1846 *Organometallics* 1984, *3*, 1846-1851

91782-18-2; $Ru_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$, 91782-19-3; $Os_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$, 91782-20-6; $Ru_3(\mu\text{-dam})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$, 91782-21-7; $Ru_3(CO)_{12}$, 15243-33-1; $[Cu(NCCH_3)_4]BF_4$, 15418-29-8; $Ru_3(\mu\text{-dpm})(CO)_{10}$, 64364-79-0; Ag, 7440-22-4; Hg, 7439-97-6; Cu, 7440-50-8; Ru, 7440-18-8.

**Supplementary Material Available:** Listings of structure factor amplitudes, thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates (28 pages). Ordering information is given on any current masthead page.

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# Preparation and Structure of the [2]Ferrocenophane $(\eta^5\text{-}C_5H_4\overline{Fe(CO)Cp)Fe(\eta^5\text{-}C_5H_4}PPh_2)$ and Related Compounds

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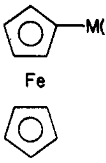
Reaction of (1,1′-ferrocenediyl)phenylphosphine with phenyllithium in diethyl ether at −78 °C followed by treatment of the product mixture with $Fe(CO)_2CpI$ gives a number of compounds including the ferrocenophanes $(\eta^5\text{-}C_5H_4\overline{Fe(CO)Cp)Fe(\eta^5\text{-}C_5H_4}PPh_2)$ (7) and $(\eta^5\text{-}C_5H_4C(O)\overline{Fe(CO)Cp)Fe(\eta^5\text{-}C_5H_4}PPh_2)$ (8). Treatment of an identical solution with $Fe(CO)(PPh_3)CpI$ also gives 7. The reaction of (1,1′-ferrocenediyl)phenylarsine with phenyllithium in a similar manner and subsequent reaction with $Fe(CO)_2CpI$ give primarily $(\eta^5\text{-}C_5H_4Fe(CO)_2Cp)Fe(\eta^5\text{-}C_5H_4AsPh_2)$ (10). A synthetically useful ferrocenyl byproduct, $(\eta^5\text{-}C_5H_4I)Fe(\eta^5\text{-}C_5H_4PPh_2)$ (6), was also isolated during these syntheses. The crystal and molecular structure of 7 has been determined by single-crystal X-ray diffraction analysis. The crystals are triclinic of space group $P\bar{1}$ with $a$ = 10.540 (1) Å, $b$ = 11.507 (2) Å, $c$ = 9.737 (3) Å, $\alpha$ = 100.41 (1)°, $\beta$ = 98.49 (1)°, $\gamma$ = 88.95 (1), $V$ = 1148.6 (5) Å$^3$, and $Z$ = 2. The data were refined to $R$ = 0.030 on the basis of 4765 reflections.

## Introduction

A significant number of sigma bonded ferrocene-transition metal complexes of the type 1 are known,[1-4] for example, Fp–ferrocene 2,[4] which may readily be prepared by reaction of a haloferrocene with NaFp or by reaction of a metalated ferrocene with FpX (X = Cl, I; Fp = $Fe(CO)_2Cp$).



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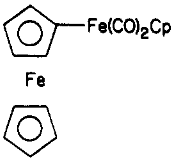

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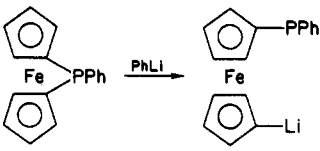
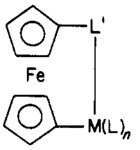
We have recently been concerned with ligand substitution reactions of 2 using acetylenes and phosphines[5] and also with the preparation of unsymmetrically, 1,1′-disubstituted ferrocene compounds such as $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4P\text{-}t\text{-}Bu_2)$ principally for use as ligands in catalysts and catalyst precursors. The ring opening reaction of (1,1′-ferrocenediyl)phenylphosphine[7,9] with phenyllithium discovered by Seyferth and Withers[10,11] has proven to be of great synthetic utility in this work (eq 1).



(1)

3 4

It seemed possible that convergence of these two lines of research could result in the preparation of ferrocenophane compounds such as 5 in which *intramolecular* ligand substitution has occurred. Such compounds would be of interest in view of our previous work and because these would be the first examples of [2]ferrocenophanes with transition metals in the bridge. This paper documents some work in this area utilizing 3 as a key reagent.



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## Experimental Section

All reactions were carried out under an inert atmosphere (Ar or $N_2$) using conventional Schlenk techniques. Phenyllithium was supplied by the Aldrich Chemical Co. as a 1.9 M solution in

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hexane. $Fe(CO)_2CpI$ was prepared from $[Fe(CO)_2Cp]_2$ by the conventional procedure.[12] All solvents were predried and freshly distilled. Mass spectra were recorded on a Kratos MS-50 instrument; only the major peaks are reported with relative intensities given in brackets. $^1H$ NMR spectra were obtained by using Bruker WP-80 and WH-400 spectrometers. Microanalyses were performed by Mr. Peter Borda of this department.

