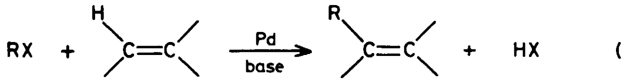
Preparation and *X*-Ray Crystal-structure Determinations of Structural Isomers of Ferrocenyl-substituted Dihydrofurans †

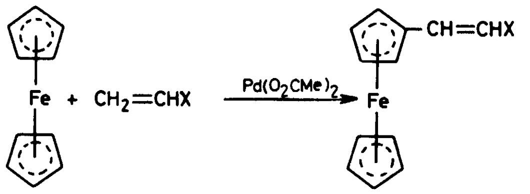
Nita A. Lewis,* Bhavini Patel, and Peter S. White *
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

The reaction of tris(3-iodopentane-2,4-dionato)cobalt(III) with vinylferrocene in the presence of triphenylphosphine and a catalytic amount of Pd^{II} produced two structural isomers. The characterisation of these isomers, 2- and 3-ferrocenyl-4-acetyl-2,3-dihydro-5-methylfuran [(B) and (C), respectively] is described. Their structures have been determined by single-crystal *X*-ray diffractometry: (B) is orthorhombic, space group *Pbca* with a = 9.821(2), b = 10.414(4), c = 27.761(6) Å, final R = 0.031, R' = 0.050 for 1 706 reflections; (C) is monoclinic, space group $P2_1/c$ with a = 9.692(1), b = 7.678(5), c = 19.082(3) Å, β = 97.76(1)°, final R = 0.031, R' = 0.048 for 1 641 reflections.

About a decade ago, Mizoroki *et al.*[1,2] and Heck and co-workers [3,4] independently discovered the palladium-catalysed substitution of vinylic hydrogen by aryl and vinyl halides [reaction (i)]. Asano *et al.*[5,6] later showed that ferrocene would undergo substitution with vinyl compounds in the same fashion [reaction (ii)]. The studies on ferrocene compounds were extended by Kasahara *et al.*[7] and Henry *et al.*[8] Encouraged by these reports, we attempted to use this procedure to synthesise large molecules containing both organometallic and co-ordination complex centres. The reactants we selected were vinylferrocene and tris(3-iodopentane-2,4-dionato)-cobalt(III), with the expectation that the reaction would proceed according to equation (iii), giving tris[3-(2-ferrocenyl-vinyl)pentane-2,4-dionato]cobalt(III) (A). Unfortunately, the cobalt was lost from the co-ordination complex and an unexpected cyclisation reaction occurred, to give structural isomers (B) and (C) of a highly substituted dihydrofuran ring.

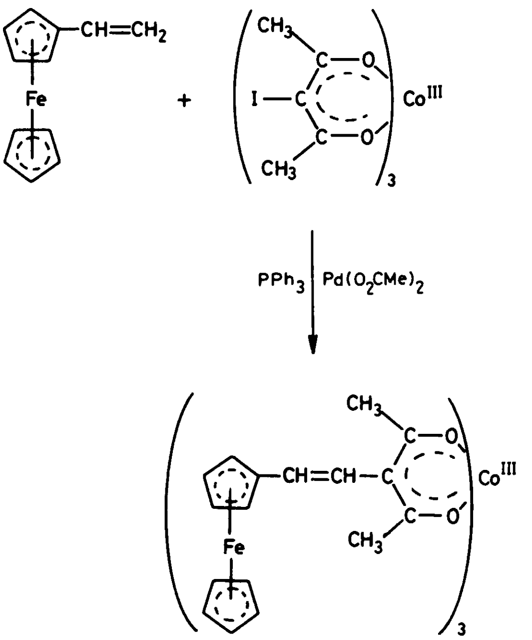


(i)



(ii)

Since it is usually difficult to prepare species of this type by standard organic methods,[9] and since the isolation of the two isomers would not be readily predicted on the basis of previous experiments,[1-8] we report our synthetic procedures and the *X*-ray crystal structures of (B) and (C). With suitable modification of the alkane used, it may be possible to use this method as a general preparative strategy for producing highly substituted dihydrofurans. The use of the cobalt(III) complex of 3-iodopentane-2,4-dione is recommended in these syntheses since the ligand alone is a powerful lachrymator.



(iii)

(A)

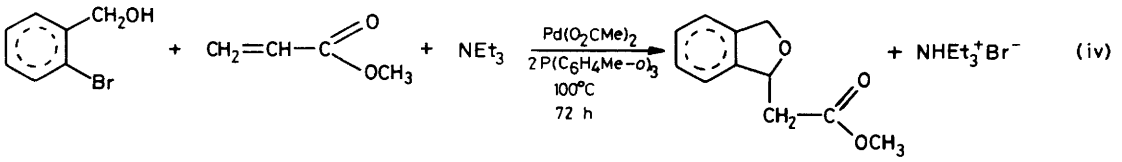
Results and Discussion

Transition-metal complexes containing pseudo-aromatic rings, especially those of pentane-2,4-dione, have been shown to undergo many typical organic aromatic substitution reactions.[10,11] One of the principal aims of the present investigation was to see if the exchange reaction of palladium could occur with the iodide derivative of a transition-metal complex of such a pseudo-aromatic ring [equation (i)]. If successful, the reaction would allow the simple preparation of a variety of large molecules incorporating both organometallic and co-ordination metal centres.

