ORGANOMETALLICS

Pentafulvenes: Versatile Synthons in Metallocene Chemistry

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The reactions of (η^5-cyclopentadienyl)(η^6-p-xylene)iron(II) hexafluorophosphate and (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium(II) hexafluorophosphate with 6-(dimethylamino)pentafulvenes are reported, establishing a novel route to unsymmetrically substituted ferrocenes and ruthenocenes carrying one or two substituents in the same ring. The method provides easy access to 1,3-difunctionalized derivatives, thus solving a long-standing problem. Ferrocenyl and ruthenocenyl iminium and amidinium salts are shown to be the primary reaction products that can be used for various further conversions. Pentafulvenes carrying strongly electron-withdrawing groups fail to yield the corresponding metallocenes while carboxyl functions and bulky alkyl groups are tolerated.

Introduction

Transition-metal chemistry of pentafulvenes has been investigated for many years, and a variety of compounds containing a pentafulvene ligand have been synthesized.[1-3] Among these are group 6A metal carbonyl complexes 1[2] of 6,6-dialkyl- and 6,6-diarylpentafulvenes (Chart I). Similar reactions of 6-(dimethylamino)- and 6,6-bis(dimethylamino)pentafulvenes led to the formation of the corresponding iminium and amidinium salts 2,[3] respectively. Other researchers have utilized the ease of conversion of pentafulvenes into cyclopentadienyl anions to synthesize a multitude of mono- and dinuclear cyclopentadienylmetal carbonyl complexes as well as simple and bridged ferrocenes,[1] e.g., 3.

Obviously however, only a few different pentafulvenes have been used in these investigations. Our intention has been to make use of the growing knowledge about 6-aminopentafulvenes (4)[1,4] for convenient syntheses of organometallic compounds. For this purpose we have studied their reactions with (η^5-cyclopentadienyl)(η^6-p-xylene)iron(II) hexafluorophosphate (5) (Scheme I, Table I) and (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium(II)
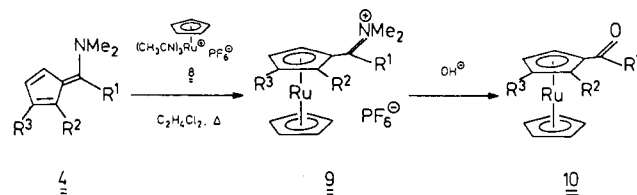
Chart I

M = Cr, Mo, W   R = Me, Et, Ph   R' = H, Me₂N
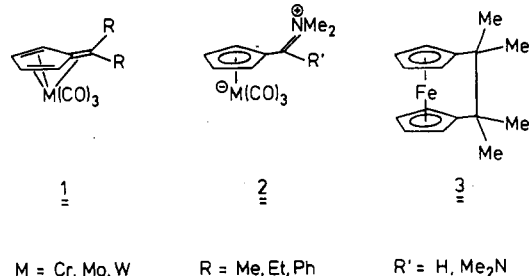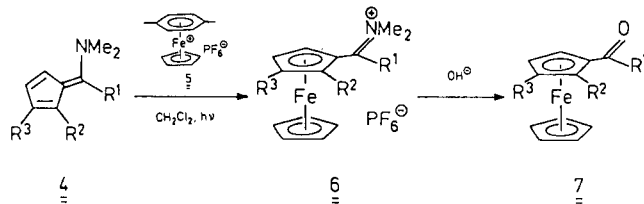
Scheme I

Scheme II

hexafluorophosphate (8) (Scheme II, Table II), which had been successfully used before as transfer reagents for the respective cyclopentadienyl metal units.[5,6]

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Table I. Pentafulvenes (4) Reacting via Scheme I To Yield Ferrocenes (7)

penta-fulvene	R[1]	R[2]	R[3]	ferro-cene	yield, %
4a	H	H	H	7a[a]	53
4b	CH₃	H	H	7b[a]	44
4c	CH₂-	-CH₂	H	7c[b]	65
4d	H	CHO	H		c
4e	CH₂-	-CO-	H		c
4f	COOMe	H	t-Bu		d
4g	H	COOEt	H	7g	67
4h	H	H	COOEt	7h	80
4i	NMe₂	H	H	7i[e]	68
4j	NMe₂	H	t-Bu	7j	72
4k	NMe₂	H	CONMe₂	7k	91
4l	NMe₂	NNPhNO₂-p	H		d
4m[f]					c

[a] Identified by comparison with authentic material.
[b] See ref 23 and 24. [c] Decomposition of pentafulvene.
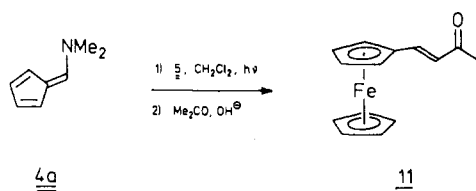[d] Pentafulvene was recovered. [e] See ref 30.
[f] 6-(2'-(Dimethylamino)vinyl)pentafulvene.

