Journal of Organometallic Chemistry, 320 (1987) 339–348
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND STUDY OF CYCLIC POLYNUCLEAR FERROCENES DERIVED FROM $(C_6H_5)_2PCH_2CH_2Si(CH_3)_2C_5H_4Li$ AS A BRIDGING LIGAND

SAVITHRI R. IYER *, DAVID R. TUETING and NEIL E. SCHORE **
Department of Chemistry, University of California, Davis, Davis, CA 95616 (U.S.A.)

(Received June 19th, 1986)

Summary

The synthesis of the potential bridging ligand $(C_6H_5)_2PCH_2CH_2Si(CH_3)_2C_5H_4$ (**3**) is described. The ferrocene (**6**) derived from **3** has been found to form macrocyclic complexes with metal fragments $NiCl_2$, $NiBr_2$, and $Co_2(CO)_6$. Although monomeric, bimetallic products might have been expected based upon the reduced steric demands of ligand **3** relative to an analogous ligand, $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_4$ (**1**), it appears that the increased flexibility in **3** is the overriding factor leading to a preference for inter- rather than intramolecular coordination of the second phosphine function in **6**.

Introduction

It has been recently shown in our laboratories that the suitability of any individual heterodifunctional ligand for construction of complexes displaying specific spatial relationships between two metal centers is a sensitive function of the ligand structure. Ligand **1**, as incorporated into ferrocene **2**, is revealed to be an excellent building block for macrocyclic, polynuclear systems. However, its application in the construction of simple monomeric cyclic complexes is quite limited due to severe steric interactions that inhibit complexation to a single metal atom in even a relatively unhindered ligand environment. Based on the examination of models, we inferred that a ligand potentially better suited to the latter purpose would be the two methylene analogue of **1**, ligand **3** [1].

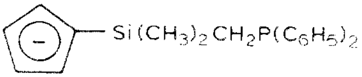
We have carried out a study of metallocenes derived from ligand **3** in our laboratories and will here describe results indicating that their chemistry is considerably less complex than that of ferrocene **2**. Models indicate much greater flexibility

---

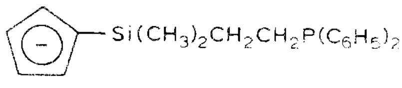
* Formerly Savithri Sundar.

** Camille and Henry Dreyfus Teacher-Scholar, 1981–86.

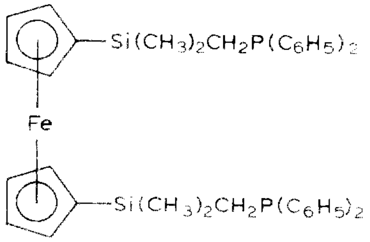
0022-328X/87/$03.50



(1)



(3)



(2)

in bimetallic complexes of **3** relative to **1**, with a very wide range of metal–metal distances available due to the greater conformational mobility of the system.

In addition, the synthesis of **1** required the preparation and isolation of the diphenylphosphinomethyllithium-TMEDA reagent, a procedure best carried out in a dry box. The purity of the final product was highly dependent on the complete removal of non-ionic impurities at various stages in the synthesis. The synthesis of ligand **3** described here avoids these difficulties and is well suited for large scale preparation. The following section outlines the preparation of [dimethyl(2-diphenylphosphinoethyl)silyl]cyclopentadienyllithium (**3**), an isolable cyclopentadienide salt possessing a free, remote phosphine [2].

Results and discussion

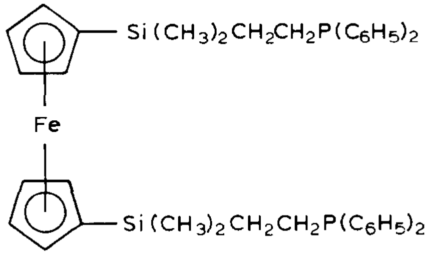
Ligand synthesis

Reaction between diphenylphosphine and chlorodimethylvinylsilane is readily carried out under photochemical conditions [3] at 25 °C in benzene solution. In the proton NMR, the product **4** shows a multiplet at δ 0.90 ppm due to the methylene attached to silicon, and another at δ 2.16 ppm, assigned to the methylene attached to phosphorus. The silane is isolated as a colorless oil in > 80% yield, is stable indefinitely at room temperature under nitrogen, and can be distilled at reduced pressure if necessary.