**Reaction of 1′-Lithio-1-(diphenylphosphino)ferrocene with FpI and $Fe(CO)(PPh_3)CpI$.** To a well-stirred diethyl ether solution (ca. 30 mL) of phenyllithium (5 mL, 1.9 M in hexane), maintained at −78 °C by means of a dry ice/acetone bath, was added dropwise (1,1′-ferrocenediyl)phenylphosphine (**3**, 1.18 g, 4.0 mmol) in the minimum quantity of ether required for complete solution. Following the addition, the reaction solution was allowed to warm slowly to approximately 0 °C (ca. 5 min) to allow the formation of **4**. (The solution becomes clear orange, and this reaction may be monitored by TLC (hexane eluant)). The solution was then rechilled (−78 °C) before adding the appropriate transition-metal complex (9.5 mmol). The resulting solution was allowed to warm slowly to room temperature and then stirred for a further 30 min. Following filtration to remove the precipitated lithium iodide and insoluble byproducts, the reaction mixture was examined by TLC (90/10 hexane/diethyl ether) and worked up as described below.

**(i) FpI Reaction.** Following TLC examination, which showed the presence of four colored compounds, the solvent volume of the reaction mixture was reduced under vacuum to ca. 4 mL. The resulting oil was then chromatographed on a neutral alumina (activity grade 1) column, and the fractions were eluted by using progressively polar mixtures of *n*-hexane, diethyl ether, and dichloromethane.[13] Each of the four fractions were collected. The first yellow fraction, eluted with 50/50 hexane/diethyl ether and obtained in low yield, was identified as **6** by comparison with an authentic sample obtained as described below. The second fraction, eluted with 80/20 diethyl ether/hexane as an orange band, gave red needles identified as **7** after solution concentration and crystallization (from hexane) (30% yield based on the ferrocenophane).

**7**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.25–7.75 (br m, 10 H), 4.77 (m, 2 H), 4.42 (m, 7 H), 4.48 (s, 5 H, free Cp), 4.30 (m, 2 H), 4.05 (m, 1 H), 3.88 (m, 1 H); IR ($CDCl_3$) $\nu_{CO}$ 1927 $cm^{-1}$, (cyclohexane) 1917 $cm^{-1}$; mass spectrum, *m/e* 518 ($M^+$, relative intensity 25.89), 419 (34.13), 490 (100.00), 489 (18.50), 488 (52.34), 487 (43.01), 486 (49.46), 410 (16.01), 370 (14.77), 317 (11.41), 304 (58.23), 245 (23.80), 121 (13.32). anal. Calcd for $C_{28}H_{18}Fe_2OP$: C, 64.91; H, 4.44. Found: C, 64.27; H, 4.79.

The third (red/brown) fraction eluted with diethyl ether was identified as $[Fe(CO)_2Cp]_2$ by comparison with an authentic sample. The fourth (yellow) fraction eluted with 50/50 ether/dichloromethane was identified as **8**. **8** was obtained in low (<5%) yield.

**8**: $^1H$ NMR $\delta$ 7.30–7.80 (m, 10 H), 5.15 (m, 1 H), 4.67 (m, 1 H), 4.51 (d, 5 H), 4.38 (m, 2 H), 3.98–4.21 (m, 4 H); IR ($CHCl_3$) $\nu_{CO}$ 1906, 1536 $cm^{-1}$; mass spectrum, *m/e* 546 ($M^+$, 2.08), 518 (30.59), 490 (100.00), 410 (14.51), 370 (27.83), 317 (17.57), 304 (74.94), 259 (7.30), 245 (14.68), 226 (9.67). Anal. Calcd for $C_{29}H_{23}Fe_2PO_2$: C, 63.77; H, 4.24. Found: C, 63.12; H, 4.21.

**(ii) $Fe(CO)(PPh_3)CpI$.** TLC examination showed the presence of two major products. However, only one band that eluted with 40/60 hexane/diethyl ether was isolated on column chromatography. Following solvent removal and crystallization two distinct types of crystals were observed, one yellow and one red. These were easily separated by hand to give compounds **6** and **7**.

**6**: yellow-orange crystals; $^1H$ NMR ($CDCl_3$) $\delta$ 7.12–7.60 (m, 10 H), 4.66 (s, 2 H), 4.20 (t, 4 H), 3.95 (q, 2 H); mass spectrum, *m/e* 496 ($M^+$, 100.00), 369 (93.73), 303 (14.24), 226 (8.03), 183 (22.19), 170 (19.61). Anal. Calcd for $C_{22}H_{18}FeIP$: C, 53.75;, H, 3.65. Found: C, 53.26; H, 3.66.

**Reaction of (1,1′-Ferrocenediyl)phenylarsine with Phenyllithium and $Fe(CO)_2CpI$.** The reaction of the arsenical (1.10 g, 3.77 mmol) was carried out with phenyllithium (4 mL, 1.9 M) using a procedure identical with that in reaction i). FpI (2.5 g, 8.2 mmol) was added to the solution of **4** thus obtained. Following TLC examination two major products were observed: the first was found to be $(Fp)_2$ and the second **10**. The latter was isolated following column chromatography and was crystallized from a 50/50 mixture of hexane/diethyl ether.

