$Co_2(CO)_6DPM$, 1, in CH_2Cl_2 and stirring in the presence of 90% ^{13}CO and 5% Pd/charcoal. Enriched samples of 1 were then used to prepare 2–5 by literature methods.[1,3] The level of enrichment was estimated by infrared spectroscopy to be ca. 20%.

Acknowledgment. We thank the Research Corp. and the State of Virginia for support of this research. We thank Mr. Tom Glass for assistance in obtaining the low-temperature NMR data.

Registry No. 1, 52615-19-7; 2, 55925-97-8; 3, 52659-27-5; 4, 82864-95-7.

Synthesis of Some Ring-Substituted [1]Ferrocenophanes and the Structure of Four Representative Examples

Ian R. Butler,[1a] William R. Cullen,*,[1a] Frederick W. B. Einstein,[1b] Steven J. Rettig,[1a] and Anthony J. Willis[1b]

Chemistry Departments, University of British Columbia, Vancouver, British Columbia, and Simon Fraser University, Burnaby, British Columbia, Canada

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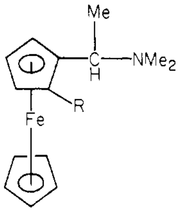
The reaction of 1,1′-dilithioferrocenes $(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3R^1Li)$ [R^1 = H, CHMeNMe$_2$, or CH(CHMe$_2$)NMe$_2$] with Cl_2PPh, I_2AsPh, and $Cl_2P\text{-}t\text{-}Bu$ [X_2ER^2] affords the appropriate [1]ferrocenophanes $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_3R^1ER^2)$. The crystal structures of four such complexes have been determined: R^1 = H, E = P, R^2 = Ph; *Pbca*, a = 7.3427 (8) Å, b = 27.078 (4) Å, c = 12.682 (2) Å, Z = 8, R = 0.045 for 1544 reflections; R^1 = H, E = P, R^2 = *t*-Bu; $P2_1/n$, a = 6.1007 (5) Å, b = 20.1851 (8) Å, c = 10.2303 (9) Å, β = 93.284 (4)°, Z = 4, R = 0.036 for 2427 reflections; R^1 = CH(CHMe$_2$)NMe$_2$, E = P, R^2 = Ph; $P2_1/c$, a = 8.2775 (9) Å, b = 15.4055 (8), c = 15.7558 (19) Å, β = 103.908 (5)°, Z = 4, R = 0.030 for 2730 reflections; R^1 = CHMeNMe$_2$, E = As, R^2 = Ph; $P\bar{1}$, a = 9.0873 (8) Å, b = 10.2776 (7) Å, c = 11.0240 (8) Å, α = 65.974 (7)°, β = 66.451 (6)°, γ = 76.959 (6)°, Z = 2, R = 0.024 for 3404 reflections. In the three phosphorus-bridged [1]ferrocenophanes, the mean tilt of the cyclopentadienyl rings is 27.0 (1)°, and the mean bridgehead angle at phosphorus is 90.8 (4)°. The corresponding parameters for the arsenic derivatives are 22.9 and 87.90 (7)°, respectively. The mean Fe–(cyclopentadienyl ring centroid) distance for all four molecules is 1.636 (6) Å.

Introduction

There has been considerable interest in reactions catalyzed by ferrocenyl phosphine derivatives of metals such as Ni, Pd, and Rh.[2-11] It is clear that rather dramatic changes in reaction products and yields can be achieved by changes in the metal and ligand. For example, it has been found that the dialkylphosphine 1 [R = $P(C(CH_3)_3)_2$] affords rhodium(I) complexes which are unexpectedly effective as asymmetric hydrogenation catalysts.[5] Complexes of the related diphenylphosphine 1 [R = $P(C_6H_5)_2$] are actually less effective in some cases. Kumada and co-workers[11] have shown that the regeo chemistry of Grignard cross coupling reactions can be varied by using either the nickel or palladium derivatives of 2 [R = $P(C_6H_5)_2$] as catalysts.



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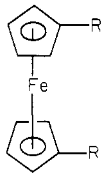

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In order to extend this chemistry, it is desirable to have available a range of compounds related to 1 and 2 with a variety of substituents and stereochemistries. The reported[12] cleavage reaction of the bridged ferrocene derivative 3 (eq 1) appeared to offer a general convenient synthetic route as indicated in eq 2. This route has been found to be viable.[12,13]

This paper describes the structure determination of bridged phosphines and arsines related to 3 which are synthetically useful starting materials for ligand preparation. The structure determination of 3 was reported[14] during the course of this study but as our own results for

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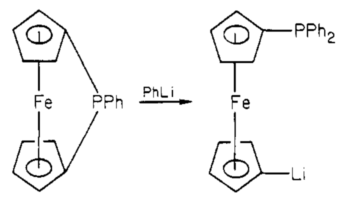

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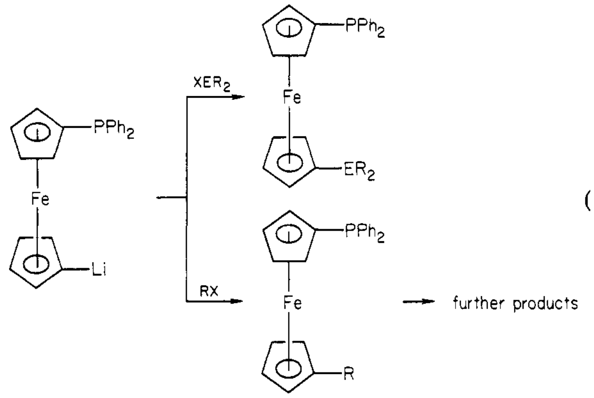

(2)

this compound afford slightly better residuals these are also included.

Compounds such as **3**, in which the cyclopentadienyl rings of the ferrocene moiety are connected by a single atom bridge, are known as [1]ferrocenophanes. The preparation and characterization of a number of these compounds with Si, Ge, and As as bridging atoms have been recently reported.[12,15-17] X-ray structure determinations have been published for three such compounds: 1,1′-ferrocenediyldiphenylsilane,[18] 1,1′-ferrocenediyldiphenylgermane,[14] and, as mentioned above, 1,1′-ferrocenediylphenylphosphine, **3**.[14]

Experimental Section

All manipulations were performed under an atmosphere of dry nitrogen. Microanalyses were performed by Mr. P. Borda of the Chemistry Department, University of British Columbia. ^{1}H NMR spectra were recorded on either a Bruker W.P. 80 operating at 80 MHz, a Varian XL100 at 100 MHz, or a Bruker WM 400 at 400 MHz. All solvents were predried and freshly distilled.

Preparation of 1,1′-Ferrocenediylphenylphosphine (3),[17] 1,1′-Ferrocenediyl-*tert*-butylphosphine (4), and 1,1′-Ferrocenediylphenylarsine (5).[12] The compounds **3** and **5** were prepared according to the published procedures.[12,17,19] Compound **4** was prepared by a similar method using *tert*-butyldichlorophosphine.[20] Careful chromatography is required in the latter preparation to separate the red 1,1′-ferrocenediyl-*tert*-butylphosphine from a white phosphine byproduct.