The fact that the cyclic derivatives (B) and (C) were obtained means that the cobalt atom must have become detached from the ligand while the palladium(II) catalyst was still present, rather than at some later stage in the purification procedure. If the cobalt had remained on the 3-iodopentane-2,4-dione ligand, the cyclisation reaction, which depends for its success on the presence of a free oxygen atom to attack the double bond (see Scheme) would have been prevented. Other examples

---

† *Supplementary data available* (No. SUP 23570, 31 pp.): thermal parameters, hydrogen atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



(iv)

of palladium-catalysed cyclisation reactions are known but they are uncommon. Heck and co-workers [12a] reported a clean cyclisation in the reaction of *o*-bromobenzyl alcohol with methyl acrylate [reaction (iv)].

By analogy with the extensive work by Heck and his colleagues,[3,12] the first step in the reaction is likely to be the replacement of the iodide on the pentane-2,4-dione by palladium. The organopalladium adduct then adds across the double bond of the vinyl substituent on the ferrocene, the usually postulated σ- and π-intermediates being assumed present.[13] No mechanistic information was obtained in the study under discussion because the palladium metal is precipitated slowly as the reaction proceeds.

The cobalt may be lost either before or after the palladium β-hydride elimination to give the pentane-2,4-dione derivative of vinylferrocene. This loss is probably the result of a redox reaction with Pd^0 producing the labile Co^{II} species.

Finally, the OH on the pentane-2,4-dione may undergo acid-catalysed addition across the double bond of the vinyl group to give the observed cyclic product in each case [isomers (B) and (C)].* When base was added to the reaction mixture to try to prevent this self-condensation, the reaction did not proceed at all. Several different bases were tried (triethylamine, di-isopropylamine, pyridine, and sodium hydrogencarbonate). It has been reported that the iodide exchange reactions proceed in the absence of triphenylphosphine to stabilise Pd^0, whereas bromine exchanges require this stabilising influence.[14] In our case, the reaction did not occur without triphenylphosphine. Using tri-*o*-tolylphosphine instead gave lower yields. The same products may be obtained using acetonitrile in place of tetrahydrofuran, but the yields were lower in this solvent.

Earlier investigations [15,16] indicated that the unstable organo-palladium intermediates prepared by the exchange reactions with halogen compounds or organo-mercury, -lead, or -tin derivatives tend to add to alkenes in such a way that the organic group ends up on the least-substituted carbon of the double bond. Usually, steric factors tend to be much more important than electronic ones. Apparently, palladium is effectively the smallest part of the organopalladium species. The relatively long palladium-carbon bond and square-planar geometry about the palladium combine to produce a relatively small effective size for the palladium end as compared with the rather bulky organic end, with its trigonal or tetrahedral carbon groups.[16]

Thus, on steric grounds one would expect that isomer (B) (arising from attack of the organic portion on the least substituted carbon) would be formed in much higher yield than isomer (C) (arising from attack of the organic portion on the most substituted carbon; see Scheme). The transition state leading to isomer (C) must be extremely crowded, with a single carbon having a ferrocenyl substituent and a pentane-2,4-dione substituent simultaneously. The role of triphenylphosphine, if any, in this reaction is unknown. Usually it is added to stabilise the palladium(0) state, but it is often unnecessary in iodide exchange reactions.[14] If, in our experiments, the triphenylphosphine is present as a ligand on palladium in the transition state, then the palladium end may well be more bulky than the organic end, thus favouring isomer (C).