Table I. Crystallographic Data[a]

| | |
|---|---|
| formula | $C_{28}H_{23}Fe_2OP$ |
| fw | 518.16 |
| cryst system | triclinic |
| space group | $P\bar{1}$ |
| *a*, Å | 10.540 (2) |
| *b*, Å | 11.507 (2) |
| *c*, Å | 9.737 (3) |
| $\alpha$, deg | 100.41 (1) |
| $\beta$, deg | 98.49 (1) |
| $\gamma$, deg | 88.95 (1) |
| *V*, Å$^3$ | 1148.6 (5) |
| *Z* | 2 |
| $D_{calcd}$, g/cm$^3$ | 1.498 |
| *F*(000) | 532 |
| cryst dimens, mm | 0.25 × 0.30 × 0.45 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 13.49 |
| scan type | $\omega$-2$\theta$ |
| scan speed, deg/min | 0.84-10.06 |
| scan range, deg in $\omega$ | 0.65 + 0.35 tan $\theta$ |
| data collected | $\pm h, \pm k, \pm l$ |
| $2\theta_{max}$, deg | 30 |
| unique reflctns | 6661 |
| reflctions with $I \geqslant 3\sigma(I)$ | 4765 |
| no. of variables | 381 |
| *R* | 0.030 |
| $R_w$ | 0.038 |
| goodness of fit | 1.706 |
| max $\Delta/\sigma$ | 0.56 |
| residual density, e/Å$^3$ | −0.58 + 0.37 (near Fe) |

[a] Temperature 22 °C; Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å); graphite monochromator; takeoff angle 2.7°; aperature (2.0 + tan $\theta$) × 4.0 mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background measurement; $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (*S* = scan count; *B* = normalized background count); function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. [b] Conventional reduced cell.

**10**: $^1H$ NMR $\delta$ 7.20–7.45 (m, 10 H), 4.75 (s, 5 H), 4.21 (t, 2 H), 4.15 (t, 2 H), 3.93 (t, 2 H), 3.74 (t, 2 H); IR ($CHCl_3$) $\nu_{CO}$ 2015, 1957 $cm^{-1}$; mass spectrum, *m/e* 590 ($M^+$) (21.57), 534 (32.74), 490 (7.26), 414 (26.88), 337 (20.86), 305 (46.83), 304 (52.48), 226 (22.26); 198 (44.05), 182 (55.93), 105 (100.00). Anal. Calcd for $C_{29}H_{23}AsFe_2O_2$: C, 59.23; H, 3.94. Found: C, 59.46; H, 4.08.

**X-ray Crystallographic Analysis of 7.** Crystallographic data are given in Table I. The crystal was sealed under an inert atmosphere in a Lindemann glass capillary and mounted in a nonspecific orientation on an Enraf-Nonius CAD4-F diffractometer. Final unit cell parameters were based on careful measurement of 2$\theta$ values for 25 reflections (2$\theta$ = 45–50°) with Mo K$\alpha$ radiation ($\lambda$ = 0.709 30 Å). The intensities of three check reflections measured each hour of X-ray exposure time throughout the data collection showed only small random fluctuations. The data were processed,[14] those reflections having $I \geq 3\sigma(I)$ being employed in the solution and refinement of the structure. Due to irregularity of the crystal surface no absorption correction was applied.

The centrosymmetric space group $P\bar{1}$ was indicated by both the *E* statistics and the Patterson function, from which the coordinates of the Fe and P atoms were determined. The remaining atoms, including hydrogen, were positioned from subsequent difference syntheses. Non-hydrogen atoms were refined with

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[13] The initial eluate contained some PhFp of known properties. Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[14] Computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses by A. Zalking; ORTEP II, illustrations by C. K. Johnson.