Reaction of **4** with sodium cyclopentadienide is instantaneous at 0 °C in THF resulting essentially in a single product in > 85% yield, dimethyl(2-diphenylphosphinoethyl)silylcyclopentadiene (**5**). This neutral silylcyclopentadiene shows no tendency to dimerize either neat or in hydrocarbon solvent.

Dropwise addition of n-BuLi to a very dilute solution of **5** in n-hexane at 0 °C initially gives a milky suspension which, after further addition gives rise to a yellow solution with the precipitation of cyclopentadienide **3** as a pale yellow to pure white air and water sensitive solid. This material is insoluble in hydrocarbon solvents, soluble in tetrahydrofuran and slightly soluble in ethyl ether. It is readily characterized spectroscopically as well as chemically; in particular, the anion reacts readily with metal halides in appropriate solvents to give rise to the corresponding metallocene systems.

Ferrocene complex (6)



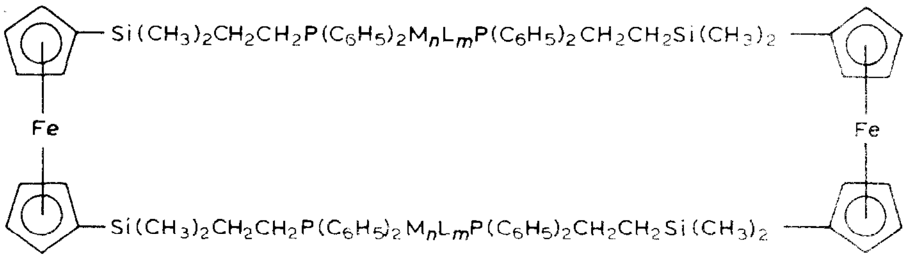
(**6**)

Direct reaction of anhydrous $FeCl_2$ with **3** in ether affords good yields of ferrocene **6** after vigorous stirring of the heterogeneous mixture for several days, followed by filtration and removal of solvent. The crude product, a brown oil, exhibits NMR absorptions that are not only broadened but shifted in position relative to the purified ferrocene itself. This perhaps indicates complexation of the free phosphine moieties with unreacted $FeCl_2$. Purification of **6** is effected by chromatography on alumina I with benzene, giving rise to an oil which slowly crystallizes upon standing under nitrogen. The orange crystalline solid melts at 89–91°C. The purified ferrocene is air stable both in the absence of solvent and in solution and exhibits NMR and electronic spectral characteristics consistent with normal, unperturbed ferrocene and tertiary phosphine functionalities. As expected, no evidence of interaction between the metallocene portion of the molecule and the phosphines is obtained.

Ferrocene-nickel(II) chloride complex (7)

The chloride **7** is prepared as a brick red solid in high yield by reaction between **6** and hydrated nickel(II) chloride. It is soluble in ethers as well as halogenated and aromatic solvents and exists in only one solid form, unlike the analogous complex of ferrocene **2** ($\mathbf{2} \cdot NiCl_2$), which has two distinct solid-state isomers, a 'benzene-soluble' and a 'benzene-insoluble' form [1]. Somewhat surprisingly, a molecular weight determination in benzene reveals **7** to be dimeric (monomer calc, 855; found, 1622), in contrast to the predominantly monomeric $\mathbf{2} \cdot NiCl_2$. Although the steric congestion associated with forming a cyclic monomeric binuclear complex is undoubtedly reduced in going from **2** to **6**, the additional degrees of conformational freedom in the latter clearly mitigate against intramolecular (vs. intermolecular) complexation of the second phosphine unit to a single Ni^{II} center.

Magnetic susceptibility measurements indicate that **7** exists as an equilibrium mixture of diamagnetic square-planar and paramagnetic tetrahedral isomers, both forms being present in nearly equal proportions (Table 1). Thus it contrasts with $\mathbf{2} \cdot NiCl_2$ which has been shown to exist predominantly in a diamagnetic square planar form. This is not unexpected on the basis of a similar observation reported in



(**7**, M_nL_m = $NiCl_2$;
8, M_nL_m = $NiBr_2$;
9, M_nL_m = $Co_2(CO)_6$)

dpe and dpp complexes of Ni^{II} [4] which showed the dpe complexes to be entirely diamagnetic in solution while the more flexible dpp complexes existed as equilibrium mixtures of the two forms. The electronic spectrum of **7** displays a more intense absorption at 840 nm that does **2**·$NiCl_2$ (Table 2) confirming the greater proportion of the tetrahedral form in the equilibrium mixture of **7**. Finally, far IR data provides evidence for the presence of tetrahedral and, specifically, *trans* square planar isomers at Ni (Table 3).