1,1′-Ferrocenediyl-*tert*-butylphosphine: red needles, decomp pt >95 °C yield 46%; ^{1}H NMR δ 4.10–5.10 (m, 8), 1.40 (d, 9). Anal. Calcd for $C_{14}H_{17}FeP$: C, 61.80; H, 6.30. Found: C, 61.82; H, 6.50.

Preparation of [2-(α-Dimethylamino)ethyl)-1,1′-ferrocenediyl]phenylphosphine (6) and [2-(α-(Dimethylamino)-β-methylpropyl)-1,1′-ferrocenediyl]phenylphosphine (7). (a) Isolation of the Dilithioferrocenyl Tetramethylethylenediamine Adducts. α-R-*N*,*N*-dimethyl-α-ferrocenylmethylamine derivatives (**6a**, R = CH_3, and **7a**, R = *i*-C_3H_7) were prepared by the published procedures.[21-23]

A solution of *n*-butyllithium in hexane (18 mL, 1.6 M) was added dropwise to a well stirred solution of **6a** or **7a** (7.20 g, 7.98 g, 28 mmol) in *n*-hexane (30 mL) and diethyl ether (50 mL). The solution was stirred for 1 h before a mixture of *n*-butyllithium (19 mL, 1.6 M) and tetramethylethylenediamine (TMED) (3.48 g, 30 mmol) was added dropwise. The solution was stirred for a further 10 h. A pale orange precipitate of 1,1′-dilithio-2-(α-R-α-(dimethylamino)methylferrocene–tetramethylethylenediamine (**6b**, R = Me, and **7b**, R = *i*-Pr) formed. This adduct was isolated by filtration and washed several times with *n*-hexane. The yield of the pyrophoric adducts is 70–80%.

(b) Reaction of the Adducts with Chlorophosphines. To a well-stirred suspension of **6b** or **7b** (1.80 g, 1.88 g, 4.7 mmol) in diethyl ether (50 mL), maintained at −78 °C, was added *P*,*P*-dichlorophenylphosphine (0.9 g, 5 mmol) in diethyl ether (10 mL). The solution was allowed to warm to room temperature slowly and was stirred for a further 1 h. The product mixture was hydrolyzed (H_2O, 20 mL), the ethereal layer separated and dried over anhydrous $MgSO_4$, and the solution volume reduced to approximately 10 mL. The resulting red oil was chromatographed on neutral alumina, eluting with diethyl ether. The second deep red band was collected, the solution volume reduced to approximately 10 mL, and *n*-hexane (5 mL) added. The solution was then cooled to −20 °C overnight. Red crystals were obtained, yield 40–60%. **6**, R = Me: mp 113–114 °C; ^{1}H NMR δ 7.10–7.90 (m, 5), 4.00–4.70 (m, 7), 3.05 (q, 1), 1.85 (s, 6), 1.90 (d, 3). Anal. Calcd for $C_{20}H_{22}FeNP$: C, 66.10; H, 6.06; N, 3.85. Found: C, 66.70; H, 6.20; N, 3.76. **7**, R = *i*-Pr: mp 128–129 °C; ^{1}H NMR δ 7.10–7.70 (m, 5), 4.00–4.80 (m, 8), 3.72 (m, 1), 2.05 (s, 6), 1.56 (2d, 3, 3). Anal. Calcd for $C_{22}H_{26}FeNP$: C, 67.88; H, 6.90; N, 3.60. Found: C, 67.53; H, 6.70; N, 3.58.

Preparation of [2-α-Dimethylamino)ethyl)-1,1′-ferrocenediyl]-*tert*-butylphosphine (8) and [2-(α-(Dimethylamino)ethyl)-1,1′-ferrocenediyl]phenylarsine (9). A procedure identical with that of the preceding preparations was used employing *tert*-butyldichlorophosphine[20] and *As*,*As*-diiodophenylarsine, respectively, in place of *P*,*P*-dichlorophenylphosphine; yields 45–65%. **8**: mp 91.5–92.5 °C ^{1}H NMR δ, 4.25–4.80 (m, 7), 4.08 (m, 1), 2.10 (s, 6), 1.54 (d, 3), 1.40 (d, 9). Anal. Calcd for $C_{18}H_{26}FeNP$: C, 62.99; H, 7.64; N, 4.08. Found: C, 63.09; H, 7.68; N, 4.07. **9**: decomp pt >108 °C; ^{1}H NMR δ 7.25–7.70 (m, 5), 4.00–4.50 (m, 8), 2.18 (s, 6), 1.56 (d, 3). Anal. Calcd for $C_{20}H_{22}AsFeN$: C, 58.91; H, 5.45; N, 3.44. Found: C, 58.86; H, 5.52; N, 3.45.

X-ray Crystallographic Analyses of 3, 4, 7, and 9. Crystallographic data for all four compounds are given in Table I. Space groups were determined from preliminary X-ray photographs (Cu Kα, λ = 1.5418 Å, or Mo Kα radiation, λ = 0.710 73 Å). Crystals of **3** were mounted on an automated Picker FACS-I diffractometer and crystals of **4**, **7**, and **9** on an Enraf-Nonius CAD4-F diffractometer; all in nonspecific orientations. Final unit-cell dimensions were obtained by least squares from the setting angles of 28 accurately centered reflections (with $25 < 2\theta < 31°$) for **3** and by least squares on 2 ($\sin \theta)/\lambda$ values for 25 reflections (with $40 < 2\theta < 50°$, $35 < 2\theta < 49°$, and $45 < 2\theta < 49°$ for **4**, **7**, and **9**, respectively) measured with Mo Kα_1 radiation (λ = 0.709 30 Å).

For **3**, two standards were measured after every 80 reflections and showed small, almost sinusoidal, variations in intensity (maximum of 4% from mean). A five-point smoothed curve was derived from the standards and used to rescale the data. The peak profiles of 2236 independent relections yielded 1544 reflections with $I > 2.3\sigma(I)$ which were regarded as observed and were used in the structure solution and refinement. Background counts of 0.1 × (scan time) were taken at each side of the very scan. Intensities and their associated errors were derived by a peak profile analysis.[24]

For **4**, **7**, and **9** the intensities of three check reflections were measured every hour throughout the data collections, showing only random fluctuations for **7** and **9**, and a uniform decrease of 7.9% in the case of **4** was accounted for by application of an isotropic decay correction. Totals of 3664, 4459, and 4989 in-

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Table I. Crystallographic Data[a]