Table II. Pentafulvenes (4) Reacting via Scheme II To Yield Ruthenocenes (10)

penta-fulvene	R[1]	R[2]	R[3]	rutheno-cene	yield, %
4a	H	H	H	10a[a]	43
4g	H	COOEt	H	10g	60
4h	H	H	COOEt	10h	55
4i	NMe₂	H	H	10i	84
4k	NMe₂	H	CONMe₂	10k	96

[a] See ref 31.

Scheme III

Results and Discussion

When electron-rich 6-(dimethylamino)pentafulvenes (4) were treated with (η^5-cyclopentadienyl)(η^6-p-xylene)iron(II) hexafluorophosphate (5) or (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium(II) hexafluorophosphate (8), ligand exchange on the transition metal could easily be achieved under the conditions that have been reported previously.[5,6] In general, the reactions led to ferrocenyl or ruthenocenyl iminium or amidinium salts 6 or 9, which could be isolated as such or reacted in situ with ethanol and aqueous 2 N NaOH to give the corresponding aldehydes, ketones, or carboxamides 7 or 10, respectively. This hydrolysis procedure turned out to be of some convenience.

When acetone was used as the solvent instead of dichloromethane, condensation occurred with the intermediate ferrocenyl dimethyliminium salt, e.g., 6a, yielding 1-(3'-oxobut-1-enyl)ferrocene (11) under conditions that otherwise would have effected hydrolysis (Scheme III).

Conversion of 6-(dimethylamino)pentafulvenes (4) to variably functionalized metallocenes worked perfectly well as long as no strongly electron-withdrawing group was present at the pentafulvene molecule. Indeed, alkoxy-

carbonyl and dialkylcarbamoyl substituents in position 1 or 2 of the pentafulvene were tolerated and gave rise to a number of disubstituted metallocenes that could not or could not easily be prepared otherwise. No ferrocenes could be isolated, however, when a carbaldehyde, keto, or azo function was located on the pentafulvene ring. Those observations have precedence in the attempted coupling of 1,1'-diacetylferrocene with benzenediazonium chloride where the ferrocene was cleaved and the azopentafulvene was obtained.[20] This result was also accounted to insufficient electron density for an effective stabilization of the intermediate. Similarly, Nesmeyanov and co-workers[21] were able to prepare 6,6-diphenylpentafulvene from 1-(diphenylhydroxymethyl)ferrocene and 1,1'-bis(diphenylhydroxymethyl)ferrocene by treatment with acid.

Not surprisingly then, no ferrocene could be isolated when a methoxycarbonyl group was present at the 6-position of the pentafulvene, e.g., 4f. This can be understood in terms of diminished electron density in the five-membered ring as well as in terms of decreased stabilization of the corresponding iminium salt 6f, although methoxalylferrocene is a well-characterized though unstable compound.[22] Steric bulk on part of the pentafulvene, however, did not hinder the reaction. Thus, N,N-dimethyl-3-tert-butyl-1-ferrocenecarboxamide (7j) could easily be obtained from 2-tert-butyl-6,6-bis(dimethylamino)pentafulvene (4j).

Conclusions

The reaction of pentafulvenes with cyclopentadienyl metal transfer reagents has turned out to be a powerful tool for the synthesis of ferrocenes and ruthenocenes carrying one or two substituents in the same ring. Since all the starting materials are available in quantity and the yields are generally good to excellent, this novel method can well compete with some traditional procedures, e.g., the preparation of 2,3-ferrocenocyclopentenone (7c), which has been achieved before by Nozaki[23] and Eilbracht[24] through multistep syntheses. It clearly provides easy access to 1,3-disubstituted ferrocenes so far being tediously

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prepared from 1,3-diacetylferrocene.[25,26] No method of synthesis has yet been reported for 1,3-disubstituted ruthenocenes. 1,3-Difunctionalized metallocenes are of considerable interest in metallocenophane chemistry.[26]

The scope of this method is extended further by the work of Watts,[27] Patin,[28] Dixneuf,[29] and their co-workers, who intensively studied the properties and synthetic use of ferrocenyl iminium salts prepared from ferrocene precursors.