At −45°C two signals of unequal intensity, separated by 1 ppm, appear in ^{31}P NMR. Warming the solution induces coalescence of these peaks near −40°C followed by further broadening such that the only signal visible at 0°C is a very small one due to the free ligand. By analogy with **2**·$NiCl_2$ we suspect that the −45°C spectrum reflects the presence of two *trans* planar complexes differing in ligand conformation, while the behavior at higher temperature is consistent with the onset of a square planar ⇄ tetrahedral equilibrium. The absence of *cis* coordination is confirmed by the lack of an appropriate absorption in the low temperature spectrum [5] (Table 4).

The temperature dependencies of the PMR spectra of this complex reveal the expected changes. At room temperature and above signals averaged over the square planar and tetrahedral isomers are seen. At higher temperatures the equilibrating

TABLE 1

MAGNETIC SUSCEPTIBILITY DATA[a]

Compound	μ_{eff} (μ_B)	N_t[b]
2·$NiCl_2$	1.36	0.18
6·$NiCl_2$ (**7**)	2.37	0.55
2·$NiBr_2$	1.93	0.36
6·$NiBr_2$ (**8**)	2.74	0.74

[a] In benzene at 20°C using the method of Evans: D.F. Evans, J. Chem. Soc., (1959) 2003. [b] Fraction of the paramagnetic isomer in solution: L.H. Pignolet, W.D. Horrocks, Jr. and R.H. Holm, J. Am. Chem. Soc., 92 (1970) 1855, and G.N. La Mar and E.O. Sherman, J. Am. Chem. Soc., 92 (1970) 2691.

TABLE 2

UV/VISIBLE SPECTRAL DATA[a]

Compound	λ_{max}, nm (log ϵ)
$Fe(C_5H_4SiMe_2CH_2PPh_2)_2$ (**2**)	254 (4.35), 277 (sh, 4.03), 339 (sh, 2.48), 437 (2.31)
$Fe(C_5H_4SiMe_2CH_2CH_2PPh_2)_2$ (**6**)	254 (5.28), 263 (sh, 5.21), 330 (sh, 2.36), 450 (2.17)
2·$Mo(CO)_4$	248 (4.62), 337 (sh, 3.56), 3.70 (sh, 3.36), 450 (sh, 2.36)
2·$NiCl_2$	252 (sh, 4.41), 382 (4.17), 482 (2.77), 839 (1.29)
6·$NiCl_2$ (**7**)	253 (sh, 4.37), 502 (2.94), 840 (2.02)
2·$NiBr_2$	248 (sh, 4.43), 317 (sh, 3.72), 408 (3.92), 507 (2.67), 854 (1.80)
6·$NiBr_2$ (**8**)	334 (sh, 3.65), 404 (3.86), 560 (2.85), 860 (2.23)
2·$Co_2(CO)_6$	255 (4.66), 277 (4.35), 388 (4.54), 450 (sh, 3.72)
6·$Co_2(CO)_6$ (**9**)	255 (2.63), 276 (2.44), 386 (4.64)

[a] Spectra were recorded in CH_2Cl_2 at 25°C; only the most intense band in 245–265 nm region is listed.

mixture shows three broads signals at about δ 6.3, 7.1, and 8.5 ppm for the *para*, *ortho*, and *meta* protons on the phenyl rings, respectively. At −64°C the only signals that are observable are due entirely to the square planar form (δ 7–8 ppm). The proportion of tetrahedral isomer present in solution diminishes so rapidly with cooling that no unequivocal identification of any of its NMR signals has been possible. However, it is reasonably clear that **7** exists as a simple dimeric complex undergoing square planar $\rightleftarrows$ tetrahedral interconversion at ambient temperature in solution. The proton spectra of **2**·$NiCl_2$ are much more complex, revealing the presence of four different species, two monomers, at least one dimer, and perhaps other oligomeric forms (Table 5).

*Ferrocene-nickel(II) bromide complex (**8**)*

The nickel bromide complex has been prepared as dark green powder by the reaction between hydrated nickel bromide and ferrocene **6** in n-butanol in > 85% yield. As is the case with **7**, **8** analyzes as a dimer in benzene.