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

| atom | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$[a] | atom | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$[a] |
|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 5012 (2) | 38988 (2) | 23260 (3) | 32 | C(25) | 20788 (26) | −841 (22) | −25041 (28) | 62 |
| Fe(2) | 38165 (2) | 32450 (2) | 25463 (3) | 38 | C(26) | 19556 (26) | 7912 (24) | −32982 (27) | 64 |
| P | 24278 (4) | 18078 (4) | 15694 (5) | 34 | C(27) | 19669 (27) | 19521 (24) | −26381 (26) | 62 |
| O | 36816 (18) | 27926 (18) | 53283 (20) | 76 | C(28) | 21392 (22) | 22263 (19) | −11842 (23) | 51 |
| C(1) | 23881 (15) | 44145 (15) | 26469 (19) | 36 | H(2) | 1856 (21) | 4770 (19) | 682 (26) | 49 (6) |
| C(2) | 16731 (19) | 48983 (16) | 15092 (22) | 41 | H(3) | 44 (20) | 5982 (19) | 1378 (22) | 42 (5) |
| C(3) | 6396 (19) | 55919 (16) | 19830 (23) | 46 | H(4) | 134 (24) | 5883 (21) | 4008 (26) | 56 (6) |
| C(4) | 6946 (19) | 55865 (17) | 34460 (23) | 45 | H(5) | 2027 (19) | 4679 (18) | 4771 (22) | 40 (5) |
| C(5) | 17681 (16) | 48730 (16) | 38479 (20) | 39 | H(7) | −144 (20) | 2407 (19) | −234 (23) | 45 (5) |
| C(6) | 7809 (14) | 21577 (14) | 18147 (18) | 32 | H(8) | −1961 (21) | 3331 (19) | 963 (23) | 44 (5) |
| C(7) | −1993 (16) | 25148 (15) | 7791 (19) | 37 | H(9) | −1343 (22) | 3238 (20) | 3597 (24) | 51 (6) |
| C(8) | −12148 (16) | 30208 (17) | 14884 (22) | 44 | H(10) | 848 (21) | 2374 (20) | 4097 (26) | 58 (6) |
| C(9) | −8991 (17) | 29737 (18) | 29358 (23) | 44 | H(11) | 5868 (29) | 4436 (30) | 4291 (35) | 92 (10) |
| C(10) | 3253 (16) | 24413 (16) | 31513 (20) | 38 | H(12) | 6204 (52) | 2304 (47) | 3199 (60) | 192 (21) |
| C(11) | 56301 (22) | 40554 (29) | 31937 (39) | 78 | H(13) | 5129 (28) | 1880 (27) | 632 (33) | 88 (9) |
| C(12) | 57799 (22) | 28572 (30) | 26744 (45) | 84 | H(14) | 4395 (29) | 3788 (31) | 281 (34) | 74 (11) |
| C(13) | 52123 (26) | 26334 (29) | 12760 (41) | 82 | H(15) | 4730 (33) | 5279 (31) | 2109 (39) | 105 (12) |
| C(14) | 47043 (32) | 37030 (37) | 9270 (41) | 82 | H(18) | 4650 (26) | 519 (24) | 2549 (27) | 67 (8) |
| C(15) | 49690 (27) | 45819 (27) | 21383 (42) | 78 | H(19) | 5029 (42) | −1150 (36) | 3185 (45) | 130 (14) |
| C(16) | 36941 (18) | 29630 (18) | 42032 (23) | 47 | H(20) | 3310 (28) | −2454 (27) | 3453 (32) | 87 (9) |
| C(17) | 26948 (18) | 4098 (16) | 22093 (21) | 43 | H(21) | 1189 (25) | −1811 (23) | 2969 (27) | 67 (7) |
| C(18) | 39462 (24) | 234 (25) | 25326 (39) | 78 | H(22) | 780 (22) | 32 (20) | 2166 (24) | 52 (6) |
| C(19) | 41525 (33) | −10541 (29) | 30004 (46) | 99 | H(24) | 2295 (21) | −394 (21) | −508 (25) | 53 (6) |
| C(20) | 31549 (33) | −17214 (24) | 31613 (34) | 81 | H(25) | 2062 (25) | −809 (25) | −2809 (28) | 63 (7) |
| C(21) | 19172 (27) | −13483 (19) | 28534 (28) | 62 | H(26) | 1890 (30) | 655 (30) | −4341 (37) | 99 (10) |
| C(22) | 16882 (21) | −2896 (17) | 23724 (24) | 48 | H(27) | 1909 (29) | 2535 (27) | −3197 (33) | 87 (9) |
| C(23) | 22688 (16) | 13524 (16) | −3520 (20) | 39 | H(28) | 2211 (24) | 3002 (24) | −697 (27) | 66 (7) |
| C(24) | 22376 (21) | 1794 (18) | −10374 (25) | 50 | | | | | |

[a] $U_{eq} = {}^1/_3$ trace $U_{diag}$.

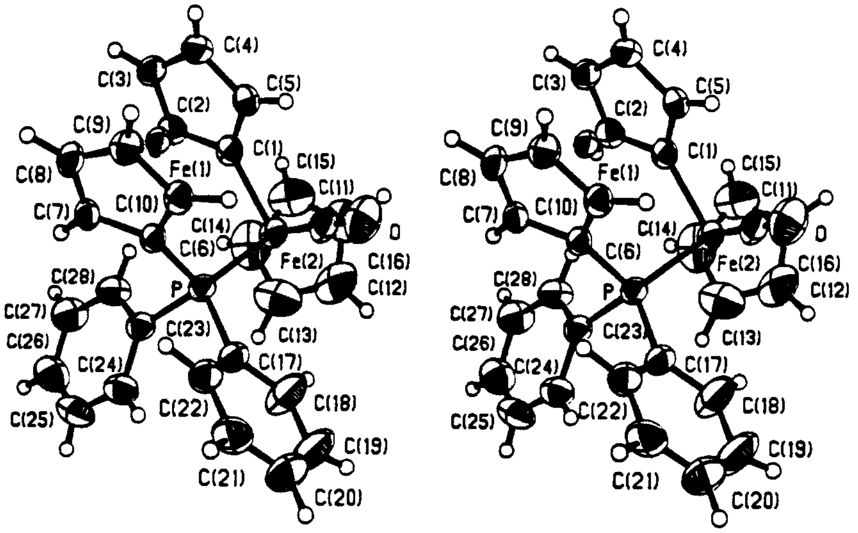

**Figure 1.** Stereoview of 7.

anisotropic thermal parameters and hydrogen atoms with isotropic thermal parameters. Neutral atom scattering factors from ref 15 were used for the non-hydrogen atoms and those of ref 16 for hydrogen atoms. Anaomalous scattering corrections[17] were applied for Fe and P atoms.