Table 1. Fractional atomic co-ordinates *

Atom	*x*	*y*	*z*
Isomer (B)			
Fe(1)	0.459 54(8)	0.323 22(7)	0.423 21(3)
C(1)	0.750 1(6)	0.248 2(5)	0.385 9(2)
C(2)	0.717 4(6)	0.158 6(5)	0.343 8(2)
C(3)	0.817 8(6)	0.199 2(5)	0.306 2(2)
C(4)	0.906 0(6)	0.282 1(5)	0.325 8(2)
O(5)	0.880 9(4)	0.310 5(3)	0.372 3(1)
C(6)	0.820 8(6)	0.151 9(5)	0.256 5(2)
C(7)	0.718 5(6)	0.049 6(6)	0.244 3(2)
O(8)	0.902 1(5)	0.190 0(4)	0.226 0(2)
C(9)	1.029 3(7)	0.346 3(7)	0.306 7(3)
C(11)	0.415 9(8)	0.202 0(6)	0.478 7(3)
C(12)	0.307 5(7)	0.285 7(6)	0.470 8(2)
C(13)	0.260 2(7)	0.268 8(8)	0.423 9(2)
C(14)	0.342 2(8)	0.173 8(6)	0.402 0(3)
C(15)	0.436 8(9)	0.134 0(7)	0.436 4(3)
C(21)	0.633 1(6)	0.420 7(5)	0.438 5(2)
C(22)	0.524 3(6)	0.508 0(5)	0.433 1(2)
C(23)	0.470 4(6)	0.493 1(6)	0.386 0(2)
C(24)	0.547 0(6)	0.395 5(5)	0.362 5(2)
C(25)	0.647 0(6)	0.350 9(5)	0.395 1(2)
Isomer (C)			
Fe(1)	0.114 05(3)	0.159 72(4)	0.138 857(15)
C(1)	0.441 0(2)	0.256 0(3)	0.157 7(1)
C(2)	0.541 1(2)	0.364 8(3)	0.120 7(1)
C(3)	0.603 6(2)	0.260 5(3)	0.077 6(1)
O(4)	0.571 6(2)	0.089 9(2)	0.084 9(1)
C(5)	0.496 7(3)	0.074 9(3)	0.146 1(1)
C(6)	0.554 1(2)	0.552 0(3)	0.132 4(1)
C(7)	0.656 8(3)	0.656 2(3)	0.097 8(2)
O(8)	0.481 9(2)	0.623 9(2)	0.171 9(1)
C(9)	0.694 3(3)	0.289 8(4)	0.022 1(1)
C(11)	0.064 8(3)	0.092 1(4)	0.235 4(1)
C(12)	−0.054 9(3)	0.086 6(4)	0.185 9(2)
C(13)	−0.031 5(3)	−0.033 4(4)	0.132 9(2)
C(14)	0.104 4(3)	−0.104 5(4)	0.150 4(2)
C(15)	0.165 8(3)	−0.025 1(4)	0.214 6(2)
C(21)	0.196 9(3)	0.404 0(3)	0.148 0(1)
C(22)	0.073 1(3)	0.403 3(3)	0.098 9(2)
C(23)	0.092 5(3)	0.286 2(4)	0.044 3(1)
C(24)	0.227 4(3)	0.213 5(4)	0.058 9(1)
C(25)	0.294 1(2)	0.286 4(3)	0.123 9(1)

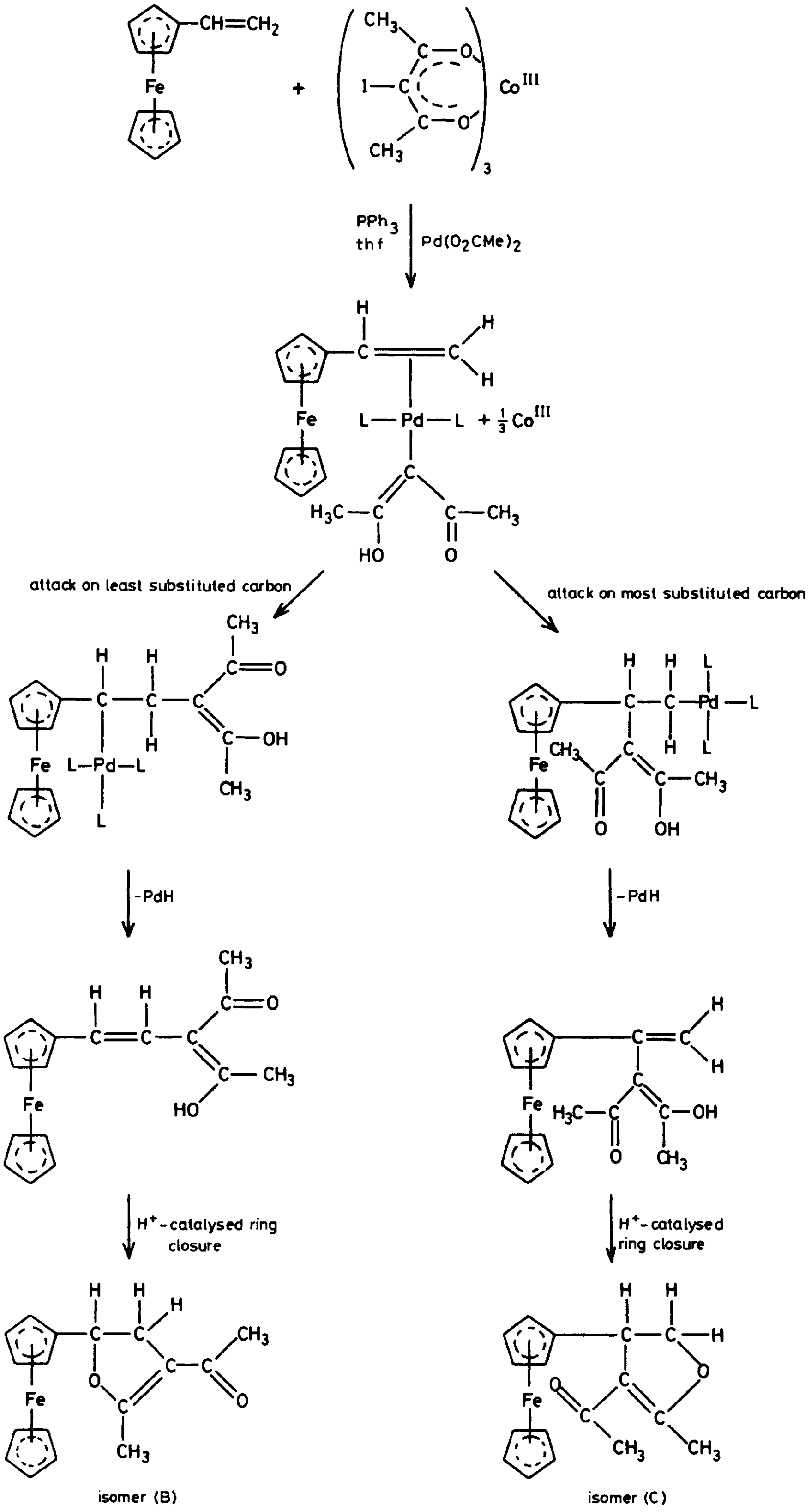
* Estimated standard deviations in parentheses.