Magnetic susceptibility measurements indicate that **8** exists predominantly in the tetrahedral form with $\mu_{eff} = 2.74$ μ_B. This value is somewhat larger than that of the corresponding chloro compound and much larger than that of analogous ferrocene-$NiBr_2$ complex **2**·$NiBr_2$ which has been shown to exist predominantly in square-planar form [1]. For **8**, the equilibrium mixture contains nearly 75% of tetrahedral isomer. The trend in N_t values of the various ferrocene-Ni^{II} halides we have prepared is consistent with that observed by others, e.g. for $Ni[Ar_2RP]_2X_2$ [6] and

TABLE 3

FAR-INFRARED DATA[a]

Compound	Wavenumber (cm^{-1})
2·$NiCl_2$	407 [b], 354 [c], 339 [c], 302 [c], 260 [b]
6·$NiCl_2$ (**7**)	400 [b], 330 [c], 295 [c]
2·$NiBr_2$	320 [b], 261 [b,c], 229 [c]
6·$NiBr_2$ (**8**)	290 [b], 260 [b,c], 220 [c]

[a] Spectra were recorded in mineral oil mulls at 25°C. [b] Assigned to Ni–X stretch of *trans* isomer. [c] Assigned to Ni–X stretch of tetrahedral isomer.

for other phosphine-Ni^{II} complexes [4,7]. Evidence for the increased proportion of the tetrahedral form is further provided by electronic and far IR spectral data, which again show the presence of only tetrahedral and *trans* square planar isomers at nickel.

The variations in the ^1H NMR spectra with temperature parallel those of the corresponding $NiCl_2$ complex **7**, the high temperature measurements giving signals for the phenyl protons averaged over both the forms, but more strongly shifted from the diamagnetic region. As the temperature is lowered only the signals of the planar form remain (δ 6.5–8.5) in the NMR spectrum. As before, at −64°C in the completely frozen out spectra signals due to paramagnetic isomer are not visible, indicating not only the predominance of square planar form in the equilibrium mixture, but also the extremely slow planar $\rightleftarrows$ tetrahedral interconversion at low temperatures. Thus **8** exists as a single solid state dimer undergoing square planar $\rightleftarrows$ tetrahedral interconversion at ambient temperatures, again, in contrast to the more complex behavior of the analogous complex of ferrocene **2**.

Ferrocene-cobalt carbonyl complex (9)

Complex **9** can be prepared as a brown solid in > 90% yield by reaction between **6** and $Co_2(CO)_8$ in benzene at room temperature. A small amount of benzene insoluble residue obtained during the preparation of **9** does not give any carbonyl absorption in the IR. The IR of **9** in THF displays major carbonyl bands at 1965sh and 1942vs cm^{-1} characteristic of the presence of the bis(phosphine)hexacarbonyldicobalt structural unit [8]. IR data are consistent with local D_{3d} symmetry with no appreciable quantity of bridged isomer. The NMR of **9** in C_6D_6 displays a broadened multiplet in the phenyl region indicating the complexation of the phosphine sites to the metal center. ^{31}P NMR gives an absorption at −66.3 ppm, representing a substantial downfield shift of the signal upon coordination of the free ferrocene phosphines to the cobalt centers. The UV spectrum of **9** in CH_2Cl_2 shows an intense absorption at 386 nm, typical of the absorption bands observed in related complexes [9]. Complex **9** is dimeric.

Reduction of a THF solution of **9** has been carried out. Reaction of **9** with an equivalent amount of KH in THF [10] gives rise to an olive green solution with major IR bands at 1840vs, 1880br, and 1920s cm^{-1}. Addition of bis(triphenylphosphine) iminium chloride precipitates KCl and produces a yellow solution exhibiting IR bands consistent with the presence of the corresponding cobaltate species, $Fe[C_5H_4Si(CH_3)_2CH_2CH_2P(C_6H_5)_2Co(CO)_3^-]_2\ 2PPN^+$, contaminated with a small amount of $Co(CO)_4^-$: IR (THF) 1835vs, 1880s, and 1921s cm^{-1}. These data are nearly identical with those for $Co(CO)_3P(C_6H_5)_3^-\ PPN^+$ as well as for the corresponding analogue derived from **2**. Attempts to isolate this substance in pure form were unsuccessful due to a tendency to separate from solution as a strongly solvent-occluding oil.