Bond distances have been corrected for thermal motion using the TLS approach.[18,19] The root-mean-square (rms) error in the temperature factors, $\Delta U_{ij}$ (derived from the least-squares analysis), is 0.0012 Å$^2$. Analysis of the entire molecule (rms $\Delta U_{ij}$ = 0.0092 Å$^2$) indicated significant independent motion of structural subunits. Six molecular fragments were analyzed: two PPh groups, three $FeC_5$ groups, and Fe(1)Fe(2)(C(1)–C(10))PC(16) (rms $\Delta U_{ij}$ = 0.0007–0.0020 Å$^2$).

Final positional and isotropic thermal parameters are listed in Table II. Bond distances (corrected and uncorrected) and angles involving the nonhydrogen atoms are given in Tables III and Table IV, respectively. Anisotropic thermal parameters, bond lengths and angles involving hydrogen, a complete listing of torsion angles, and measured and calculated structural factors (Tables V–IX) are included as supplementary material.

A stereoview of the molecule is shown in Figure 1.

## Results and Discussion

The documented ring cleavage reaction[10,11] of (1,1′-ferrocenediyl)phenylphosphine was carried out in the presence of excess phenyllithium at −78 °C to give 1′-lithio-1-(diphenylphosphino)ferrocene, 4. Excess phe-

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Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses[a]

| | | | |
|---|---|---|---|
| Fe(1)-C(1) | 2.049 (2) | C(3)-C(4) | 1.418 (3) |
| Fe(1)-C(2) | 2.038 (2) | C(4)-C(5) | 1.435 (3) |
| Fe(1)-C(3) | 2.047 (2) | C(6)-C(7) | 1.442 (2) |
| Fe(1)-C(4) | 2.046 (2) | C(6)-C(10) | 1.434 (3) |
| Fe(1)-C(5) | 2.026 (2) | C(7)-C(8) | 1.418 (3) |
| Fe(1)-C(6) | 2.002 (2) | C(8)-C(9) | 1.410 (3) |
| Fe(1)-C(7) | 2.049 (2) | C(9)-C(10) | 1.422 (3) |
| Fe(1)-C(8) | 2.071 (2) | C(11)-C(12) | 1.395 (4) |
| Fe(1)-C(9) | 2.051 (2) | C(11)-C(15) | 1.381 (5) |
| Fe(1)-C(10) | 2.009 (2) | C(12)-C(13) | 1.384 (5) |
| Fe(2)-P | 2.2116 (5) | C(13)-C(14) | 1.411 (5) |
| Fe(2)-C(1) | 2.002 (2) | C(14)-C(15) | 1.405 (5) |
| Fe(2)-C(11) | 2.102 (2) | C(17)-C(18) | 1.394 (3) |
| Fe(2)-C(12) | 2.099 (2) | C(17)-C(22) | 1.388 (3) |
| Fe(2)-C(13) | 2.092 (3) | C(18)-C(19) | 1.399 (4) |
| Fe(2)-C(14) | 2.096 (3) | C(19)-C(20) | 1.357 (5) |
| Fe(2)-C(15) | 2.105 (2) | C(20)-C(21) | 1.374 (4) |
| Fe(2)-C(16) | 1.725 (2) | C(21)-C(22) | 1.387 (3) |
| P-C(6) | 1.815 (2) | C(23)-C(24) | 1.392 (3) |
| P-C(17) | 1.830 (2) | C(23)-C(28) | 1.394 (3) |
| P-C(23) | 1.833 (2) | C(24)-C(25) | 1.391 (3) |
| O-C(16) | 1.149 (3) | C(25)-C(26) | 1.370 (4) |
| C(1)-C(2) | 1.437 (2) | C(26)-C(27) | 1.373 (4) |
| C(1)-C(5) | 1.436 (3) | C(27)-C(28) | 1.379 (3) |
| C(2)-C(3) | 1.421 (3) | | |

[a] Values are uncorrected.

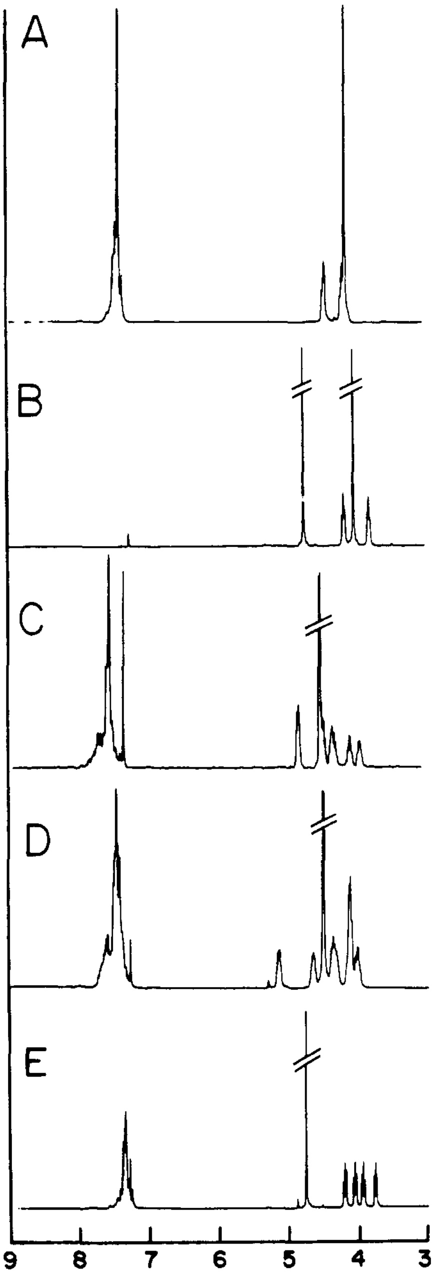
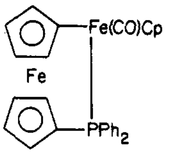