Furthermore, possibilities to modify the cyclopentadienyl metal transfer reagents with respect to the cyclopentadienyl part as well as the metal can be visualized.

Experimental Section

General Comments. ^{1}H NMR spectra were determined with a Varian XL-100 spectrometer with tetramethylsilane as internal standard (δ scale). UV spectra were obtained with a Beckman 5240 spectrometer (nm, log ϵ). IR spectra were measured with a Beckman IR 5A instrument (cm^{-1}). Mass spectra were obtained with a Varian MAT 311A spectrometer (electron impact: MS-EI, 70 eV; field desorption: MS-FD). Elemental analyses were carried out in the microanalytical laboratory of the Institut für Organische Chemie, Technische Hochschule Darmstadt. Melting points were determined in a Büchi SMP-20 apparatus and are uncorrected.

A. Preparation of Pentafulvenes (4). 6-(Dimethylamino)pentafulvene (4a),[7] 6-methyl-6-(dimethylamino)pentafulvene (4b),[8] 1-formyl-6-(dimethylamino)pentafulvene (4d),[9] 3-(dimethylamino)-1,2-dihydropentalen-1-one (4e),[10] 6,6-bis(dimethylamino)pentafulvene (4i),[8] 2-*tert*-butyl-6,6-bis(dimethylamino)pentafulvene (4j),[4] 2-((*p*-nitrophenyl)azo)-6,6-bis(dimethylamino)pentafulvene (4l),[11] and 6-(2'-(dimethylamino)vinyl)pentafulvene (4m)[12,13] were prepared according to literature procedures.

3-(Dimethylamino)-1,2-dihydropentalene (4c).[13] A solution of 5.0 g (34 mmol) of 6-(2'-(dimethylamino)vinyl)pentafulvene (4m) in 50 mL of freshly destilled piperidine was heated to reflux for 90 min. The solution was then concentrated in vacuo. Crystallization of the residue from 350 mL of ether with addition of charcoal at -25 °C gave 3.5 g (70%) of yellow needles, mp 122 °C: ^{1}H NMR (CDCl$_3$) 3.03 (m, 4 H, 1,2-H), 3.25 (s, 6 H, CH$_3$), 5.91 (m; 1 H, 6-H), 6.21 (m, 1 H, 4-H), 6.91 (m; 1 H, 5-H); UV (*n*-hexane) 309 (4.43), 314 (4.43), 214 (3.98). Anal. Calcd for C$_{10}$H$_{13}$N (147.21): C, 81.58; H, 8.90; N, 9.52. Found: C, 81.71; H, 8.75; N, 9.64.

2-*tert*-Butyl-6-(dimethylamino)-6-(methoxycarbonyl)pentafulvene (4f).[14] A solution of 13.1 g (0.1 mol) of methyl dimethyloxamate in 150 mL of dichloromethane was reacted with 17.3 g (0.1 mol) of triethyloxonium tetrafluoroborate. After the solution had cooled to room temperature it was added to 200 mL (0.1 mol) of a 0.5 M solution of lithium *tert*-butylcyclopentadienide in *n*-hexane at -15 °C. The mixture was then allowed to warm to room temperature, stirred for 24 h, and hydrolyzed by addition of 100 mL of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted three times with 50 mL of *n*-hexane. The organic layers were combined, dried (Na$_2$SO$_4$), concentrated, and filtered over a short column of alumina (B III). The filtrate was again concentrated. Recrystallization of the residue from *n*-hexane gave 13.0 g (55%) of yellow crystals as a mixture of the Z and E isomers of 4f, mp 86 °C: ^{1}H NMR (CDCl$_3$) 1.20 1.23 (2 s, 9 H, *t*-Bu), 3.16, 3.18 (2 s, 6 H, NMe$_2$), 3.91, 3.94 (2 s, 3 H, COOMe), 5.84 (t, J = 2.2 Hz, 0.5 H), 6.10–6.34 (m, 1.5 H), 6.58 (m, 2 H, ring-H); UV (dioxane) 260 (3.29), 335

(4.42). Anal. Calcd for C$_{14}$H$_{21}$NO$_2$ (235.33): C, 71.46; H, 8.99; N, 5.95. Found: C, 71.56; H, 9.17; N, 5.97.