Conclusions

Ferrocene complex **6**, containing the potential bridging ligand $C_5H_4SiMe_2$-$CH_2CH_2PPh_2$ (**3**), is a readily prepared metallocene-based bis-phosphine which is capable of complexation to a variety of other transition metal fragments. The products obtained are easily characterized, readily purified homogeneous materials with considerably simpler spectroscopic properties than analogous complexes of ferrocene **2**, containing the smaller ligand system $C_5H_4SiMe_2CH_2PPh_2$. Remarkably, however, every 'bimetallic' system prepared in this study has been found to be dimeric, including complexes of the relatively unhindered NiX_2 fragments for which the corresponding complexes with **2** were found to be mostly monomers. As these preparations have generally been carried out under moderately dilute (ca. 10^{-2} *M*) conditions (more dilute than for **2**), it is clear that ligand **6** will not provide a convenient entry towards simple bimetallic monomers, although with modification of reaction solvents and conditions these might ultimately become available. Nevertheless, as ferrocene **6** was intended to serve only as a model system for the construction of bimetallics containing metallocenes based on other metals besides iron, we have pursued the use of ligand **3** in this latter capacity. The results of the first of these studies are presented in the accompanying paper.

Experimental

All preparations were carried out under an atmosphere of N_2 by using either standard Schlenk techniques or a Vacuum Atmospheres Drilab. Suitable solvents were rendered water and oxygen free by distillation from sodium benzophenone ketyl or dianion. Halogenated solvents were dried over 3Å molecular sieves and degassed before use. Diphenylphosphine and dicobalt octacarbonyl were obtained from Pressure Chemical Corporation and used as received. Chlorodimethylvinylsilane was obtained from SiLar Laboratories and purged with Argon before use. All other organic reagents were distilled under N_2 and degassed before use. Solid inorganic reagents were obtained from Alfa/Ventron and transferred into the dry box after being held at high vacuum for at least 12 h. Spectroscopic measurements utilized the following instrumentation: UV/visible, Cary 17; IR/far, Beckman IR-8, Perkin-Elmer 180; ^1H NMR, Varian A60-A; EM-390, Nicolet NT-360, ^{31}P NMR, Nicolet NT-200 (at 81 MHz). Proton chemical shifts are quoted in ppm downfield from tetramethylsilane. The NMR coupling constants are expressed in Hz. Elemental analyses and molecular weight determinations were carried out by the Galbraith Microanalytical Laboratory or the U.C. Berkeley Microanalytical Laboratory.

TABLE 4

PROTON-DECOUPLED ^{31}P NMR DATA

Compound	^{31}P	$\Delta\delta$ (Coordination)
$Fe(C_5H_4SiMe_2CH_2PPh_2)_2$ (**2**)	−30.4	
$Fe(C_5H_4SiMe_2CH_2CH_2PPh_2)_2$ (**6**)	−9.1	
2·$NiCl_2$	−6.4 (−60°C)	+24.0
6·$NiCl_2$ (**7**)	−27.3 (−45°C)	−18.3
2·$NiBr_2$	+2.4 (−60°C)	+32.8
6·$NiBr_2$ (**8**)	+15.1 (−60°C)	+24.2
2·$Co_2(CO)_6$	+46.3	+76.7
6·$Co_2(CO)_6$ (**9**)	+66.3	+75.3

TABLE 5

PROTON NMR DATA[a] δ (ppm) (m, J (Hz))