	3	4	7	9
formula	$C_{16}H_{13}FeP$	$C_{14}H_{17}FeP$	$C_{22}H_{26}FeNP$	$C_{20}H_{22}AsFeN$
fw	292.10	272.11	391.28	407.17
cryst system	orthorhombic	monoclinic	monoclinic	triclinic[b]
space group	*Pbca*	$P2_1/n$[c]	$P2_1/c$	$P\bar{1}$
a, Å	7.3427 (8)	6.1007 (5)	8.2775 (9)	9.0873 (8)
b, Å	27.078 (4)	20.1851 (8)	15.4055 (8)	10.2776 (7)
c, Å	12.682 (2)	10.2303 (9)	15.7558 (19)	11.0240 (8)
α, deg	90	90	90	65.974 (7)
β, deg	90	93.284 (4)	103.908 (5)	66.451 (6)
γ, deg	90	90	90	76.959 (6)
V, Å^3	2521.5 (6)	1257.7 (2)	1950.2 (3)	859.6 (1)
Z	8	4	4	2
D_{calcd}, g cm^{-3}	1.539	1.437	1.333	1.573
F(000)	1200	568	824	416
cryst dimens, mm	0.30 × 0.14 × 0.47	0.34 × 0.36 × 0.44	0.24 × 0.25 × 0.31	0.11 × 0.43 × 0.43
μ(Mo Kα), cm^{-1}	12.96	12.93	8.56	27.81
transmission factors	0.66–0.84	0.61–0.69	0.80–0.83	0.51–0.77
scan type	$\omega-2\theta$	$\omega-\theta$	$\omega-{}^4/_3\theta$	$\omega-2\theta$
ω scan speed, deg min^{-1}	1.00	1.55–10.06	1.34–10.06	1.34–10.06
scan range (deg in ω)[d]	0.80 + 0.35 tan θ	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ	0.60 + 0.35 tan θ
data collected	*h,k,l*	$h,k,\pm l$	$\pm h,k,l$	$h,\pm k,\pm l$
$2\theta_{\max}$, deg	50	60	55	60
cryst decay	negligible	7.9%	negligible	negligible
unique reflctns	2236	3664	4459	4989
observed reflctns	1544	2427	2730	3404
no. of variables	216	213	330	296
R(observed reflctns)	0.045	0.036	0.030	0.024
R_w(observed reflctns)	0.062	0.050	0.034	0.030
R(all data)		0.067	0.058	0.052
error in observn of unit weight		1.000	1.938	1.329

[a] Temperature 21 ± 1 °C; Mo Kα radiation, graphite monochromator, λ = 0.709 30 Å (α_1), 0.713 59 Å (α_2); function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2)^{1/2}$, $w = 1/(\sigma^2(F) + 0.0004F^2)$ for **3** and $w = 1/\sigma^2(F)$. $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (*S* = scan count; *B* = background count) for **4**, **7**, and **9**. [b] Lattice constants refer to reduced cell. [c] Nonstandard setting of $P2_1/c$, equivalent positions $\pm(x, y, z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$. [d] For **4**, **7** and **9** the scan range was extended by 25% on each side for background measurement.

dependent data were measured and processed for **4**, **7**, and **9**, respectively. Of these, 2427, 2730, and 3404 had $I > 3\sigma(I)$ and were used in the solution and refinement of the structures. Absorption corrections were applied to all four data sets, transmission factor ranges appearing in Table I.

The structures were all solved by conventional heavy-atom techniques; all atoms (including hydrogen) not located from the Patterson function were positioned from successive difference maps. In the case of **9**, the centrosymmetric space group $P\bar{1}$ was indicated by the Patterson function and was verified by the subsequent successful refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms with isotropic thermal parameters. An extinction parameter[25] was included in the refinement of **3**. Neutral-atom scattering factors and anomalous scattering corrections (for As, Fe, and P) were taken from ref 26.

Maximum parameter shifts on the last cycles of refinement corresponded to 0.10σ, 0.28σ, 1.8σ, and 1.1σ for **3**, **4**, **7**, and **9**, respectively; for **7** and **9** the maximum shifts were associated with hydrogen atom parameters, those for non-hydrogen atoms all being less than 0.10σ. Final difference maps showed no unusual features. Refinement of **3** was by block-diagonal (Gauss-Siedel) least squares. All calculations for **3** involved computer programs[27] run on an in-house PDP-8e computer. Full-matrix least-squares refinement was employed for **4**, **7**, and **9**, calculations being performed on an Amdahl 470/V8 computer using programs listed in ref 28. Final positional and isotropic (or equivalent isotropic, U_{eq} = 1/3 trace *U*) thermal parameters are given for **3**, **4**, **7**, and **9** in Tables II–V, respectively. Anisotropic thermal parameters (Tables VI–IX) and measured and calculated structure factors for the four structures are included as supplementary material.

Table II. Final Positional (Fractional, ×10^4; Fe and P, ×10^5; H, ×10^3) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses for 1,1′-Ferrocenediylphenylphosphine (3)

atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Fe	21415 (9)	7520 (2)	49700 (4)	44
P	46793 (16)	13839 (4)	40731 (9)	49
C(1)	2820 (6)	995 (2)	3549 (3)	49
C(2)	3060 (7)	467 (2)	3603 (3)	58
C(3)	1351 (8)	248 (2)	3835 (3)	67
C(4)	55 (7)	624 (2)	3900 (3)	62
C(5)	926 (6)	1076 (2)	3729 (3)	51
C(6)	3998 (6)	1234 (2)	5441 (3)	48
C(7)	4454 (6)	749 (2)	5824 (4)	58
C(8)	3039 (8)	578 (2)	6476 (3)	68
C(9)	1700 (7)	946 (2)	6521 (3)	63
C(10)	2264 (6)	1352 (2)	5897 (3)	49
C(11)	3743 (6)	1996 (2)	3879 (3)	47
C(12)	3910 (6)	2369 (2)	4637 (3)	52
C(13)	3338 (6)	2844 (2)	4416 (4)	60
C(14)	2613 (6)	2959 (2)	3453 (4)	62
C(15)	2419 (7)	2598 (2)	2702 (4)	60
C(16)	2982 (6)	2120 (2)	2908 (3)	53
H(2)	414 (5)	29 (1)	356 (3)	42 (10)
H(3)	136 (6)	−6 (1)	391 (3)	71 (13)
H(4)	−120 (5)	59 (1)	408 (3)	61 (12)
H(5)	48 (6)	139 (1)	381 (3)	61 (12)
H(7)	551 (5)	60 (2)	564 (3)	64 (12)
H(8)	304 (6)	23 (1)	678 (3)	70 (14)
H(9)	60 (5)	94 (1)	688 (3)	62 (12)
H(10)	166 (4)	163 (1)	576 (2)	34 (9)
H(12)	433 (5)	229 (1)	529 (3)	42 (10)
H(13)	356 (6)	312 (2)	495 (2)	59 (13)
H(14)	223 (5)	328 (1)	328 (3)	56 (12)
H(15)	190 (6)	268 (2)	211 (4)	82 (15)
H(16)	284 (5)	188 (1)	235 (3)	60 (12)

Bond lengths and angles for the four structures are given in Tables X and XI, respectively. Important structural parameters for **3**,

