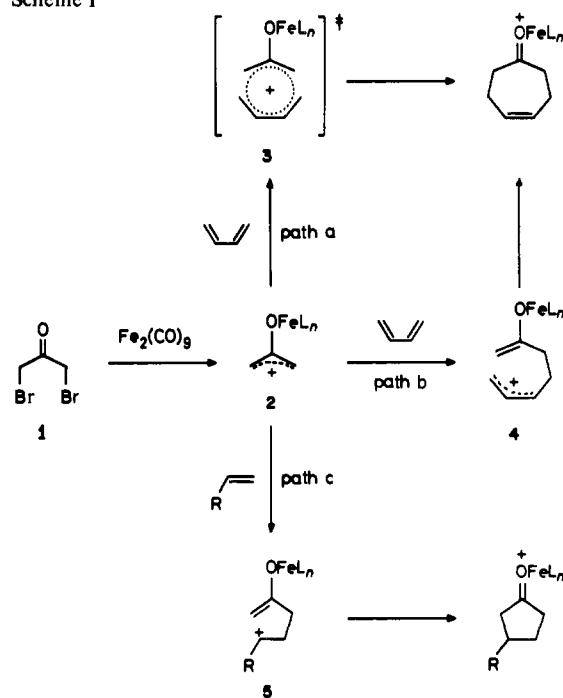
Regioselectivity of the Iron Carbonyl Promoted Cyclocoupling Reaction of α,α' -Dibromo Ketones with Olefins and Dienes¹

Sir:

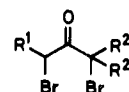
Reaction of α,α' -dibromo ketone **1** and $\text{Fe}_2(\text{CO})_9$ generates the reactive 2-oxallyl-Fe(II) species **2**² which can cycloadd across 1,3-dienes in a [3 + 4 \rightarrow 7] fashion to give the corresponding 4-cycloheptenones.^{3,4} In addition, the reactive intermediate **2** can be trapped by certain olefins in a [3 + 2 \rightarrow 5] manner, producing cyclopentanone derivatives.⁵ Discovery of such cationic cycloadditions has led to two fundamental questions, *viz.*, the concertedness of such reactions and the origin of the regioselectivity in the reaction of unsymmetrically substituted reactants.

The [3 + 4] reaction of **2** and dienes is classified as a [π 2 + π 4] process. If this cationic cycloaddition of symmetry-allowed type proceeds indeed in a concerted manner through the transition state **3** (path a in Scheme I), the regioselectivity

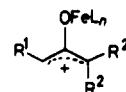
Scheme I



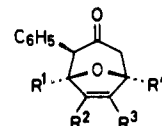
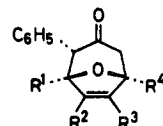
L = Br, CO, solvent, etc.



- 6, $\text{R}^1 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{H}$
 7, $\text{R}^1 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{CH}_3$
 8, $\text{R}^1 = \text{R}^2 = \text{CH}_3$



- 9, $\text{R}^1 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{H}$
 10, $\text{R}^1 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{CH}_3$
 11, $\text{R}^1 = \text{R}^2 = \text{CH}_3$



- 12, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$; $\text{R}^2 = \text{CH}_3$ 14, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$; $\text{R}^2 = \text{CH}_3$
 13, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{CH}_3$ 15, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{CH}_3$
 16, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$; $\text{R}^2 = \text{Br}$ 18, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$; $\text{R}^2 = \text{Br}$
 17, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{Br}$ 19, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{Br}$
 20, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$; $\text{R}^2 = \text{COOC}_2\text{H}_5$
 21, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{COOC}_2\text{H}_5$
 22, $\text{R}^1 = \text{COOC}_2\text{H}_5$; $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$
 23, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$; $\text{R}^4 = \text{COOC}_2\text{H}_5$
 24, $\text{R}^1 = \text{COOCH}_3$; $\text{R}^2 = \text{CH}_3$; $\text{R}^3 = \text{R}^4 = \text{H}$
 25, $\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^3 = \text{CH}_3$; $\text{R}^4 = \text{COOCH}_3$
 26, $\text{R}^1 = \text{COOCH}_3$; $\text{R}^2 = \text{R}^3 = \text{H}$; $\text{R}^4 = \text{CH}_3$
 27, $\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{R}^3 = \text{H}$; $\text{R}^4 = \text{COOCH}_3$
 28, $\text{R}^1 = \text{COOCH}_3$; $\text{R}^4 = \text{H}$; $\text{R}^3 = \text{CH}_3$
 29, $\text{R}^1 = \text{R}^3 = \text{H}$; $\text{R}^2 = \text{CH}_3$; $\text{R}^4 = \text{COOCH}_3$

would be controlled by frontier MOs of the cycloaddends.⁶ On the other hand, if the cycloaddition went in a stepwise manner via path b, the orientation would be determined by the relative stabilities of the regioisomeric zwitterions of type **4**.

Thus the dibromo ketone **6** was treated with $\text{Fe}_2(\text{CO})_9$ and the resulting oxallyl species **9** was trapped with various furan derivatives, leading to the bicyclic adducts **12**–**29**. The results are summarized in Table I. Apparently, the experimental findings are not consistent with the stepwise mechanism but agree with the concerted process where the regioselectivity is under frontier MO control. Unless other special factors are operating, the more stable regioisomeric transition state arises through interaction of the *reaction sites* having the larger MO coefficient and of those with the smaller coefficient (primary MO interaction). The validity has been demonstrated by the reaction of furans bearing three different kinds of substituents (methyl, halogen, and ester) at C-3 position (runs 1–3); these furans have similar MO shapes with respect to the C-2 and C-5 positions (Figure 1)⁷ and therefore the reaction exhibits the same regioselectivity. The results obtained with certain 2-furoates, except for one case, do fit in with the prediction, but the bias toward the prediction of the major isomer, we feel, is far greater than that expected from the degree of MO inclination (particularly run 4). This is presumably due to the operation of the secondary MO interactions between the *substituents* where frontier MOs develop to a considerable extent. In view of the relative magnitude of the C-2 and C-5 coefficients of 4-methyl-2-furoate, its reaction might have been conceived to give **29** as the major product. In fact, however, the regioisomer **28** formed predominantly (run 7), because there exists strong MO interaction between ortho carbon in phenyl ring of **9** and carbonyl oxygen of the furoate.

The [3 + 2 \rightarrow 5] cycloaddition exhibits a different feature