Compound	Solvent	C_5H_4	$SiMe_2$	$SiCH_2$	CH_2P	PPh_2
$ClSiMe_2CH_2PPh_2$	C_6D_6		0.42(d, 0.95)	1.82(br s)		7.2–7.9(m)
$ClSiMe_2CH_2CH_2$-PPh_2 (**4**)	C_6D_6		0.10(s)	0.86(m)	2.11(m)	6.9–7.5(m)
	$CDCl_3$		0.33(s)	0.80(m)	2.00(m)	7.2–7.5(m)
$LiC_5H_4SiMe_2CH_2$-PPh_2 (**1**)	THF-d_8	5.97(m)	0.20(d, 0.7)	1.55(d, 2.3)		7.1–7.7(m)
$LiC_5H_4SiMe_2CH_2$-CH_2PPh_2 (**3**)	THF-d_8	5.93(br s)	0.13(s)	0.80(m)	2.00(m)	7.1–7.6(m)
$Fe(C_5H_4SiMe_2CH_2$-$PPh_2)_2$ (**2**)	C_6D_6	4.12('t', 1.8) 4.32('t', 1.7)	0.34(d, 0.9)	1.66(d, 0.6)		7.08–7.34(m)
$Fe(C_5H_4SiMe_2CH_2$-$CH_2PPh_2)_2$ (**6**)	C_6D_6	3.90('t', 1.7) 4.13('t', 1.7)	0.20(s)	0.92(m)	2.13(m)	7.03–7.72(m)
2·$NiCl_2$ [b]	$CDCl_3$	3.88, 3.90 3.95, 4.04 4.15, 4.17 4.19, 4.26	0.62 0.69 0.73 0.79(s)	unobserved		See Ref. 1
6·$NiCl_2$ [b] (**7**)	$CDCl_3$	4.15, 4.30 (br s)	0.25(s)	0.85(m)	1.25(m)	8.25, 7.15 6.48(br s)
2·$NiBr_2$ [b]	$CDCl_3$	3.95(br s) 4.18(br s) 4.05(br s) 4.29(br s)	1.04(br s)	unobserved		−3.9, 2.6 4.6, 5.5, 9.4, 12.3 (br s)
6·$NiBr_2$ [b] (**8**)	$CDCl_3$	4.20, 4.33(br s)	0.35(s)	0.89(m)	1.28(m)	9.55, 5.98 4.88(br s)
2·$Co_2(CO)_6$	C_6D_6	4.00(br s), 4.20(br s)	0.60(br s)	2.30(br d, 12)		7.10(br m) 7.80(br m)
6·$Co_2(CO)_6$ (**9**)	C_6D_6	4.00(br s), 4.25(br s)	0.15(s)	0.6–1.5(m)	2.2–3.0(m)	7.35(br m) 7.48(br m)

[a] All spectra were recorded at 60 or 90 MHz and ambient temp. unless otherwise indicated. Chemical shifts are given in δ followed by multiplicity and J values in parentheses. "t" = apparent triplet, followed by peak to peak splitting. [b] Spectra were recorded at 360 MHz at ambient temperature.

Chlorodimethyl(2-diphenylphosphinoethyl)silane (4)

A quartz tube was charged with 6.32 g (50.6 mmol, 20% excess) of chlorodimethylvinylsilane, 7.84 g (42.2 mmol) of diphenylphosphine and 25 ml dry benzene. The tube was stoppered and agitated until a clear, colorless, homogeneous solution was obtained. Irradiation (450W Hanovia medium-pressure lamp) was carried out at 27°C for 120 h. In vacuo removal of solvent and excess silane resulted in a white, cloudy semisolid. The gel was extracted with 3 × 20 ml 4/1 n-hexane/ethyl ether. The extracts were filtered, combined, cooled to −30°C and the supernatant collected. After solvent removal, a colorless oil weighing 10.5 g (34.2 mmol, 81%) was obtained, in all respects identical with that prepared by Stobart, et al. [3d]. The silane was used without further purification. ^1H NMR (CDCl)$_3$: δ 0.33 (s, 6H), 0.60–0.95 (m, 2H), 1.90–2.15 (m, 2H), 7.20–7.50 (m, 10H). ^1H NMR (C_6D_6): δ 0.10 (s, 6H), 0.80–0.92 (m, 2H), 2.07–2.16 (m, 2H), 6.95–7.10 (m, 4H), 7.40–7.50 (m, 6H). B.p. 145–150°C/10^{-2} mmHg. Anal. found: C, 61.27; H, 6.81. $C_{16}H_{20}ClPSi$ calc: C, 62.63; H, 6.57%.

[Dimethyl(2-diphenylphosphinoethyl)silyl]cyclopentadiene (5)

A Schlenk vessel was charged with 18.9 g (60.0 mmol) of $ClSi(CH_3)_2CH_2CH_2P(C_6H_5)_2$ and 70 ml THF. The clear, colorless solution was cooled to 0°C. Dropwise addition of 5.62 g (64.0 mmol) $Na(C_5H_5)$ in 70 ml THF, warming to 27°C and stirring for 3 h resulted in a cloudy solution. Solvent removal in vacuo yielded a yellow oil. The oil was extracted with 3 × 40 ml n-hexane, the extracts filtered and the filtrate concentrated to obtain 18.2 g (52.8 mmol, 88%) of a bright yellow oil. The oil was used without further purification. Isomeric mixtures of substituted cyclopentadienes were obtained. The isomers were not separated. ^1H NMR ($CDCl_3$): δ −0.05 (s, 6H), 0.50–0.73 (m, 2H), 1.90–2.20 (m, 2H), 6.42–6.80 (br m, 5H), 7.20–7.80 (m, 10H).