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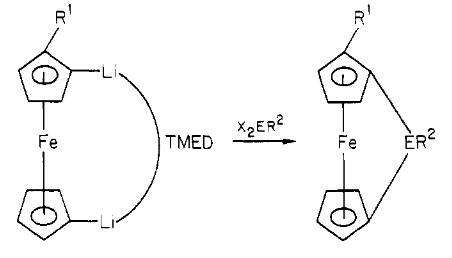
Table III. Final Positional (Fractional, $\times 10^4$; Fe and P, $\times 10^5$; H, $\times 10^3$) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses for 1,1′-Ferrocenediyl-*tert*-butylphosphine (4)

atom	x	y	z	U_{eq}/U_{iso}
Fe	21270 (7)	45294 (2)	30336 (4)	32
P	38307 (14)	36407 (5)	13059 (10)	43
C(1)	2350 (6)	4440 (2)	1116 (3)	40
C(2)	129 (6)	4584 (2)	1414 (3)	45
C(3)	87 (7)	5209 (2)	2059 (4)	50
C(4)	2243 (7)	5458 (2)	2165 (4)	52
C(5)	3644 (7)	5008 (2)	1582 (4)	48
C(6)	3193 (6)	3604 (2)	3054 (4)	45
C(7)	1073 (7)	3641 (2)	3587 (4)	49
C(8)	1174 (8)	4057 (2)	4717 (4)	57
C(9)	3365 (8)	4280 (2)	4909 (4)	56
C(10)	4605 (7)	4007 (2)	3916 (4)	50
C(11)	2247 (6)	2972 (2)	408 (4)	46
C(12)	2985 (11)	3007 (3)	−998 (5)	71
C(13)	3043 (10)	2326 (2)	1052 (6)	67
C(14)	−244 (8)	3005 (3)	372 (7)	69
H(2)	−121 (8)	430 (2)	120 (5)	70 (14)
H(3)	−120 (7)	541 (2)	239 (4)	50 (11)
H(4)	256 (8)	583 (3)	251 (5)	73 (15)
H(5)	524 (7)	504 (2)	148 (4)	47 (11)
H(7)	−18 (6)	344 (2)	324 (4)	41 (10)
H(8)	−10 (8)	417 (2)	519 (5)	71 (15)
H(9)	399 (7)	453 (2)	561 (5)	65 (13)
H(10)	593 (6)	410 (2)	381 (3)	32 (9)
H(12a)	467 (10)	298 (2)	−106 (5)	83 (16)
H(12b)	224 (11)	265 (4)	−151 (7)	126 (24)
H(12c)	254 (10)	338 (3)	−135 (6)	94 (21)
H(13a)	255 (11)	230 (4)	207 (7)	131 (25)
H(13b)	246 (9)	201 (3)	67 (6)	86 (18)
H(13c)	457 (8)	230 (2)	111 (5)	65 (14)
H(14a)	−71 (10)	297 (3)	120 (6)	97 (21)
H(14b)	−79 (8)	339 (3)	−6 (5)	66 (15)
H(14c)	−89 (8)	260 (3)	−17 (5)	83 (16)

4, **7**, and **9**, are compared with those of other [1] ferrocenophanes in Table XII. Bond distances and angles involving hydrogen atoms and torsion angles (Tables XIII–XXIII) are included as supplementary material.

Results and Discussion

The previously known [1]ferrocenophanes **3** and **5** were prepared from 1,1′-dilithioferrocene by the literature procedure (eq 3, R^1 = H, X_2ER^2 = I_2AsPh, Cl_2PPh). A simple extension using Cl_2P-*t*-Bu allows the isolation of the previously unknown **4**. Best yields are obtained when the isolated TMED adduct is used. An excess of X_2ER^2 should be avoided because of a reaction of this with the ferrocenophane product.



10

3, R^1 = H, R^2 = Ph, E = P
4, R^1 = H, R^2 = *t*-Bu, E = P
5, R^1 = H, R^2 = Ph, E = As
6, R^1 = CH(Me)NMe_2, R^2 = Ph, E = P
7, R^1 = CH($CHMe_2$)NMe_2, R^2 = Ph, E = P
8, R^1 = CH(Me)NMe_2, R^2 = *t*-Bu, E = P
9, R^1 = CH(Me)NMe_2, R^2 = Ph, E = As

Table IV. Final Positional (Fractional, $\times 10^4$; Fe and P, $\times 10^5$; H, $\times 10^3$) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses for [2-(α-(Dimethylamino)-β-methylpropyl)-1,1′-ferrocenediyl]phenylphosphine (7)

atom	x	y	z	U_{eq}/U_{iso}
Fe	33666 (4)	28659 (2)	35932 (2)	33
P	53454 (8)	41943 (4)	44538 (4)	32
N	5670 (3)	4614 (1)	1948 (1)	43
C(1)	5552 (3)	3388 (1)	3599 (1)	30
C(2)	4474 (3)	3479 (2)	2721 (1)	31
C(3)	4019 (3)	2621 (2)	2415 (2)	37
C(4)	4794 (4)	2018 (2)	3061 (2)	44
C(5)	5748 (3)	2480 (2)	3782 (2)	38
C(6)	3435 (3)	3654 (2)	4604 (2)	38
C(7)	1947 (3)	3823 (2)	3933 (2)	41
C(8)	976 (3)	3057 (2)	3772 (2)	51
C(9)	1798 (4)	2411 (2)	4346 (2)	55
C(10)	3302 (4)	2763 (2)	4857 (2)	45
C(11)	6984 (3)	3835 (2)	5384 (2)	34
C(12)	6725 (3)	3658 (2)	6200 (2)	41
C(13)	8052 (4)	3459 (2)	6892 (2)	48
C(14)	9645 (4)	3438 (2)	6783 (2)	54
C(15)	9922 (4)	3624 (2)	5976 (2)	61
C(16)	8615 (3)	3823 (2)	5282 (2)	52
C(17)	4158 (3)	4323 (2)	2212 (2)	34
C(18)	7021 (4)	4883 (3)	2659 (2)	54
C(19)	6277 (5)	4012 (3)	1382 (3)	66
C(20)	2677 (3)	4283 (2)	1399 (2)	42
C(21)	1031 (4)	4136 (3)	1645 (2)	61
C(22)	2563 (5)	5116 (3)	849 (3)	68
H(3)	331 (4)	251 (2)	188 (2)	48 (8)
H(4)	467 (3)	143 (2)	298 (2)	43 (7)
H(5)	638 (3)	223 (1)	432 (1)	23 (6)
H(7)	174 (3)	435 (2)	365 (2)	40 (8)
H(8)	−11 (3)	303 (2)	339 (2)	44 (7)
H(9)	134 (4)	185 (2)	444 (2)	64 (9)
H(10)	403 (3)	247 (2)	524 (2)	27 (6)
H(12)	556 (4)	366 (2)	632 (2)	51 (8)
H(13)	786 (4)	330 (2)	744 (2)	74 (10)
H(14)	1055 (4)	334 (2)	727 (2)	66 (9)
H(15)	1102 (4)	362 (2)	589 (2)	48 (8)
H(16)	882 (4)	394 (2)	476 (2)	78 (11)
H(17)	395 (2)	479 (1)	260 (1)	17 (5)
H(18a)	669 (4)	523 (2)	301 (2)	60 (11)
H(18b)	736 (4)	518 (2)	247 (2)	50 (8)
H(18c)	765 (4)	444 (2)	302 (2)	65 (10)
H(19a)	538 (5)	393 (2)	91 (3)	83 (13)
H(19b)	724 (5)	427 (2)	123 (2)	81 (11)
H(19c)	668 (4)	349 (2)	171 (2)	76 (12)
H(20)	283 (3)	384 (2)	107 (2)	29 (7)
H(21a)	14 (4)	408 (2)	113 (2)	75 (11)
H(21b)	101 (3)	362 (2)	202 (2)	61 (9)
H(21c)	89 (4)	462 (2)	205 (2)	69 (11)
H(22a)	171 (4)	507 (2)	32 (2)	65 (9)
H(22b)	243 (5)	557 (3)	130 (3)	106 (15)
H(22c)	349 (5)	517 (3)	68 (2)	92 (14)

The monolithiation of α-dimethylamino ferrocenes is well-known to be stereospecific. Dilithiation easily affords the substituted 1,1′-dilithioferrocenes **6b** and **7b** (**10**, R = CH(Me)NMe_2, CH($CHMe_2$)NMe_2) which can be isolated as TMED adducts. These compounds also react as shown in eq **3**, giving the substituted ferrocenophanes **6**–**9**.