It has also been reported [16] that electron-withdrawing substituents at or near the double bond favour substitution of the organic moiety at the least substituted carbon of the bond. Ferrocene is strongly electron donating, which should favour isomer (C) and may partly account for the rather large amount of this isomer formed (see Experimental section).

The atomic co-ordinates determined from the *X*-ray structure analysis are given in Table 1. Bond distances and

---

* Our experiments do not indicate whether or not the palladium participates in the cyclisation process, for example by displacement from the ferrocene derivative by oxygen. We show the palladium β-hydride elimination occurring before cyclisation in the Scheme since the organic portion is quite likely to undergo ring formation without the assistance of the metal.

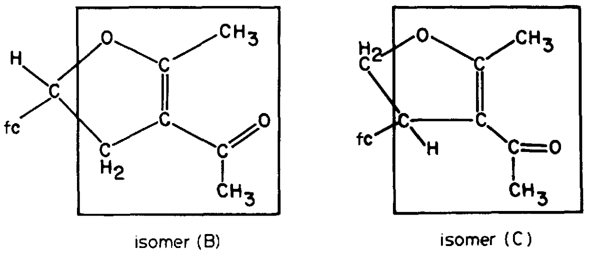

Fe
Co^{III}
PPh$_3$
thf
Pd(O$_2$CMe)$_2$
L—Pd—L + $\frac{1}{3}$Co^{III}
attack on least substituted carbon
attack on most substituted carbon
-PdH
-PdH
H$^+$-catalysed ring closure
H$^+$-catalysed ring closure
isomer (B)
isomer (C)

Scheme.

Table 2. Bond lengths (Å) *

Isomer (B)			
Fe(1)–C(11)	2.038(6)	C(3)–C(6)	1.464(8)
Fe(1)–C(12)	2.032(6)	C(4)–O(5)	1.347(7)
Fe(1)–C(13)	2.038(7)	C(4)–C(9)	1.481(9)
Fe(1)–C(14)	2.024(6)	C(6)–C(7)	1.503(9)
Fe(1)–C(15)	2.016(7)	C(6)–O(8)	1.230(7)
Fe(1)–C(21)	2.029(5)	C(11)–C(12)	1.393(11)
Fe(1)–C(22)	2.045(6)	C(11)–C(15)	1.388(11)
Fe(1)–C(23)	2.052(6)	C(12)–C(13)	1.395(9)
Fe(1)–C(24)	2.036(5)	C(13)–C(14)	1.413(11)
Fe(1)–C(25)	2.020(6)	C(14)–C(15)	1.395(12)
C(1)–C(2)	1.529(8)	C(21)–C(22)	1.411(8)
C(1)–O(5)	1.488(7)	C(21)–C(25)	1.412(7)
C(1)–C(25)	1.495(8)	C(22)–C(23)	1.419(8)
C(2)–C(3)	1.496(8)	C(23)–C(24)	1.423(8)
C(3)–C(4)	1.338(8)	C(24)–C(25)	1.415(7)
Isomer (C)			
Fe(1)–C(11)	2.033(3)	C(3)–O(4)	1.357(3)
Fe(1)–C(12)	2.049(3)	C(3)–C(9)	1.483(4)
Fe(1)–C(13)	2.039(3)	O(4)–C(5)	1.460(3)
Fe(1)–C(14)	2.044(3)	C(6)–C(7)	1.497(4)
Fe(1)–C(15)	2.039(3)	C(6)–O(8)	1.227(3)
Fe(1)–C(21)	2.039(3)	C(11)–C(12)	1.394(4)
Fe(1)–C(22)	2.038(3)	C(11)–C(15)	1.425(5)
Fe(1)–C(23)	2.035(3)	C(12)–C(13)	1.410(5)
Fe(1)–C(24)	2.039(2)	C(13)–C(14)	1.423(4)
Fe(1)–C(25)	2.051(2)	C(14)–C(15)	1.424(4)
C(1)–C(2)	1.524(3)	C(21)–C(22)	1.419(4)
C(1)–C(5)	1.519(4)	C(21)–C(25)	1.425(3)
C(1)–C(25)	1.500(3)	C(22)–C(23)	1.408(4)
C(2)–C(3)	1.348(3)	C(23)–C(24)	1.414(4)
C(2)–C(6)	1.457(3)	C(24)–C(25)	1.432(3)