**Figure 2.** The $^1H$ NMR spectra (80 MHz, $CDCl_3$): A, $Ph_2PFc$; B, FpFc 2; C, 7; D, 8; E, 10.



7

nyllithium was used to prevent ring cleavage of 3 by 4.[11] The solution of 4 was treated with dicarbonylcyclopentadienyliron iodide (FpI) principally because of our continuing interest in $\sigma$-bound Fp compounds of ferrocene.[5] After product separation by column chromatography and crystallization, four reaction products were isolated, two of which were present in minor amounts. The major products consisted of the well-known dimer $[Fe(CO)_2Cp]_2$ and a red crystalline compound. The latter was initially assigned the structure 7 on the basis of analytical and spectroscopic results and later confirmed by a crystal structure determination (Figure 1). The $^1H$ NMR of this compound shows the presence of a disubstituted ferrocene derivative that contains a coordinated diphenylphosphine moiety. This spectrum is shown in Figure 2c together with the spectra of (diphenylphosphino)ferrocene and Fp–ferrocene for comparison. At 80 MHz two sharp singlets are observed in the non-ferrocenyl ($\eta^5$-$C_5H_5$) region; however, at 400 MHz only the expected singlet is seen. One $\nu_{CO}$ band is present in the solution ($CHCl_3$) infrared spectrum (1927 $cm^{-1}$), and the mass spectrum shows a strong parent at $m/e$ 518. The monomer 7 would be expected to exhibit some tilting of the ferrocenyl Cp rings to accommodate the coordination of the phosphine to the sigma bound iron center. However, this ring tilt would be

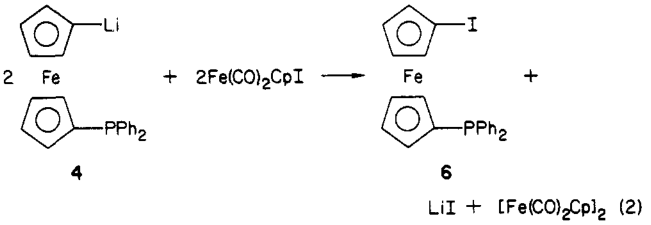
Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

| | | | | | |
|---|---|---|---|---|---|
| P-Fe(2)-C(1) | 90.46 (5) | C(1)-C(5)-C(4) | 110.3 (2) | P-C(17)-C(22) | 122.11 (14) |
| P-Fe(2)-C(16) | 90.59 (7) | P-C(6)-C(7) | 125.80 (13) | C(18)-C(17)-C(22) | 118.6 (2) |
| C(1)-Fe(2)-C(16) | 91.73 (8) | P-C(6)-C(10) | 125.29 (12) | C(17)-C(18)-C(19) | 119.4 (3) |
| Fe(2)-P-C(6) | 114.08 (5) | C(7)-C(6)-C(10) | 106.92 (15) | C(18)-C(19)-C(20) | 121.1 (3) |
| Fe(2)-P-C(17) | 116.00 (6) | C(6)-C(7)-C(8) | 108.0 (2) | C(19)-C(20)-C(21) | 120.1 (2) |
| Fe(2)-P-C(23) | 116.89 (6) | C(7)-C(8)-C(9) | 108.6 (2) | C(20)-C(21)-C(22) | 119.9 (2) |
| C(6)-P-C(17) | 103.23 (8) | C(8)-C(9)-C(10) | 108.4 (2) | C(17)-C(22)-C(21) | 120.9 (2) |
| C(6)-P-C(23) | 101.56 (8) | C(6)-C(10)-C(9) | 108.1 (2) | P-C(23)-C(24) | 123.84 (15) |
| C(17)-P-C(23) | 103.08 (9) | C(12)-C(11)-C(15) | 109.3 (3) | P-C(23)-C(28) | 118.41 (15) |
| Fe(2)-C(1)-C(2) | 127.84 (14) | C(11)-C(12)-C(13) | 107.7 (3) | C(24)-C(23)-C(28) | 117.7 (2) |
| Fe(2)-C(1)-C(5) | 127.57 (13) | C(12)-C(13)-C(14) | 108.0 (3) | C(23)-C(24)-C(25) | 119.9 (2) |
| C(2)-C(1)-C(5) | 104.4 (2) | C(13)-C(14)-C(15) | 107.6 (3) | C(24)-C(25)-C(26) | 121.3 (2) |
| C(1)-C(2)-C(3) | 110.6 (2) | C(11)-C(15)-C(14) | 107.4 (3) | C(25)-C(26)-C(27) | 119.5 (2) |
| C(2)-C(3)-C(4) | 107.6 (2) | Fe(2)-C(16)-O | 176.3 (2) | C(26)-C(27)-C(28) | 119.8 (2) |
| C(3)-C(4)-C(5) | 107.1 (2) | P-C(17)-C(18) | 119.3 (2) | C(23)-C(28)-C(27) | 121.8 (2) |