The reaction of these ferrocenophanes have been investigated according to the scheme shown in eq 2. This chemistry and the use of the derived ligands in catalytic hydrogenation reactions will be described in forthcoming publications.

The remainder of this paper is concerned with a description of the structures of a representative selection of the ferrocenophanes.

The crystal structures of **3**, **4**, **7**, and **9** each consist of discrete molecules separated by normal van der Waals

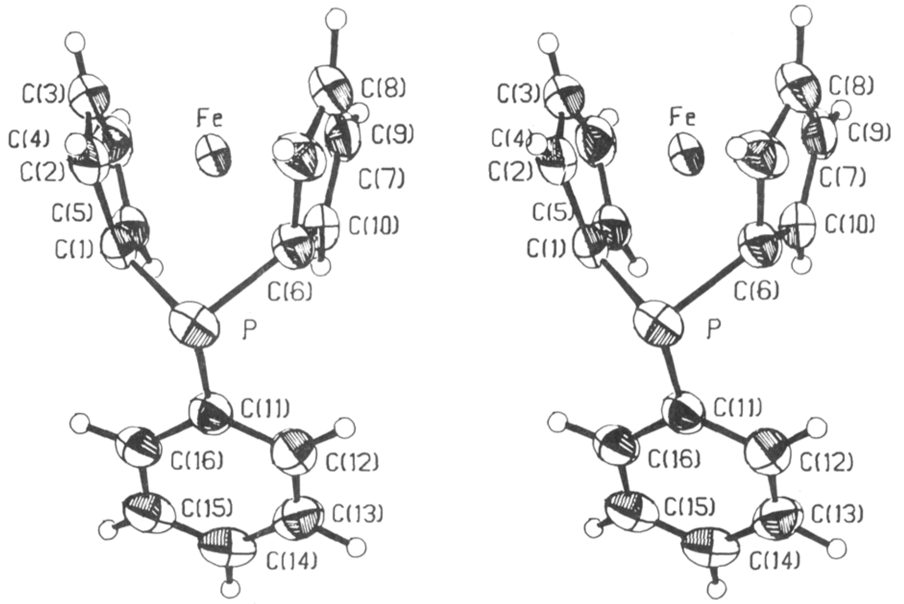


Figure 1. Stereoview of the structure of the ferrocenophane **3**.

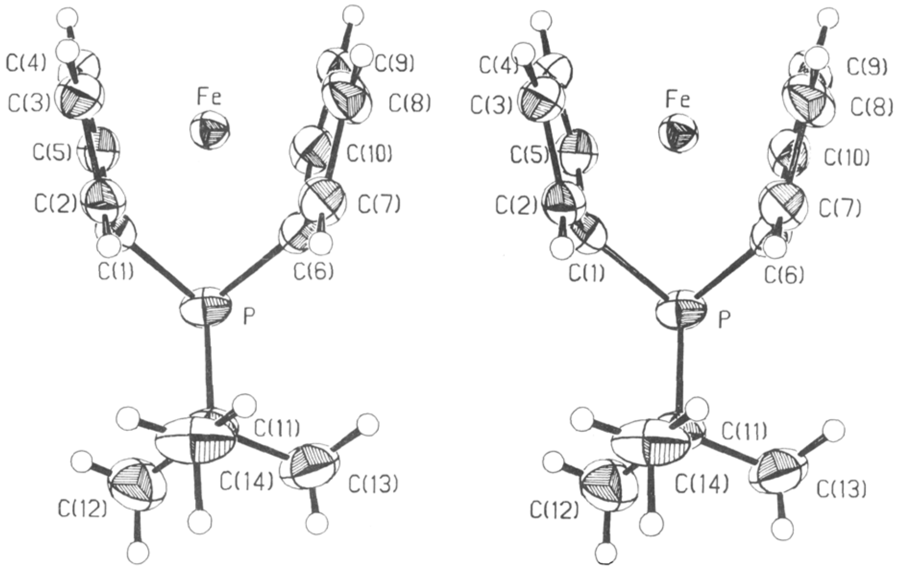


Figure 2. Stereoview of the structure of the ferrocenophane **4**.

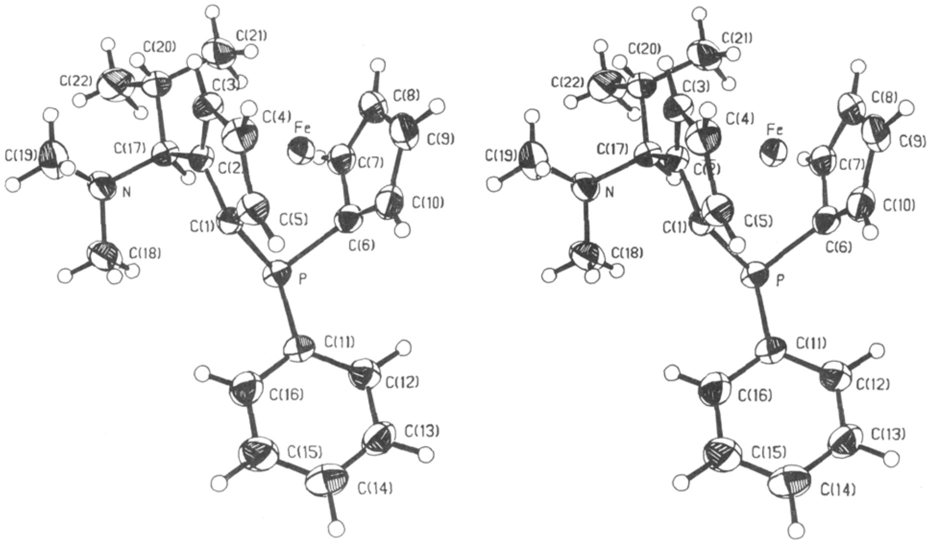


Figure 3. Stereoview of the structure of the ferrocenophane **7**.

distances. Stereoscopic views of the four molecules are shown in Figure 1–4. The unsubstituted molecules **3** and **4** have approximate mirror symmetry, the plane of symmetry containing atoms Fe, P, and C(11).