* Estimated standard deviations in parentheses.



isomer (B) isomer (C)

Figure 1. Line drawings of structural isomers showing planar portions in boxes (fc = ferrocenyl)

Table 3. Bond angles (°) *

Isomer (B)			
C(2)–C(1)–O(5)	104.7(4)	C(7)–C(6)–O(8)	120.4(5)
C(2)–C(1)–C(25)	115.2(5)	C(15)–C(11)–C(12)	107.4(7)
O(5)–C(1)–C(25)	108.4(4)	C(11)–C(12)–C(13)	108.8(6)
C(1)–C(2)–C(3)	102.9(4)	C(12)–C(13)–C(14)	107.5(7)
C(2)–C(3)–C(4)	109.0(5)	C(13)–C(14)–C(15)	107.0(6)
C(2)–C(3)–C(6)	125.1(5)	C(14)–C(15)–C(11)	109.3(7)
C(4)–C(3)–C(6)	125.9(5)	C(25)–C(21)–C(22)	108.3(5)
C(3)–C(4)–O(5)	114.4(5)	C(21)–C(22)–C(23)	108.0(5)
C(3)–C(4)–C(9)	132.4(6)	C(22)–C(23)–C(24)	107.7(5)
O(5)–C(4)–C(9)	113.2(5)	C(23)–C(24)–C(25)	107.9(4)
C(1)–O(5)–C(4)	107.8(4)	C(24)–C(25)–C(21)	108.1(5)
C(3)–C(6)–C(7)	115.9(5)	C(21)–C(25)–C(1)	125.5(5)
C(3)–C(6)–O(8)	123.6(6)	C(24)–C(25)–C(1)	126.5(5)
Isomer (C)			
C(2)–C(1)–C(5)	100.0(2)	C(7)–C(6)–O(8)	119.9(2)
C(2)–C(1)–C(25)	110.0(2)	C(15)–C(11)–C(12)	109.4(3)
C(5)–C(1)–C(25)	114.6(2)	C(11)–C(12)–C(13)	107.9(3)
C(1)–C(2)–C(3)	108.9(2)	C(12)–C(13)–C(14)	108.4(3)
C(1)–C(2)–C(6)	121.1(2)	C(13)–C(14)–C(15)	107.7(3)
C(3)–C(2)–C(6)	130.0(2)	C(14)–C(15)–C(11)	106.7(3)
C(2)–C(3)–O(4)	112.5(2)	C(25)–C(21)–C(22)	108.8(2)
C(2)–C(3)–C(9)	134.8(2)	C(21)–C(22)–C(23)	107.8(2)
O(4)–C(3)–C(9)	112.7(2)	C(22)–C(23)–C(24)	108.6(2)
C(3)–O(4)–C(5)	107.7(2)	C(23)–C(24)–C(25)	108.3(2)
C(1)–C(5)–C(4)	105.6(2)	C(24)–C(25)–C(21)	106.6(2)
C(2)–C(6)–C(7)	120.6(2)	C(21)–C(25)–C(1)	126.2(2)
C(2)–C(6)–O(8)	119.5(2)	C(24)–C(25)–C(1)	127.1(2)

* Estimated standard deviations in parentheses.

angles are collected in Tables 2 and 3. The ferrocenyl substituents in both isomers are eclipsed, with mean Fe–C distances of 2.033(10) and 2.041(5) Å for (B) and (C), respectively. This is in good agreement with the results of room temperature studies on ferrocene itself by Seiler and Dunitz.[17] In isomer (B), the unsubstituted ring has significantly higher thermal parameters than the substituted one, indicating some libration in the plane of the ring. This effect is also observed, to a lesser degree, in isomer (C).