1-(Ethoxycarbonyl)-6-(dimethylamino)pentafulvene (4g) and 2-(Ethoxycarbonyl)-6-(dimethylamino)pentafulvene (4h).[14,15] To 53.8 mL (0.1 mol) of a solution (1.86 M) of sodium cyclopentadienide[16] in tetrahydrofuran under nitrogen was added 11.8 g (0.1 mol) of diethyl carbonate. The mixture was heated to reflux for 20 h. Then 200 mL of dry tetrahydrofuran and, subsequently, 19.9 g (0.1 mol) of (dimethylamino)methoxycarbenium methyl sulfate[17] were added while the mixture was kept boiling. Two hours after the addition had been completed, it was allowed to cool and stand at room temperature for another 12 h. Hydrolysis was then achieved by treatment with 300 mL of cold, saturated ammonium chloride solution. After addition of 500 mL of ethyl acetate, the mixture was shaken vigorously and the layers were separated. The organic layer was dried (Na$_2$SO$_4$), concentrated, and filtered over a short column of alumina (N III). The filtrate was then chromatographed over alumina (N III) with *n*-hexane/ethyl acetate, 2:1. Elution of the first light yellow band and evaporation of the solvent yielded 5.1 g (28%) of 4g, mp 92 °C: ^{1}H NMR (CDCl$_3$) 1.33 (t, J = 7 Hz, 3 H, CH$_2$–CH$_3$), 3.28 (s, 6 H, NMe$_2$), 4.25 (q, J = 7 Hz, 2 H, CH$_2$–CH$_3$), 6.41 (ddd, J$_1$ = 4.6 Hz, J$_2$ = 3.2 Hz, J$_3$ = 0.7 Hz, 1 H, 3-H), 6.81 (dd, J$_1$ = 4.6 Hz, J$_2$ = 1.8 Hz, 1 H, 4-H), 7.17 (dd, J$_1$ = 3.2 Hz, J$_2$ = 1.8 Hz, 1 H, 2-H), 8.81 (s, 1 H, 6-H); UV (dioxane) 244 (3.22), 235 sh (4.14), 352 (4.39). Anal. Calcd for C$_{11}$H$_{15}$NO$_2$ (193.25): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.58; H, 7.77; N, 7.29.

Elution of the second light yellow band and evaporation of the solvent yielded 4.2 g (23 %) of 4h as a mixture of the Z and E isomers, mp 119 °C: ^{1}H NMR (CDCl$_3$) 1.32, 1.34 (2 t, J = 7 Hz, 3 H, CH$_2$–CH$_3$), 3.27 (s, 6 H, NMe$_2$), 4.26, 4.28 (2 q, J = 7 Hz, 2 H, CH$_2$–CH$_3$), 6.37 (dd, J$_1$ = 4.8 Hz, J$_2$ = 2.4 Hz, 0.5 H, 4-H, Z), 6.50 (dd, J$_1$ = 5.0 Hz, J$_2$ = 2.4 Hz, 0.5 H, 4-H, E), 6.71 (dd, J$_1$ = 4.8 Hz, J$_2$ = 1.6 Hz, 0.5 H, 3-H, Z), 6.89 (ddd, J$_1$ = 5.0 Hz, J$_2$ = 2.0 Hz, J$_3$ = 0.9 Hz, 0.5 H, 3-H, E), 7.11 (dd, J$_1$ = 2.4 Hz, J$_2$ = 2.0 Hz, 0.5 H, 1-H, E), 7.25 (m, 1 H, 1-H plus 6-H, Z/E), 7.32 (s, 0.5 H, 6-H, Z/E); UV (dioxane) 245 (4.14), 337 (4.58). Anal. Calcd for C$_{11}$H$_{15}$NO$_2$ (193.25): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.21; H, 7.66; N, 7.45.