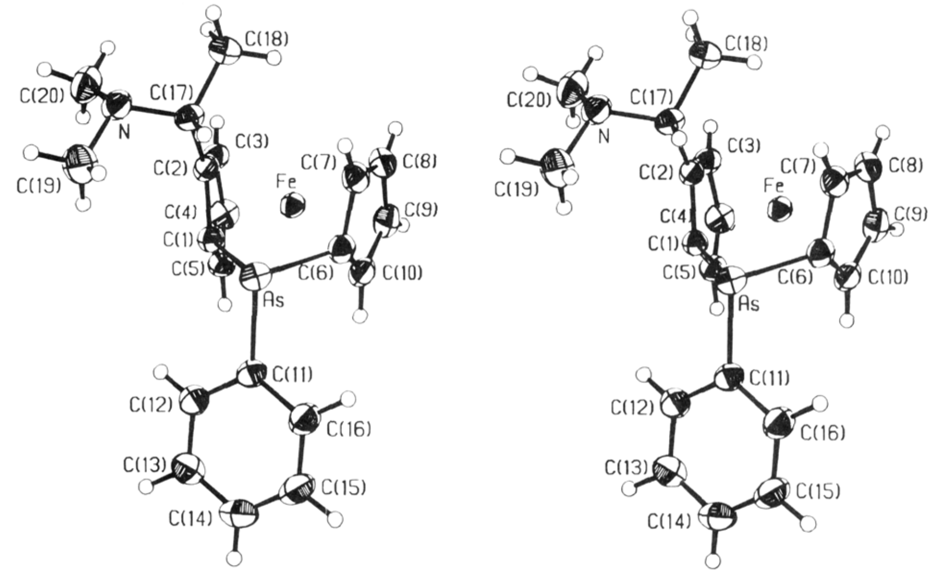


Figure 4. Stereoview of the structure of the ferrocenophane **9**.

Table V. Final Positional (Fractional, ×10^4; As and Fe, ×10^5; H, ×10^3) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses for [2-(α-(Dimethylamino)ethyl)-1,1′-ferrocenediyl]phenylarsine (**9**)

atom	x	y	z	U_{eq}/ U_{iso}
As	59259 (2)	40160 (2)	70728 (2)	33
Fe	74152 (3)	15753 (3)	62550 (3)	30
N	2049 (2)	1856 (2)	7473 (2)	40
C(1)	5580 (2)	1948 (2)	7873 (2)	30
C(2)	4988 (2)	1414 (2)	7130 (2)	30
C(3)	5768 (2)	33 (2)	7210 (2)	35
C(4)	6830 (3)	−311 (2)	7977 (2)	39
C(5)	6716 (2)	861 (2)	8381 (2)	35
C(6)	7885 (2)	3619 (2)	5571 (2)	35
C(7)	7603 (3)	3356 (2)	4494 (2)	40
C(8)	8762 (3)	2278 (3)	4113 (2)	44
C(9)	9788 (3)	1874 (3)	4920 (2)	46
C(10)	9252 (2)	2682 (2)	5817 (2)	40
C(11)	6815 (2)	4104 (2)	8374 (2)	34
C(12)	6161 (3)	3351 (2)	9820 (2)	41
C(13)	6638 (3)	3565 (3)	10768 (2)	48
C(14)	7759 (3)	4539 (3)	10286 (3)	50
C(15)	8398 (3)	5286 (3)	8863 (3)	51
C(16)	7948 (3)	5069 (2)	7904 (2)	43
C(17)	3702 (2)	2168 (2)	6473 (2)	34
C(18)	3964 (3)	1871 (3)	5152 (2)	47
C(19)	1564 (4)	2469 (4)	8570 (3)	63
C(20)	1746 (3)	354 (3)	8100 (3)	56
H(3)	565 (3)	−41 (3)	681 (3)	47 (7)
H(4)	749 (3)	−125 (3)	828 (3)	48 (6)
H(5)	722 (3)	91 (3)	890 (3)	46 (6)
H(7)	676 (3)	377 (3)	416 (3)	43 (6)
H(8)	894 (4)	187 (3)	353 (3)	54 (8)
H(9)	1074 (3)	113 (3)	488 (3)	39 (6)
H(10)	971 (3)	267 (3)	646 (3)	57 (8)
H(12)	540 (3)	277 (2)	1012 (2)	36 (5)
H(13)	606 (4)	315 (3)	1178 (3)	49 (8)
H(14)	806 (3)	467 (3)	1091 (3)	55 (8)
H(15)	919 (3)	592 (3)	851 (3)	57 (7)
H(16)	840 (3)	560 (3)	687 (3)	56 (7)
H(17)	370 (3)	323 (3)	620 (3)	52 (7)
H(18a)	381 (3)	86 (3)	537 (3)	53 (7)
H(18b)	507 (4)	212 (4)	445 (4)	83 (10)
H(18c)	310 (4)	234 (3)	473 (3)	62 (8)
H(19a)	222 (4)	199 (3)	922 (3)	65 (8)
H(19b)	40 (5)	241 (4)	911 (4)	81 (10)
H(19c)	164 (4)	346 (4)	810 (3)	66 (8)
H(20a)	204 (4)	−7 (4)	740 (4)	87 (11)
H(20b)	227 (4)	−29 (4)	879 (4)	83 (10)
H(20c)	67 (5)	27 (4)	854 (4)	83 (10)

Table X. Bond Lengths (Å) for **3**, **4**, **7**, and **9** with Estimated Standard Deviations in Parentheses (E = P or As)

bond	**3**	**4**	**7**	**9**
Fe–C(1)	1.982 (4)	1.983 (3)	1.978 (2)	2.000 (2)
Fe–C(2)	2.014 (4)	2.003 (3)	2.056 (2)	2.039 (2)
Fe–C(3)	2.067 (4)	2.069 (4)	2.089 (3)	2.077 (2)
Fe–C(4)	2.076 (5)	2.078 (4)	2.069 (3)	2.075 (2)
Fe–C(5)	2.011 (4)	2.038 (4)	2.011 (3)	2.014 (2)
Fe–C(6)	1.979 (4)	1.978 (4)	1.992 (2)	2.005 (2)
Fe–C(7)	2.014 (4)	1.998 (4)	2.036 (3)	2.033 (2)
Fe–C(8)	2.075 (4)	2.081 (4)	2.086 (3)	2.073 (2)
Fe–C(9)	2.062 (4)	2.083 (4)	2.080 (3)	2.075 (2)
Fe–C(10)	2.007 (4)	2.015 (4)	2.011 (3)	2.020 (2)
E–C(1)	1.849 (5)	1.854 (3)	1.870 (2)	1.987 (2)
E–C(6)	1.850 (5)	1.854 (3)	1.851 (2)	1.986 (2)
E–C(11)	1.811 (4)	1.870 (4)	1.827 (2)	1.946 (2)
C(1)–C(2)	1.443 (6)	1.435 (5)	1.462 (3)	1.453 (2)
C(1)–C(5)	1.426 (6)	1.456 (5)	1.431 (4)	1.436 (3)
C(2)–C(3)	1.419 (7)	1.424 (5)	1.427 (3)	1.421 (3)
C(3)–C(4)	1.396 (8)	1.406 (6)	1.412 (4)	1.422 (3)
C(4)–C(5)	1.399 (7)	1.405 (6)	1.410 (4)	1.416 (3)
C(6)–C(7)	1.440 (6)	1.434 (6)	1.440 (3)	1.444 (3)
C(6)–C(10)	1.435 (7)	1.447 (5)	1.441 (4)	1.435 (3)
C(7)–C(8)	1.406 (7)	1.427 (6)	1.416 (4)	1.418 (3)
C(8)–C(9)	1.401 (8)	1.414 (6)	1.406 (5)	1.421 (3)
C(9)–C(10)	1.415 (6)	1.413 (6)	1.418 (4)	1.417 (3)
C(11)–C(12)	1.398 (6)	1.532 (6)	1.381 (4)	1.392 (3)
C(11)–C(16)	1.393 (6)		1.397 (4)	1.389 (3)
C(12)–C(13)	1.382 (6)		1.383 (3)	1.386 (3)
C(13)–C(14)	1.369 (7)		1.371 (4)	1.385 (3)
C(14)–C(15)	1.372 (7)		1.375 (4)	1.372 (4)
C(15)–C(16)	1.385 (6)		1.376 (4)	1.383 (3)
C(11)–C(13)		1.529 (6)		
C(11)–C(14)		1.520 (6)		
N–C(17)			1.480 (3)	1.477 (3)
N–C(18/20)			1.441 (4)	1.452 (3)
N–C(19)			1.457 (4)	1.457 (3)
C(2)–C(17)			1.517 (3)	1.517 (2)
C(17)–C(20/18)			1.547 (3)	1.524 (3)
C(20)–C(21)			1.520 (4)	
C(20)–C(22)			1.538 (4)	