There are no significant inter- or intra-molecular contacts. The portions of the structures (B) and (C) shown in boxes in Figure 1 are essentially planar, with a resulting shortening of the formally single bonds [isomer (B), C(2), C(3), C(4), O(5), C(6), C(7), O(8), C(9), maximum deviation 0.08 Å; isomer (C), C(1), C(2), C(3), O(4), C(6), C(7), O(8), C(9), maximum deviation 0.13 Å, C(5) 0.40 Å out of the plane].

The physical data for the isomers are collected in Table 4. The most unusual features are exhibited by isomer (B), which has a carbonyl stretching frequency shifted to 1 660 cm^{-1} from its expected position [*ca.* 1 740 cm^{-1}; see isomer (C)]. This is probably due to conjugation of the carbonyl with the cyclopentadiene ring through the ether oxygen, which cannot occur in isomer (C) (see Figure 1). This effect may also be responsible for the more intense u.v. spectrum of isomer (B). Table 5 documents the electrochemical properties of the two compounds. Again, isomer (B) shows electronic properties markedly different from those of the parent ferrocene. This implies that the iron atom is also electronically coupled to the substituent, probably by the same mechanism as suggested for the i.r. and u.v. spectra. Little effect on the $E_{\frac{1}{2}}$ value is observed for the substituent on isomer (C) relative to ferrocene itself.

In conclusion, it appears that transition-metal complexes might be used as a source of organic reagents in palladium-catalysed reactions. In order to keep the metal from becoming detached from the organic ligand, it appears that it will be necessary to choose metal atoms which are inert in their lower oxidation states. On the other hand, if the metal atom in the transition-metal complex is not wanted in the final product, cobalt seems to be a good choice in the experimental design.

Experimental

Reagents.—Bis(cyclopentadienyl)iron(II), palladium acetate, and tetra-n-butylammonium hexafluorophosphate were purchased from Alfa. Triphenylphosphine was obtained from Aldrich, and Silica Gel G from B.D.H. Chemicals. Analytical reagent grade anhydrous methanol was purchased from Mallinckrodt, and acetonitrile (distilled in glass) came from Burdick and Jackson Laboratories Inc. All reagents were used without further purifications except for the tetrahydrofuran and the $N(C_4H_9)_4{}^+PF_6{}^-$. The former was A.C.S. grade solvent obtained from Anachemic Chemicals Ltd.; it was

Table 4. Physical data for the structural isomers (B) and (C)

	I.r. (cm^{-1})	^1H N.m.r. (δ)	$\lambda_{max.}/cm^{-1}$ (ε)
Isomer (B)			
	$\nu_{C=O}$, 1 660sharp $\nu_{C=C}$ (aromatic) 1 595br cyclopentadiene 1 100, 1 005, 800—900 ν_{C-O-C} 1 050, 1 150, 1 230 (strong)	2.20 [3 H, t, C(5)H_3], 2.28 (3 H, s, CH_3CO), 3.20 [2 H, dq, C(3)H_2], 4.15 (9 H, m, unsubstituted ferrocene ring), 5.40 [1 H, t, C(2)H]	435 (102 ± 3) 278 (12 700 + 200)
Isomer (C)			
	$\nu_{C=O}$, 1 740 $\nu_{C=C}$ (aromatic) 1 595br cyclopentadiene 1 100, 1 002, 800—900 ν_{C-O-C} 1 210s	2.12 [3 H, s, C(5)H_3], 2.23 (3 H, s, CH_3CO), 4.08 (9 H, m, unsubstituted ferrocene ring), 4.68 [2 H, d, C(2)H_2], 4.82 [1 H, d, C(3)H]	440 (115 ± 5) 273 (8 800 ± 400)

Table 5. Electrochemical data on the isomers (B) and (C) and ferrocene

Compound	$E_{\frac{1}{2}}{}^a$/mV	Conditions	Ref.
Ferrocene	596	0.1 mol dm^{-3} NEt_4ClO_4 in acetonitrile	*b*
Isomer (B)	656	0.1 mol dm^{-3} $N(C_4H_9)_4PF_6$ in acetonitrile	This work
Isomer (C)	600	0.1 mol dm^{-3} $N(C_4H_9)_4PF_6$ in acetonitrile	This work

[a] Relative to normal hydrogen electrode. [b] A. C. LeVanda, K. Bechaard, D. O. Cowan, and M. D. Rausch, *J. Am. Chem. Soc.*, 1977, **99**, 2964.

refluxed overnight over $LiAlH_4$, then was freshly distilled prior to use. The latter was recrystallised several times from the purified acetonitrile (Burdick and Jackson).