6,6-Bis(dimethylamino)-2-(dimethylcarbamoyl)pentafulvene (4k).[14] To a solution of 3.3 g (20 mmol) of 6,6-bis(dimethylamino)pentafulvene (4i) and 4.1 g (40 mmol) of triethylamine in 200 mL of dichloromethane at -10 °C was added 3.2 g (10 mmol) of phosgene iminium chloride[18] in portions with stirring. After the addition was complete, the mixture was heated to reflux for 3 h. Then it was allowed to cool and 100 mL of a saturated solution of potassium carbonate was added. Vigorous stirring was continued for 1 h. The layers were separated and the aqueous layer was extracted twice with 50 mL of dichloromethane. The combined organic layers were dried (Na$_2$SO$_4$) and concentrated. Chromatography of the residue on alumina (B IV) with ethyl acetate yielded 2.8 g (60%) of 4k as yellow crystals, mp 151 °C (main fraction): ^{1}H NMR (CDCl$_3$) 3.12 (s, 12 H, 6-NMe$_2$), 3.18 (s, 6 H, CONMe$_2$), 6.24 (dd, J$_1$ = 4.5 Hz, J$_2$ = 2.3 Hz, 1 H, 4-H), 6.49 (dd, J$_1$ = 4.5 Hz, J$_2$ = 2.0 Hz, 1 H, 3-H), 6.79 (dd, J$_1$ = 2.3 Hz, J$_2$ = 2.0 Hz, 1 H, 1-H); UV (CH$_3$OH) 257 (4.27), 349 (4.52). Anal. Calcd for C$_{13}$H$_{21}$N$_3$O (235.33): C, 66.35; H, 8.99; N, 17.86. Found: C, 66.17; H, 8.93; N, 18.07.

B. Reaction of (η^5-Cyclopentadienyl)(η^6-*p*-xylene)iron(II) Hexafluorophosphate (5) with Pentafulvenes (4). Standard Procedure. In a 100-mL round-bottom flask equipped with a reflux condenser and a nitrogen bubbler, a solution of 2.0 mmol (0.74 g) of 5 and 3.0 mmol of the appropriate pentafulvene (4) in 40 mL of dichloromethane was irradiated for 14 h with a 300-W sunlamp (Osram) in an atmosphere of nitrogen while being stirred magnetically. The heat of the lamp caused the solvent to boil. After it had been allowed to cool to room temperature, the solution was filtered, if necessary. Then 15 mL of ethanol and 15 mL of 2 N NaOH were added and stirring was continued for another 90 min. After the layers had been separated, the aqueous layer was diluted to 60 mL and subsequently extracted once with dichloromethane (2 N HCl was added in case an emulsion had formed). The combined organic layers were washed twice with water, dried (Na$_2$SO$_4$), and concentrated. The residue was chromatographed over a short column of alumina (B II) with *n*-hexane/ether (1:1), ether, or dichloromethane as eluent, de-

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Table III. Melting Points and Spectroscopic and Analytical Data for Metallocenes 7 and 10