The geometry of the bridged ferrocene moiety in each of the three phosphorus-bridged species is essentially the same as that reported earlier for **3**.[14] The parameters listed in Table XII are virtually identical for **3** and **4**, the only significant difference being the shorter Fe···P distance in **4**, a result consistent with the slightly larger value of β in **4**. In the substituted molecule **7** the values of $\bar{\beta}$ and θ are slightly larger than those in **3** and **4** resulting in a small

Table XI. Bond Angles (deg) for **3**, **4**, **7**, and **9** with Estimated Standard Deviations in Parentheses (E = P or As)

atoms	**3**	**4**	**7**	**9**
C(1)-E-C(6)	90.7 (2)	90.48 (15)	91.28 (10)	87.90 (7)
C(1)-E-C(11)	101.1 (2)	110.0 (2)	101.43 (11)	100.13 (7)
C(6)-E-C(11)	103.1 (2)	108.3 (2)	104.73 (11)	102.34 (8)
E-C(1)-C(2)	117.2 (3)	127.9 (3)	118.5 (2)	117.54 (13)
E-C(1)-C(5)	125.1 (3)	113.5 (3)	122.0 (2)	122.56 (13)
C(2)-C(1)-C(5)	105.4 (4)	105.8 (3)	107.4 (2)	106.9 (2)
C(1)-C(2)-C(3)	108.4 (4)	108.6 (3)	106.4 (2)	107.21 (15)
C(1)-C(2)-C(17)			124.8 (2)	125.8 (2)
C(3)-C(2)-C(17)			128.2 (2)	126.9 (2)
C(2)-C(3)-C(4)	108.1 (4)	108.1 (4)	109.2 (2)	109.3 (2)
C(3)-C(4)-C(5)	108.5 (4)	108.9 (4)	108.6 (2)	107.6 (2)
C(4)-C(5)-C(1)	109.6 (4)	108.5 (4)	108.4 (2)	109.0 (2)
E-C(6)-C(7)	117.0 (3)	127.5 (3)	115.6 (2)	115.62 (14)
E-C(6)-C(10)	124.7 (3)	114.5 (3)	126.0 (2)	124.85 (14)
C(7)-C(6)-C(10)	105.9 (4)	104.9 (4)	105.5 (2)	106.3 (2)
C(6)-C(7)-C(8)	109.0 (4)	109.9 (4)	109.2 (3)	108.6 (2)
C(7)-C(8)-C(9)	108.0 (4)	107.3 (4)	108.0 (3)	108.1 (2)
C(8)-C(9)-C(10)	108.9 (4)	108.5 (4)	108.5 (3)	108.2 (2)
C(9)-C(10)-C(6)	108.2 (4)	109.4 (4)	108.8 (3)	108.8 (2)
E-C(11)-C(12)	112.2 (3)	104.9 (3)	123.7 (2)	120.22 (15)
E-C(11)-C(16/13)	119.5 (3)	105.2 (3)	117.6 (2)	120.28 (15)
P-C(11)-C(14)		118.0 (3)		
C(12)-C(11)-C(16/13)	118.0 (4)	109.9 (4)	118.4 (2)	118.9 (2)
C(12)-C(11)-C(14)		108.8 (4)		
C(13)-C(11)-C(14)		109.9 (4)		
C(11)-C(12)-C(13)	120.4 (4)		120.4 (2)	120.3 (2)
C(12)-C(13)-C(14)	120.8 (4)		120.8 (3)	120.2 (2)
C(13)-C(14)-C(15)	119.8 (4)		119.4 (3)	119.5 (2)
C(14)-C(15)-C(16)	120.3 (4)		120.5 (3)	120.9 (2)
C(15)-C(16)-C(11)	120.8 (4)		120.6 (3)	120.2 (2)
C(17)-N-C(20/18)			114.8 (2)	114.7 (2)
C(17)-N-C(19)			114.7 (2)	112.3 (2)
C(19)-N-C(20/18)			110.0 (3)	110.4 (2)
N-C(17)-C(2)			111.0 (2)	113.48 (15)
N-C(17)-C(20/18)			109.6 (2)	109.4 (2)
C(2)-C(17)-C(20/18)			113.9 (2)	113.0 (2)
C(17)-C(20)-C(21)			112.0 (2)	
C(17)-C(20)-C(22)			111.2 (2)	
C(21)-C(20)-C(22)			109.3 (3)	

Table XII. Selected Structural Data for [1]Ferrocenophanes $[(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3R)Fe]X$

	a	*b*	**3**[b]	**3**[c]	**4**[c]	**7**[c]	**9**[c]
X	$Si(C_6H_5)_2$	$Ge(C_6H_5)_2$	PC_6H_5	PC_6H_5	$P(t\text{-}C_4H_9)$	PC_6H_5	AsC_6H_5
R	H	H	H	H	H	$CH[N(CH_3)_2]C_3H_7$	$CH(CH_3)N(CH_3)_2$
mean Fe-Cp[d]	1.65	1.63	1.63	1.632 (3)	1.631 (2)	1.642 (2)	1.641 (1)
mean Fe-C	2.054	2.029	2.028	2.029	2.033	2.041	2.041
Fe···X[e]	2.636 (5)	2.744 (3)	2.774 (3)	2.774 (1)	2.763 (1)	2.764 (1)	2.8760 (3)
C(1)···C(6)	2.86 (1)	2.858 (14)	2.619 (12)	2.632 (6)	2.633 (5)	2.661 (3)	2.758 (3)
Cp-Fe-Cp	167	170	160	159.8	159.8	160.1	162.5
α[f]	19.2	16.6	26.7	26.9	27.1	27.0	22.9
$\bar{\beta}$[f]	40	38	32.5	32.3	32.8	33.1	32.8
θ[f]	99.1 (3)	93.6 (4)	90.6 (3)	90.7 (2)	90.5 (2)	91.3 (1)	87.90 (7)
mean Fe-C(1,6)	2.014 (11)	2.001 (14)	1.979 (4)	1.981 (2)	1.980 (3)	1.985 (7)	2.002 (3)
mean Fe-C(2,5,7,10)	2.030 (7)	2.031 (13)	2.013 (8)	2.012 (3)	2.014 (17)	2.029 (12)	2.026 (12)
mean Fe-C(3,4,8,9)	2.098 (16)	2.042 (7)	2.067 (14)	2.070 (7)	2.078 (6)	2.081 (9)	2.075 (2)

[a] Reference 18. [b] Reference 14. [c] This work. [d] Cp refers to centroid of cyclopentadienyl ring. [e] X refers to bridging atom here. [f] Defined in ref 14: α = tilt angle between Cp rings, $\bar{\beta}$ = mean angle between Cp plane and Cp-X bond, and θ = C(1)-X-C(6).

but significant increase in the C(1)···C(6) separation. The Fe···P distances in **4** and **7** are equal.