Preparation of 2- *and* 3-*Ferrocenyl*-4-*acetyl*-2,3-*dihydro*-5-*methylfuran* [(B) *and* (C), *respectively*].—A 250-ml round-bottomed flask was fitted with a nitrogen inlet and a dropping funnel. The apparatus was flame-dried. To the flask were added palladium acetate (0.01 mol) and triphenylphosphine (0.15 mol). The apparatus was then flushed with nitrogen for 30 min. Dry tetrahydrofuran (thf) was added (5 cm^3) and the mixture stirred for 30 min. Vinylferrocene (3.5 mmol) dissolved in dry tetrahydrofuran (10 cm^3) was then added dropwise over 30 min. The solution was stirred for 40 min. Then tris(3-iodopentane-2,4-dionato)cobalt(III) [18] dissolved in tetrahydrofuran (60 cm^3) was added dropwise over 3 h. The mixture was stirred for 24 h.

The solvent was then removed on a rotary evaporator. The resulting red oil was dissolved in chloroform (20 cm^3) and washed with water (2 × 20 cm^3). The organic layer was dried over magnesium sulphate and was concentrated to 3 cm^3. This concentrate was applied to a Silica Gel G column, and the products were separated by elution with 30 : 70 (v/v) ether–hexane. Four bands were separated. The eluate from the fourth band, after drying, produced an orange crystalline solid [isomer (B)] (43%) and that from the third band produced another orange solid [isomer (C)] (11%) [Found: isomer (B) C, 66.05; H, 5.7; isomer (C) C, 65.2; H, 5.8. $C_{17}H_{18}FeO_2$ requires C, 65.85; H, 5.8%].

Spectral Measurements.—The infrared spectra were run on a Perkin-Elmer 683 spectrophotometer (KBr discs). The n.m.r. spectra were obtained with a Varian T60 instrument at ambient temperature.

Electrochemical Measurements.—The electrochemical cell was of the conventional three-electrode type, with an aqueous saturated calomel electrode; platinum wires were used as the auxiliary and working electrodes. A PAR 173 potentiostat/galvanostat was used for potential control and a PAR 175 universal programmer was used as a sweep generator for the cyclic voltammetric experiments. The PAR 176 instrument was used as a current follower. Voltammograms were recorded with a Hewlett-Packard 7047-A X—Y recorder.

Analyses.—Microanalyses were performed by Canadian Microanalytical Services Ltd., Vancouver, Canada.

Crystal Structure Determinations.—After preliminary photographic investigations, suitable crystals were mounted on a Picker FACS-I diffractometer. Cell parameters and an orientation matrix were determined by a least-squares fit to the centred co-ordinates of 20 Friedel pairs of reflections with $2\theta \geqslant 30°$. In both cases two unique sets of intensity data were collected using ω—2θ scans of $2°(2\theta)\ min^{-1}$. Backgrounds were estimated by a standing count of 0.1 (scan-time) at each end of the scan, if the reflection was considered significant [$I > 2\sigma(I)$] an analysis of the peak profile was performed. Graphite-monochromated Mo-K_α radiation was used throughout both investigations.

In both cases the Fe atoms were located from the Patterson function and the positions of all the other atoms were found in subsequent difference syntheses. The structures were refined by block-matrix least-squares methods, using counter statistics weights. Scattering factors were taken from ref. 19, and those for Fe were corrected for anomalous dispersion; the function minimised was $\Sigma w(\Delta|F|)^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogens were included in the final stages of refinement with isotropic thermal parameters. The final residuals were, for isomer (B), $R = (\Sigma\Delta|F|/\Sigma|F|) = 0.031$, $R' = [\Sigma w(\Delta|F|)^2/\Sigma w|F|^2] = 0.050$ (including unobserved reflections, 0.069 and 0.068) and for isomer (C), $R = 0.031$ and $R' = 0.048$ (including unobserved reflections, 0.036 and 0.054). The crystal data are given in Table 6 and atomic co-ordinates in Table 1. The programs used were those of Larson and Gabe [20] for the PDP8/A computer.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for a co-operative grant (to N. A. L. with Professor P. M. Henry, University of Guelph, Guelph,

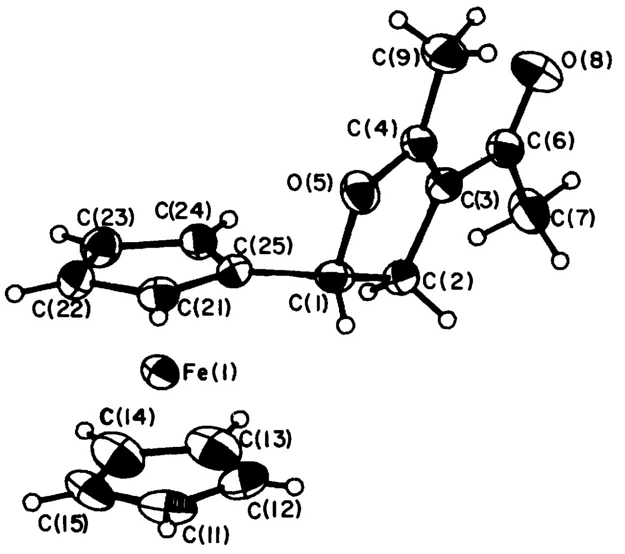


Figure 2. X-Ray structure of isomer (B)