expected to be considerably less than that observed for [1]ferrocenophanes such as **3**. This is indeed so. The tilt in **3** is 26.7° whereas the tilt in **7** is 8.6°. This probably accounts for the less intense red color of **7** as compared to **3**. Other features of the crystal structure of **7** are as follows. The crystal is made up of discrete molecules separated by normal van der Waals distances. The iron-to-$\eta^5$-Cp distances are 1.635 (2) (Fe(1)–Cp(1)), 1.637 (Fe(1)–Cp(2)), and 1.731 (3) Å (Fe(2)–Cp(3)) where Cp(1), Cp(2), and Cp(3) are the centroids of the cyclopentadienyl rings. The ferrocenyl Cp rings are almost eclipsed (stagger angle C(1)–Cp(1)···Cp(2)–C(16) = −10.3 (2)°). Cp(1)–Fe(1)–Cp(2) is distorted from linearity by 8.3 (1)°. The angles around Fe(2) are respectively 128.8 (1) (P–Fe(2)–Cp(2)), 121.9 (1) (C(1)–Fe(2)–Cp(3)), 123.0 (1) (C(16)–Fe(2)–Cp(3)), and 90.46 (5)° (P–Fe(2)–C(1)).

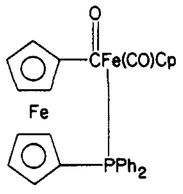
The molecule **7** is the first example of a [2]ferrocenophane with heteroatoms in the bridge and is only the second to have its structure determined, the other being 1,1′-tetramethylethyleneferrocene.[20] In this case the rings are staggered by 9° with the ring tilt being 23° mainly due to the shorter bridge C–C distance of 1.584 (14) Å. The dihedral angle C(1)–Fe(2)–P–C(6) in **7** is 18.32 (8)°; the corresponding angle in the bridge of 1,1′-tetramethylethyleneferrocene is 25°.

The two minor products obtained from the reaction producing **7** were identified as the iodo derivative **6** and the [3]ferrocenophane **8**. The iodo compound **6** can be isolated as a yellow/orange crystalline solid. This presumably results from an exchange reaction of **4** with the transition-metal iodide (eq 2). The analytical and spectroscopic data are in accord with this formulation. The $^1$H NMR spectrum shows a strong solvent dependence of the iodo-substituted ferrocene ring protons.



**6** is potentially a very useful starting material for the synthesis of a number of 1,1′-disubstituted ferrocene compounds, and results in this area will be reported later.

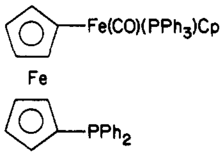
The ferrocenophane **8** has a $^1$H NMR spectrum similar to that of **7** except that a low-field proton resonance in the ferrocenyl ring proton region is observed ($\delta$ 5.15), indicating the presence of a more electronegative substituent on the ferrocenyl ring. The bridging Fe($C_5H_5$) signal is a doublet presumably due to phosphorus coupling. The solution infrared spectrum shows a broad $\nu$(CO) band at 1906 cm$^{-1}$ ($CHCl_3$) with a low-frequency metal acyl CO absorption at 1536 cm$^{-1}$. The acyl stretching frequency for the distorted benzoyl group in Cp(DPPE)FeCOPh has he unusually low value of 1510 cm$^{-1}$.[21] The mass spectrum exhibits a strong parent ion at *m/e* 546. Examples of the insertion (migration) reaction that is necessary to produce **8** are well-known. The insertion of CO into the Fe–C bond in Fp–Ph by addition of $PPh_3$ has been reported by Nesmeyanov;[22] however, under thermal conditions the CO is extruded. In the present case the conditions (low temperature) as well as relief of ring strain probably stabilize the CO inserted product **8**.



**8**

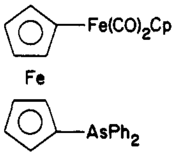
A number of other [3]ferrocenophanes with heteroatoms in the bridge are known[23] including the -S-S-S- bridged compound of known structure.[24] There are also a large number of transition-metal chelate complexes of ligands such as Fe($\eta^5$-$C_5H_4PPh_2$)$_2$ (e.g., (P–P)Mo(CO)$_4$) that are conceptually also [3]ferrocenophanes.[1,6]

The reaction of **4** was next carried out with Fe(CO)($PPh_3$)CpI under conditions identical with those of the previous reaction. This was an attempt to prepare compound **9** on the basis that it would be very unlikely that the remaining CO would be displaced by the incoming phosphine. The major product, however, was found to be **7**, the product previously observed with Fe(CO)$_2$CpI. Apparently the triphenylphosphine is readily replaced in an *intramolecular* substitution process. The iodo derivative **6** is also formed in this reaction (eq 2) as are traces of **8**.



**9**

The work was extended by using the phenylarsine-bridged ferrocenophane (analogue of **3**) as the reaction precursor. In this case the major $\sigma$-metal bound ferrocene derivative isolated was compound **10**. No evidence for a ferrocene analogue of **7** or **8** was obtained. Compound **10** exhibits a particularly interesting proton NMR spectrum in the ferrocenyl region. In essence four triplets are evident (see Figure 2) resulting from the clear separation of the resonances of the four sets of ferrocenyl proton pairs.