[[Dimethyl(2-diphenylphosphinoethyl)silyl]cyclopentadienyl]lithium (3)

A Schlenk vessel was charged with 5.28 g (15.5 mmol) of $(C_5H_5Si(CH_3)_2CH_2CH_2P(C_6H_5)_2)$ and 150 ml n-hexane. To the clear, colorless solution was added dropwise 6.15 ml of 2.6 *M* n-butyllithium (16.0 mmol) at 27°C. The mixture immediately became cloudy and pale yellow solid precipitated from solution. The mixture was stirred an additional 2 h and the solvent removed in vacuo to obtain a yellow solid. The solid was stirred with 75 ml n-hexane, filtered, rinsed with n-hexane (2 × 15 ml), ethyl ether (2 × 10 ml) and dried in vacuo. A pure white powder was isolated in a yield of 4.00 g (11.6 mmol, 75%). ^1H NMR (THF-d_8): δ 0.13 (s, 6H), 0.80 (m, 2H), 2.00 (m, 2H), 5.93 (br s, 4H), 7.10–7.60 (m, 10H).

1,1′-Bis[dimethyl(2-diphenylphosphinoethyl)silyl]ferrocene (6)

A suspension of 0.92 g (7.3 mmol) of anhydrous iron(II) chloride in 10 ml of ether was treated with a solution of 5.0 g (14.56 mmol) of **3** in 50 ml of ether and the mixture stirred at 27°C under N_2 for two days. Insoluble material was removed by filtration and warmed with 4 × 10 ml of ether. The combined filtrates were reduced to a brown oil at high vacuum. This oil was chromatographed (alumina I/benzene) yielding an orange red oil which solidified after storage for a week under N_2. Yield 1.6 g, 76%; m.p. 89–91°C. NMR (C_6D_6): δ 0.20 (s, 12H, CH_3Si), 0.92 (m, 4H, CH_2Si), 2.13 (m, 4H, CH_2P), 3.90 and 4.13 (apparent triplets, splittings = 1.7 Hz, 4H ea., Cp), 7.03–7.30 (m, 12H, *m*- and *p*-Ph), 7.35–7.72 (m, 8H, *o*-Ph). Anal. found: C, 69.61; H, 6.76; P, 8.33. $C_{42}H_{48}P_2Si_2Fe$ calc: C, 69.41; H, 6.66; P, 8.52%.

$Fe[C_5H_4Si(CH_3)_2CH_2CH_2P(C_6H_5)_2]_2NiCl_2$ (7)

A solution of 0.18 g (0.79 mmol) of nickel(II) chloride hexahydrate in 50 ml of absolute, N_2-purged ethanol was heated to reflux under N_2, treated dropwise with a solution of 0.57 g (0.79 mmol) of **6** in 80 ml of ethanol, and refluxed for an additional 30 min. The cooled reaction mixture was taken to dryness under vacuum and the residue washed with several small portions of petroleum ether to remove unreacted **6**. The resultant dark red powder (0.42 g, 0.5 mmol, 64%) had a melting point of 100–101°C.

Far-IR (mineral oil mull): 405, 350, 315, 260, 235 cm^{-1} UV/VIS/IR (CH_2Cl_2): $\lambda_{max}(\log \epsilon)$ 840 (2.02), 502 (2.94), 376 (4.22), 352 (sh) (4.37). Anal. found: C, 58.42; H, 5.49, 6.08; Cl, 8.20. $C_{42}H_{41}P_2Si_2FeNiCl_2$ calc: C, 58.91; H, 5.60; Cl, 8.29%. Molecular weight (osmometric, benzene), calc (monomeric): 855. Found: 1622.

$Fe[C_5H_4Si(CH_3)_2CH_2CH_2P(C_6H_5)_2]NiBr_2$ (8)

A solution of 0.068 g (0.2 mmol) of nickel(II) bromide trihydrate in 10 ml of N_2-purged n-butanol was heated under N_2, treated with 0.16 g (0.2 mmol) of **6** in 10 ml of n-butanol, and heated for an addition 30 min. A green solid soon separated out which was washed with several small portions of n-hexane. Yield 0.16 g (0.17 mmol), 86%. The solid had a m.p. of 132–133°C.