Table 6. Crystal data

	Isomer (B)	Isomer (C)
Formula	$C_{17}H_{18}FeO_2$	$C_{17}H_{18}FeO_2$
M	310.18	310.18
System	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a/Å	9.821(2)	9.692(1)
b/Å	10.414(4)	7.678(5)
c/Å	27.761(6)	19.082(3)
β/°		97.76(1)
U/Å^3	2 839	1 407
Z	8	4
D_c/Mg m^{-3}	1.45	1.46
Crystal size (mm)	0.2 × 0.2 × 0.4	0.3 × 0.3 × 0.4
μ/mm^{-1}	1.06	1.06
F(000)	1 296	648
λ/Å	0.710 69	0.710 69
$2\theta_{max.}$ (°)	45	45
No. of reflections measured	5 034	3 682
No. of unique reflections	2 517	1 840
No. of observed reflections [$I > 2\sigma(I)$]	1 706	1 641
$\Sigma\lvert\Delta I\rvert/\Sigma I$	0.034	0.014
No. of variables	253	253
R (including unobserveds)	0.031 (0.069)	0.031 (0.036)
R' (including unobserveds)	0.050 (0.068)	0.048 (0.054)

Ontario), and for an operating grant (to P. S. W.). We also thank Professor Henry for his encouragement of our efforts and for discussions.

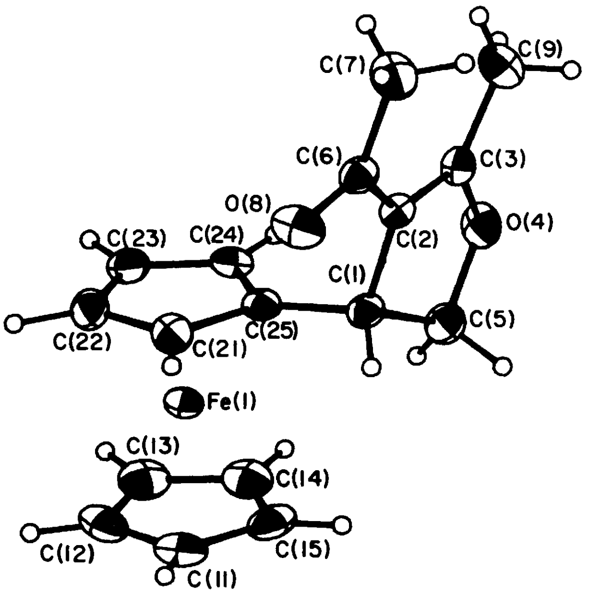


Figure 3. X-Ray structure of isomer (C)

References

1 T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 581.
2 T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1505.
3 R. F. Heck and J. P. Nolley, jun., *J. Org. Chem.*, 1972, **37**, 2320.
4 H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, 1974, **96**, 1133.
5 R. Asano, I. Moritani, Yuzo Fujiwara, and S. Teranishi, *Chem. Commun.*, 1970, 1293.
6 R. Asano, I. Moritani, A. Sonoda, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc. C*, 1971, 3691.
7 A. Kasahara, T. Izumi, G. Saito, M. Yodono, R. Saito, and Y. Goto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 895.
8 P. M. Henry, N. A. Lewis, and H. Taube, *Can. J. Chem.*, 1982, **60**, 1143.
9 S. R. Ohlsen and S. Turner, *J. Chem. Soc. C*, 1971, 3442.
10 J. P. Collman, *Adv. Chem. Ser.*, 1963, **37**, 78.
11 R. J. Balahura and N. A. Lewis, *Can. J. Chem.*, 1975, **53**, 1154.
12 (*a*) N. A. Cortese, C. B. Ziegler, jun., B. J. Hrnjez, and R. F. Heck, *J. Org. Chem.*, 1978, **43**, 2952; (*b*) C. B. Ziegler and R. F. Heck, *ibid.*, p. 2941.
13 P. M. Henry, 'Palladium Catalysed Oxidation of Hydrocarbons,' Reidel, Dordrecht, Holland, 1980.
14 J. B. Melpolder and R. F. Heck, *J. Org. Chem.*, 1976, **41**, 265.
15 R. F. Heck, *J. Am. Chem. Soc.*, 1968, **90**, 5518.
16 R. F. Heck, *J. Am. Chem. Soc.*, 1971, **93**, 6896.
17 P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1979, **35**, 1068.
18 J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, 1961, **83**, 531.
19 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
20 A. C. Larson and E. J. Gabe, Minimum Computer System for Complete Structure Determination, 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. von Koningsveld, and G. C. Bassi, Delft University Press, The Netherlands, 1978, pp. 81—89.

Received 1st September 1982; *Paper* 2/1505