**10**

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**Registry No.** **3**, 72954-06-4; **4**, 82311-95-3; **6**, 91798-57-1; **7**, 91798-58-2; **8**, 91841-52-0; **10**, 91798-59-3; $(Fp)_2$, 12154-95-9; FpI, 12078-28-3; $Fe(CO)(PPh_3)CpI$, 12099-18-2; (1,1′-ferrocenediyl)phenylarsine, 72954-08-6; 1-diphenylarsino-1′-lithioferrocene, 91798-60-6.

**Supplementary Material Available:** Tables of final anisotropic thermal parameters, bond angles and lengths involving H atoms, torsion angles and calculated and observed structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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# The X-ray Crystal and Molecular Structure of $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$: A Cationic Complex with an Agostic Metal···H···C Interaction

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The X-ray crystal and molecular structure of the complex $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ has been determined. The crystals are orthorhombic of space group $Pna2_1$ with $a$ = 20.510 (5) Å, $b$ = 12.992 (3) Å, and $c$ = 16.954 (4) Å; $R$ = 0.0478 for 3257 unique reflections. The structure reveals the existence of an agostic Ru···H···C interaction that contains a Ru···H distance of 2.08 (7) Å and a lengthened C–H bond of 1.14 (7) Å. The hydrogen atom occupies the sixth coordination site of a distorted octahedron; the other sites being taken up by the $\eta^3$-enyl portion of the cyclooctenyl ligand and the three phosphorus donor ligands (Ru–P bond distances = 2.350 (2), 2.302 (2), and 2.223 (2) Å.) The shortest Ru–P bond is situated trans to the Ru···H interaction. A discussion of the structure in comparison with analogous structures containing an agostic $\eta^3$-enyl ligand is presented.

## Introduction

We have recently reported[1] the sterically controlled isomerization of the hydrido–diene complexes $[RuH(cod)L_3][PF_6]$ which gave a series of $\eta^3$-enyl cations $[Ru(\eta^3\text{-}C_8H_{13})L_3]^+$ analogous with the species $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$.[2] As with the iron complex, the $^1H$ NMR spectra of the ruthenium compounds all contain a feature characteristic of an agostic M···H–C interaction, viz., an exchange-broadened high field signal due to the two endo hydrogen atoms adjacent to the $\eta^3$-enyl functional group, either of which can interact with the metal at any one time. For the complex $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ (**1**) it was possible to reach the slow-exchange region of this process at −90 °C using a 500-MHz instrument, indicating that the barrier to exchange is higher for this compound than for the other ruthenium compounds studied. We decided to determine the structure of **1** in order to obtain some insight into the factors giving rise to the higher exchange barrier for **1**; e.g., whether it is a function of a stronger M···H–C interaction or of steric repulsions between the bulky $P(OMe)Ph_2$ ligands and the atoms of the cyclooctenyl ligand. Although there are now a number of structural studies of M···H–C interactions,[3] only two are relevant to complex **1**. The structures of $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3][BF_4]$ (**2**)[4] and $[Mn(\eta^3\text{-}C_7H_{11})(CO)_3]$ (**3**)[5] have been thoroughly studied by both X-ray and neutron diffraction methods. In this paper the X-ray structure of **1** is presented and, by comparison with the structures **2** and **3**, an estimate of the structural effect of the Ru···H–C interaction is made.

## Experimental Section

Orange-brown multifacetted crystals suitable for X-ray examination were grown from dichloromethane–ethanol solution. Unit cell dimensions were determined by least-squares fit to the diffracting positions of 25 reflections measured on a Philips PW 1100 four-circle diffractometer. The intensities of 3557 reflections with $3 \le \theta \le 23°$ in the octant $+h,+k,+l$ were measured by using the $\omega$–$2\theta$ scan mode with a scan width of 1.00° in $\omega$ and a scan speed of 0.04° $s^{-1}$. Backgrounds were measured for 12.5 s at each end of the scan. Three reference reflections were measured every 60 min and showed no significant deviations from their mean intensities. No absorption corrections were applied.

**Crystal data:** $C_{47}H_{52}F_6O_3P_4Ru$; $M_r$ = 1003.9; orthorhombic; space group $Pna2_1$; $a$ = 20.510 (5) Å, $b$ = 12.992 (3) Å, $c$ = 16.954 (4) Å, $U$ = 4517.7 Å$^3$, $D_{calcd}$ = 1.476 Mg m$^{-3}$ for $Z$ = 4, $F(000)$ = 2064; Mo K$\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo K$\alpha$) = 0.482 mm$^{-1}$. The structure was solved by Patterson and difference electron density synthesis methods and was refined by using SHELX.[6] The $z$ coordinate of the Ru atom was fixed at 0.25 to define the origin. The H atoms of the cyclooctenyl ligand and the methyl groups were located by using a subsequent difference electron density synthesis and were refined. All other H atoms were added in calculated positions (C–H = 0.95 Å). Isotropic temperature factors were refined for the phenyl C atoms, and anisotropic temperature factors were refined for all other non-H atoms. Five common isotropic temperature factors were refined for the H atoms. Least-squares refinement using a weighting scheme $w = 1/\sigma^2(F_o)$ and with the matrix blocked so that in each group of three cycles Ru refined in cycles 1 and 2, the atoms of the ligands containing P(1) or P(2) refined in cycle 1, the atoms of the ligand containing

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