no.	mp, °C	¹H NMR (CDCl₃), δ	MS (%)ᵃ	UV (log ε), nm	IR (KBr), cm⁻¹ (C=O)	elemental analysis
7c	84	2.60–3.30 (m, 4 H, CH₂), 4.15 (s, 5 H, C₅H₅), 4.53 (t, J = 2.4 Hz, 1 H, 5-H), 4.64 (d, J = 2.4 Hz, 2 H, 4, 6-H)	240 (100), 212 (83), 146 (8), 121 (35), 56 (59)	223 (4.40), 269 (3.76), 313 (2.95), 350 (2.54), 458 (2.45)ᵇ	1680	C₁₃H₁₂FeO (240.09) calcd: C, 65.04; H, 5.04 found: C, 65.25; H, 4.98
7g	66	1.39 (t, J = 7 Hz, 3 H, CH₃), 4.32 (s, 5 H, C₅H₅), 4.36 (q, J = 7 Hz, 2 H, CH₂), 4.79 (t, J = 3 Hz, 1 H, 4-H), 5.17 (d, J = 3 Hz, 2 H, 3, 5-H), 10.69 (s, 1 H, CHO)	286 (70), 258 (10), 230 (17), 214 (23), 186 (15), 121 (45), 56 (100)	222 (4.33), 254 sh (3.87), 334 (3.02), 362 (3.09), 445 (2.72)	1710 1660	C₁₄H₁₄FeO₃ (286.11) calcd: C, 58.77; H, 4.93 found: C, 59.03; H, 4.90
7h	66	1.38 (t, J = 7 Hz, 3 H, CH₃), 4.32 (s, 5 H, C₅H₅), 4.34 (q, J = 7 Hz, 2 H, CH₂), 4.98 (dd, J_1 = 3 Hz, J_2 = 1.2 Hz, 1 H, 5-H), 5.19 (dd, J_1 = 3 Hz, J_2 = 1.2 Hz, 1 H, 4-H), 5.45 (t, J = 1.2 Hz, 1 H, CHO), 10.00 (s, 1 H, CHO)	286 (100), 258 (38), 214 (20), 186 (15), 121 (50), 56 (92)	219 (4.42), 252 sh (3.84), 275 (3.66), 335 (3.05), 357 (3.11), 458 (2.52)ᶜ	1710 1660	C₁₄H₁₄FeO₃ (286.11) calcd: C, 58.77; H, 4.93 found: C, 58.71; H, 4.84
7i	112	3.12 (s, 6 H, NMe₂), 4.23 (s, 5 H, C₅H₅), 4.30 (t, J = 2 Hz, 3, 4-H), 4.63 (t, J = 2 Hz, 2, 5-H)	257 (62), 213 (28), 185 (18), 121 (25), 56 (40), 43 (100)	259 sh (3.66), 297 sh (2.81), 329 sh (2.24), 441 (2.18)ᶜ	1620	C₁₃H₁₅FeNO (257.12) calcd: C, 60.73; H, 5.88; N, 5.45 found: C, 60.96; H, 5.83; N, 5.42
7j	116	1.25 (s, 9 H, CMe₃), 3.16 (s, 6 H, NMe₂), 4.22 (s, 5 H, C₅H₅), 4.22 (m, 1 H, 4-H), 4.56 (m, 2 H, 2, 5-H)	313 (100), 298 (50), 269 (10), 241 (5), 121 (45), 72 (34), 56 (30)	212 (4.45), 263 sh (3.66), 333 (2.23), 443 (2.20)ᶜ	1620	C₁₇H₂₃FeNO (313.23) calcd: C, 65.19; H, 7.40; N, 4.47 found: C, 65.43; H, 7.47; N, 4.44
7h	147	3.13 (s, 12 H, NMe₂), 4.29 (s, 5 H, C₅H₅), 4.77 (d, J = 1.5 Hz, 2 H, 4, 5-H), 5.07 (t, J = 1.5 Hz, 1 H, 2-H)	328 (100), 284 (47), 263 (81), 220 (42), 121 (35), 72 (27), 56 (32)	270 sh (3.72), 308 sh (3.00), 338 sh (2.71), 449 (2.28)ᵇ	1600	C₁₆H₂₀FeN₂O₂ (328.20) calcd: C, 58.56; H, 6.14; N, 8.54 found: C, 58.55; H, 6.06; N, 8.41
10a	98	4.66 (s, 5 H, C₅H₅), 4.87 (t, J = 2 Hz, 2 H, 3, 4-H), 5.10 (t, J = 2 Hz, 2 H, 2, 5-H), 9.75 (s, 1 H, CHO)	260 (55), 232 (100), 204 (11), 167 (47), 139 (20), 114 (16), 102 (15)	217 (4.04), 244 (4.00), 276 sh (3.14), 330 (2.92)ᶜ	1650	C₁₁H₁₀ORu (259.27) calcd: C, 50.96; H, 3.89 found: C, 51.23; H, 3.95
10g	101	1.33 (t, J = 7 Hz, 3 H, CH₃), 4.28 (q, J = 7 Hz, 2 H, CH₂), 4.70 (s, 5 H, C₅H₅), 4.99 (t, J = 2 Hz, 1 H, 4-H), 5.40 (d, J = 2 Hz, 2 H, 3, 5-H)	332 (100), 304 (25), 286 (40), 257 (23), 231 (37), 205 (17), 186 (14), 167 (43), 114 (9), 102 (8)	220 (4.17), 240 sh (4.00), 306 sh (3.13), 322 (3.16)ᶜ	1710 1660	C₁₄H₁₄O₃Ru (331.34) calcd: C, 50.75; H, 4.26 found: C, 50.90; H, 4.18
10h	97	1.29 (t, J = 7 Hz, 3 H, CH₃), 4.14 (q, J = 7 Hz, 2 H, CH₂), 4.68 (s, 5 H, C₅H₅), 5.23 (dd, J_1 = 1 Hz, J_2 = 3 Hz, 2 H, 5-H), 5.42 (dd, J_1 = 1 Hz, J_2 = 3 Hz, 2 H, 4-H), 5.66 (t, J = 1 Hz, 2-H)	332 (80), 304 (69), 276 (75), 259 (15), 231 (73), 204 (42), 184 (29), 167 (100), 114 (37), 102 (22)	222 (4.24), 240 sh (4.00), 293 (3.23), 330 sh (2.96)ᶜ	1720 1680	C₁₄H₁₄O₃Ru (331.34) calcd: C, 50.75; H, 4.26 found: C, 50.80; H, 4.25
10i	115	3.12 (s, 6 H, NMe₂), 4.60 (s, 5 H, C₅H₅), 4.66 (t, J = 2 Hz, 2 H, 3, 4-H), 4.96 (t, J = 2 Hz, 2 H, 2, 5-H)	303 (100), 259 (96), 231 (79), 205 (28), 167 (27), 114 (13), 102 (49)	224 sh (3.99), 320 (2.56)ᶜ	1600	C₁₃H₁₅NORu (302.34) calcd: C, 51.65; H, 5.00; N, 4.63 found: C, 51.74; H, 4.97; N, 4.61
10k	186	3.11 (s, 12 H, NMe₂), 4.66 (s, 5 H, C₅H₅), 5.08 (d, J = 1.5 Hz, 2 H, 4, 5-H), 5.36 (t, J = 1.5 Hz, 1 H, 2-H)	374 (100), 330 (77), 302 (11), 287 (13), 259 (40), 167 (23), 102 (3)	238 sh (4.05), 324 (2.67)ᵇ	1605	C₁₆H₂₀N₂O₂Ru (373.42) calcd: C, 51.46; H, 5.40; N, 7.50 found: C, 51.40; H, 5.27; N, 7.50