The mean Fe–Cp distances for all of the complexes listed in Table XVIII are near the expected value of 1.64 Å.[14] It is noteworthy, however, that the mean Fe–Cp distances in the two substituted complexes **7** and **9** are slightly longer than those in the unsubstituted molecules **3** and **4**. The arsine complex **9** displays structural parameters (Table XII) which are more similar to those of the phosphine analogues than to the germanium derivative even though the covalent radii of As and Ge are nearly identical. Strain is thus relieved in different ways in these compounds. In the silicon and germanium analogues the $\bar{\beta}$ values are large, indicating that most of the strain occurs at atoms C(1) and C(6). The phosphorus and arsenic derivatives have smaller (and in fact equal) values of $\bar{\beta}$, additional strain being compensated for by larger ring tilts (α) and smaller bridgehead angles θ. The smaller values of θ for the phosphorus and arsenic compounds are a result of the presence of the lone pair of electrons, bond angles at tervalent P or As commonly being substantially less than the tetrahedral angle. The θ angle in **9** at 87.90 (7)° is the smallest yet observed for a [1]ferrocenophane and the Fe···As distance of 2.8760 (3) Å the longest distance between the iron and the bridging atom. The most significant difference between the phosphorus and arsenic compounds is in the ring tilt α, the value of 22.9° observed for the arsine being intermediate between the mean of 27.0

Organometallics **1983,** *2,* 135–140 135

(1)° for the phosphorus-bridged and the values of 19.2 and 16.6° for the silicon- and germanium-bridged analogues, respectively. The C(1)⋯C(6) distance and the Cp–Fe–Cp angle in **9** are also intermediate between the corresponding values observed for the phosphorus and the silicon/germanium derivatives (see Table XII).

The cyclopentadienyl and phenyl rings in all four compounds are planar to within ±0.01 Å although seven of the eleven rings exhibit statistically significant deviations from planarity (χ^2 values for the C(1) and C(6) cyclopentadienyl rings are 11.7 and 2.3 for **3**, 16.6 and 3.9 for **4**, 38.0 and 26.0 for **7**, and 0.4 and 13.6 for **9**; χ^2 = 4.3, 15.0, and 11.5, respectively, for the phenyl rings in **3**, **7**, and **9**). The mean displacements of the P or As atoms from the mean planes of the cyclopentadienyl rings are 0.988 (1), 1.004 (4), 1.015 (6), and 1.075 (4) Å for **3**, **4**, **7**, and **9**, respectively. The mean libration-corrected[29,30] distance in the cyclopentadienyl rings of 1.428 Å is in excellent agreement with the accepted value of 1.429 Å.[31] The cyclopentadienyl rings all display substituent-induced geometrical distortions, the mean bond length involving the P- or As-substituted carbon atom being 1.445 (9) Å, adjacent C–C bonds averaging 1.419 (8) Å, and the unique bonds (across the ring from the substituted atom) averaging 1.414 (9) Å. The pattern of C–C bond length variation in the 1,2-disubstituted cyclopentadienyl rings differs somewhat (see Table X), the longest distances (1.464 (3) Å in **7**, and 1.445 (2) A in **9**) being between the substituted carbon atoms. Ring bond angles at the substituted carbon atoms are contracted from the "ideal" 108.0° to 104.9 (4)–106.3 (2)° for monosubstituted 106.4 (2)–107.4 (2)° for disubstituted rings with corresponding increases in the angles at the unsubstituted carbons. Substituent-induced ring distortions for the P- and As-substituted phenyl rings are as expected.[32]

The mean bond angles at phosphorus are 98.3, 102.9, and 99.2° in **3**, **4**, and **7**, respectively, and the mean angle at As in **9** is 96.8°, all of these values being substantially smaller than the tetrahedral angle (vide supra). The mean angles at nitrogen (113.2° for **7**, 112.5° for **9**), in contrast, are larger than the tetrahedral angle, indicating some delocalization of the lone pair.

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Registry No. **3**, 72954-06-4; **4**, 83547-83-5; **5**, 72954-08-6; **6**, 83560-65-0; **6a**, 31904-34-4; **6b**, 83547-84-6; **7**, 83547-85-7; **7a**, 83601-98-3; **7b**, 83560-64-9; **8**, 83547-86-8; **9**, 83547-87-9; TMED, 110-18-9; *tert*-butyldichlorophosphine, 25979-07-1; *As,As*-diiodophenylarsine, 6380-34-3; *P,P*-dichlorophenylphosphine, 644-97-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, measured and calculated thermal parameters, bond distances and angles involving hydrogen atoms and torsion angles, and structure factor amplitudes (Tables VI–IX and XIII–XXIII) (77 pages). Ordering information is given on any current masthead page.

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An η^2-Arene Complex of Rhenium: Synthesis, Characterization, and Activation of the Aromatic Carbon–Hydrogen Bonds

James R. Sweet and William A. G. Graham*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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Investigations of a cationic η^2-arene complex of rhenium having activated aromatic carbon–hydrogen bonds are described. $[(\eta\text{-}C_5H_5)Re(NO)(CO)(3,4\text{-}\eta^2\text{-}C_6H_5CHPh_2)][PF_6]$ ($2\cdot PF_6$) forms as yellow microcrystals from the reaction of Ph_3CPF_6 with $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ in CH_2Cl_2 at −78 °C; the solid is stable at room temperature for limited periods, but solutions begin to decompose at a significant rate above −40 °C. The triphenylmethane ligand is readily displaced by PPh_3 to form $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)][PF_6]$. In CH_2Cl_2 at −78 °C, $2\cdot PF_6$ is deprotonated by Et_3N affording para and meta isomers of $(\eta\text{-}C_5H_5)Re(NO)(CO)(\eta^1\text{-}C_6H_4CHPh_2)$. ^1H NMR spectra indicate that **2** is stereochemically nonrigid over the range studied (−40 to −70 °C). Migration of the rhenium group about the coordinated ring is proposed to occur via intermediate η^1-arenium structures, a model related to that of electrophilic aromatic substitution. Formation of these intermediates in solution accounts for activation of the carbon–hydrogen bonds toward deprotonation.

Arene molecules coordinated in η^2 fashion to a transition metal have often been suggested as intermediates in the activation of carbon–hydrogen bonds or other catalytic processes.[1] The η^2-arene bonding mode is well established for d^{10} metals such as Cu^+ and Ag^+,[2] and there are several examples involving transition metals with perfluoro- or perfluoroalkyl-substituted derivatives;[3] the latter cannot be regarded as typical arenes, however. The crystal structure of a (1,2-η^2-anthracene)nickel(0) complex[4] ap-

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