Far-IR (mineral oil mull): 480, 440, 290, 260, 220 cm^{-1} UV/VIS/IR (CH_2Cl_2): $\lambda_{max}(\log \epsilon)$ 860 (2.23), 560 (2.85), 404 (3.86), 334 (sh) (3.65) nm. Anal. found: C, 52.65; H, 5.26; Br, 16.16. $C_{42}H_{48}Br_2P_2Si_2FeNi$ calc: C, 53.39; H, 5.09; Br, 16.93%. Molecular weight (osmometric, benzene), calc (monomeric): 944. Found: 1720.

$Fe[C_5H_4Si(CH_3)_2CH_2CH_2P(C_6H_5)_2]_2Co_2(CO)_6$ (9)

A filtered solution of 0.23 g (0.66 mmol) of octacarbonyldicobalt in 40 ml of benzene was treated dropwise with a solution of 0.47 g (0.65 mmol) of **6** in 50 ml of benzene under nitrogen. The solution was stirred for 1 d at room temperature. The solution was filtered and solvent removed in vacuo, leaving a red-brown solid. This solid was redissolved in minimum amount of benzene, and the solution treated with twice its volume of petroleum ether. A brown solid was collected: 0.58 g (0.57 mmol), 90% yield. NMR (C_6D_6): δ 0.15 (s, 12H), 0.6–1.5 (m, 4H), 2.2–3.0 (m, 4H), 4.0 and 4.25 (br s, 8H), 7.0–8.1 (m, 20H) ppm. IR (THF): 1942vs, 1965sh cm^{-1}. UV/VIS (CH_2Cl_2): 386 (4.64), 276 (2.44), 255 (2.64) nm. Anal. Found: C, 56.69; H, 5.02. $C_{48}H_{48}P_2Si_2FeCo_2O_6$ calc: C, 56.93; H, 4.74%. Molecular weight (osmometric, benzene), calc (monomeric): 1011. Found: 2064.

Acknowledgments

Acknowledgment is made to the Committee on Research for the University of California, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Camille and Henry Dreyfus Foundation, for the support of this research.

References

1 N.E. Schore, L.S. Benner and B.E. La Belle, Inorg. Chem., 20 (1981) 3200

2 N.E. Schore and S. Sundar, J. Organomet. Chem., 184 (1980) C44.

3 (a) H. Niebergall, Makromol. Chem. 52 (1962) 218; (b) C.H. Barnes and M.P. David, J. Org. Chem., 25 (1960) 1191; (c) J. Cerobe and U. Moller, J. Organomet. Chem., 17 (1969) 263 and 31 (1971) 157; (d) R.D. Holmes-Smith, R.D. Osei and S.R. Stobart, J. Chem. Soc. Perkin Trans. I, (1983) 861

4 G.R. Van Hecke and W.D. Horrocks, Jr., Inorg. Chem., 5 (1966) 1968.

5 Cf. R.A. Palmer, H.F. Giles, Jr. and D.R. Whitcomb, J. Chem. Soc., Dalton Trans., (1978) 1671.

6 (a) C.R.C. Coussmaker, M.H. Hutchinson, J.R. Mellor, L.E. Sutton and L.M. Venanzi, J. Chem. Soc., (1961) 2705; (b) M.C. Browning, J.R. Mellor, D.J. Morgan, S.A.J. Pratt, L.E. Sutton and L.M. Venanzi, ibid., (1962) 693; (c) R.G. Hayter and F.S. Humiec, Inorg. Chem., 4 (1965) 1701.

7 D.W. Allen, I.T. Millar, F.G. Mann, R.M. Canadine and J. Walker, J. Chem. Soc., A (1969) 1097.

8 (a) O. Vohler, Chem. Ber., 91 (1958) 1235; (b) J.A. McCleverty, A. Davison and G. Wilkinson, J. Chem. Soc., (1965) 3890; (c) A.R. Manning, J. Chem. Soc. A, (1968) 1135.

9 H.B. Abrahamson, C.C. Frazier, D.S. Ginley, H.B. Gray, J. Lilienthal, D.R. Tyler and M.S. Wrighton, Inorg. Chem., 16 (1977) 1554.

10 K. Inkrott, R. Goetze and S.G. Shore, J. Organomet. Chem., 154 (1978) 337