ᵃ Data refer to ⁵⁶Fe or ¹⁰²Ru as the predominant isotopes. ᵇ Recorded in 1,4-dioxane. ᶜ Recorded in n-hexane.

pending on the polarity of the respective ferrocene derivatives (7), which were always eluted as the first band of the column. Purification was achieved by recrystallization from ether/*n*-hexane or sublimation at 10^{-3} torr. Yields and data of the compounds thus obtained are shown in Tables I and III.

Ferrocenyl-*N*,*N*,*N'*,*N'*-tetramethylamidinium Hexafluorophosphate (6i). 6,6-Bis(dimethylamino)pentafulvene (4i) (0.49 g, 3.0 mmol) was treated with 0.74 g (2.0 mmol) of 5 according to the standard procedure. The dichloromethane solution was concentrated and the residue was triturated with ether. The crude product was collected by filtration and purified by column chromatography on alumina (B II) with acetone as eluent. After the dark red band had been eluted the solution was concentrated. Red-brown plates, mp 157 °C, were obtained upon addition of ether (0.70 g, 81%): ^{1}H NMR (CD_3COCD_3) 3.45 (s, 6 H, NMe$_2$), 4.51 (s, 5 H, C$_5$H$_5$), 4.99 (s, 4 H, 2–5-H); ^{1}H NMR (CDCl$_3$) 3.36 (s, 6 H, NMe$_2$), 4.44 (s, 5 H, C$_5$H$_5$), 4.72 (t, *J* = 2 Hz, 2 H, 3,4-H), 4.83 (t, *J* = 2 Hz, 2 H, 2,5-H); MS-FD *m/e* 285 (C$_{15}$H$_{21}$FeN$_2$$^+$); IR (KBr) 1590 (C=N), 830 (P—F); UV (CH$_3$CN) 236 (4.11), 279 (4.13), 348 (3.25–3.33; concentration dependent), 482 (3.00). Anal. Calcd for C$_{15}$H$_{21}$F$_6$FeN$_2$P (430.17): C, 41.88; H, 4.92; N, 6.51. Found: C, 41.93; H, 4.92; N, 6.21.

1-(3'-Oxobut-1-enyl)ferrocene (11). 6-(Dimethylamino)-pentafulvene (4a) (0.36 g, 3.0 mmol) was treated with 0.74 g (2.0 mmol) of 5 according to the standard procedure. The solvent was evaporated and the residue was treated with 100 mL of acetone and 30 mL of 2 N NaOH at reflux temperature for 40 min. The mixture was concentrated and 150 mL of water was added. The aqueous solution was extracted three times with 50 mL of ether. The combined organic layers were washed with water, dried (Na$_2$SO$_4$), and concentrated. Chromatography of the residue with elution of the red band gave 0.28 g (55%) of 11 as red-orange crystals, mp 85 °C, identical with authentic material.[19]

C. Reaction of (η^5-Cyclopentadienyl)tris(acetonitrile)-ruthenium(II) Hexafluorophosphate (8) with Pentafulvenes. Standard Procedure. A solution of 0.50 mmol (217 mg) of 8 and 0.75 mmol of the appropriate pentafulvene (4) in 30 mL of 1,2-dichloroethane was heated to reflux under nitrogen for 14 h.

Workup was essentially the same as for the corresponding ferrocenes; vide supra. Yields and data of the ruthenocenes thus obtained are listed in Tables II and III.

Ruthenocenyl-*N*,*N*,*N'*,*N'*-tetramethylamidinium Hexafluorophosphate (9i). 6,6-Bis(dimethylamino)pentafulvene (4i) (0.49 g, 3.0 mmol) was treated with 217 mg (0.50 mmol) of 5 according to the standard procedure. After the mixture had been allowed to cool, the solvent was evaporated and the residue was washed with ether. Filtration and recrystallization of the product from acetone/ether yielded 221 mg (93%) of 9i as red-brown plates, mp 186 °C: ^{1}H NMR (CD_3COCD_3) 3.42 (s, 6 H, NMe$_2$), 4.84 (s, 5 H, C$_5$H$_5$), 5.11 (t, *J* = 2 Hz, 2 H, 3,4-H), 5.27 (t, *J* = 2 Hz, 2 H, 2,5-H); ^{1}H NMR (CDCl$_3$) 3.35 (s, 6 H, NMe$_2$), 4.80 (s, 5 H, C$_5$H$_5$), 4.99 (s, 4 H, 2–5-H); MS-FD, *m/e* 331 (C$_{15}$H$_{21}$N$_2$Ru$^+$); IR (KBr) 1590 (C=N), 835 (P—F); UV (CH$_3$CN) 222 (3.92), 269 (4.25), 360 (3.27), 507 (1.58). Anal. Calcd for C$_{15}$H$_{21}$F$_6$N$_2$PRu (475.38): C, 37.90; H, 4.45; N, 5.89. Found: C, 38.05; H, 4.51; N, 6.14.

Syntheses and X-ray Crystal Structures of Highly Dissociated Rhodium(I) Phosphine Complexes Using Very Bulky Phosphine Ligands

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A series of rhodium(I) phosphine complexes has been prepared by treating [{RhCl(CO)$_2$}$_2$], [{RhCl(COD)}$_2$], and [{RhCl(COE)$_2$}$_2$] with the bulky phosphines PX{CH(SiMe$_3$)$_2$}$_2$ (X = Cl, H, or Me). ^{31}P and ^{1}H NMR and X-ray methods were used to identify the products of these reactions. The olefin complexes are highly dissociated in solution. The molecular structures of [RhCl(COD)(PCl{CH(SiMe$_3$)$_2$}$_2$)]·C$_7$H$_8$ (1), bis-[*trans*-{(cyclooctene)μ-chloro[bis{bis(trimethylsilyl)methyl}phosphine]dirhodium(I)}] (5), and *trans*-[RhCl(CO)(PH{CH(SiMe$_3$)$_2$}$_2$)$_2$] (8) have been determined by X-ray diffraction. The crystal data at 140 K are as follows. 1: *a* = 11.158 (3) Å, *b* = 11.930 (3) Å, *c* = 13.132 (3) Å, *α* = 97.24 (2)°, *β* = 104.02 (2)°, *γ* = 93.82 (2), *Z* = 2, space group *P*Ī. 5: *a* = 11.118 (5) Å, *b* = 16.403 (9) Å, *c* = 17.782 (11) Å, *β* = 104.77 (4)°, *Z* = 2, space group *P*2$_1$/*n*. 8: *a* = 10.620 (1) Å, *b* = 22.705 (4) Å, *c* = 20.375 (3) Å, *β* = 96.00 (1)°, *Z* = 4, space group *P*2$_1$/*n*. For 1 *R* = 0.044, for 5 *R* = 0.023, and for 8 *R* = 0.038. 1 is essentially square planar, Rh–P = 2.287 (1), Rh–Cl = 2.363 (1), and Rh–C = 2.124 (5)–2.253 (5) Å. For 5 the Rh$_2$Cl$_2$ core is planar, Rh–Rh = 3.690 (1), Rh–P = 2.203, Rh–Cl = 2.391 (1) and 2.475 (1), and Rh–C = 2.098 (3) and 2.110 (3) Å. Complex 8 is nearly square planar and does not dissociate appreciably in solution. The geometries at phosphorus in the dissociating complexes show no unusual angles or distances. This suggests that the steric effects in these ligands are more subtle than those found in the bulkiest phosphines now known.

Introduction

The catalytic hydrogenation of unsaturated substrates by rhodium(I) phosphine complexes probably involves the presence of three-coordinate intermediates such as Rh-

Cl(P)$_2$ (P = phosphine).[1] There are only a few examples of RhX(P)$_2$ complexes in the literature.[2,3] The reaction

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(1) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1978**, 692.