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IRON–SILICON BOND CLEAVAGE IN DICARBONYL(η^5-CYCLOPENTADIENYL)(TRIMETHYLSILYL)IRON USING TETRABUTYLAMMONIUM FLUORIDE

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Summary

Dicarbonyl(η^5-cyclopentadienyl)(trimethylsilyl)iron (**1**) was found to react with a 1 *M* solution of tetrabutylammonium fluoride (**2**) in tetrahydrofuran at 25°C to give dicarbonyl(η^5-cyclopentadienyl)iron anion (**5**). The anion generated under these conditions was trapped with electrophiles (R–X) to give 45–89% yields of neutral dicarbonyl(η^5-cyclopentadienyl)-alkyl, -allyl, -acyl-iron compounds and the ethylene cation. Tetrabutylammonium hydroxide also can be used in this reaction. Evidence indicates that fluoride ion instead of hydroxide attacks the silicon when tetrabutylammonium fluoride is used since fluorotrimethylsilane can be detected in the reaction product. Tetrabutylammonium fluoride and hydroxide quantitatively liberate styrene from dicarbonyl(η^5-cyclopentadienyl)(η^2-styrene)iron tetrafluoroborate, producing bis[dicarbonyl(η^2-cyclopentadienyl)iron].

Introduction

Organosilanes and silyl ethers have been used extensively in organic synthesis [1,2]. One main advantage in their synthetic utility is that the carbon–silicon and oxygen–silicon bonds can be broken with both nucleophilic and electrophilic reagents. A major advance occurred when fluoride ion was found to selectively cleave these bonds in aprotic solvents [3,4]. The apparent driving force for fluoride induced cleavage is the formation of the very stable fluorine–silicon bond [5].

The large number of organotransition metal silanes known today have synthetic potential similar to organic analogues, yet few applications have been reported. One of the first transition metal silanes prepared was dicarbonyl(η^5-cyclopentadienyl)(trimethylsilyl)iron (**1**, Fp = $Cp(CO)_2Fe$) [6]. Several electrophilic [7] and nucleophilic [8] cleavages of **1** have been reported, however, only a few synthetic applications have appeared. One of these is the preparation of a cyclopropenium salt depicted in eq. 1 [7f]. A question can be raised as to whether **1** in eq. 1 is attacked directly by the

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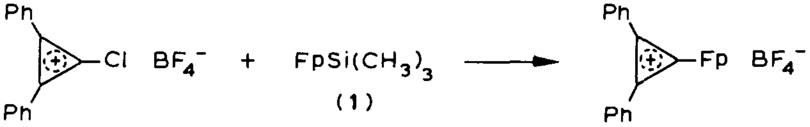

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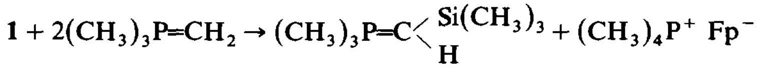
electrophilic cyclopropenium ion or if Fp anion is produced via nucleophilic attack on silicon. A phosphorus ylide was used in a nucleophilic cleavage of **1** (eq. 2) [8a],



$$1 + 2(CH_3)_3P{=}CH_2 \rightarrow (CH_3)_3P{=}C\begin{smallmatrix} Si(CH_3)_3 \\ H \end{smallmatrix} + (CH_3)_4P^+ \ Fp^- \qquad (2)$$

while an earlier study showed that KOH in methanol could cleave **1** to give Fp anion in a slow reaction [8b]. A dimethylarsenidoiron complex was prepared by **1** with chlorodimethylarsine [8c], while BuLi was found to cause the trimethylsilyl group to migrate to the cyclopentadienyl ring [8d].

Tetrabutylammonium fluoride (**2**) has been used extensively in organic synthesis as a base [9] and as a cleavage reagent for the organosilyl derivatives described above [3]. The potential for use of fluoride ion in organotransition metal chemistry can be seen in the recent report by Alper and Damude where metal carbonyl anions were prepared [10]. A specific example is depicted in eq. 3. Whether fluoride ion acts as a

$$\underset{}{Fe_3(CO)_{12}} + \underset{\mathbf{(2)}}{Bu_4N^+F^-} \xrightarrow[THF]{H_2O} Bu_4N^+[HFe_3(CO)_{11}]^- \qquad (3)$$

base or a nucleophile in this reaction is yet to be established.

We report here new applications of **1** and **2** in organotransition metal chemistry, including the efficient cleavage of the iron–silicon bond in **1** with **2**. This cleavage produces Fp anion and fluorotrimethylsilane which are identified through trapping experiments (Fp^-) and spectroscopy ($FSi(CH_3)_3$).

Results and discussion

When dicarbonyl(η^5-cyclopentadienyl)(trimethylsilyl)iron (**1**) was treated at room temperature with one equivalent of tetrabutylammonium fluoride (commercial 1 *M* solution in THF), the light yellow solution immediately darkened. The infrared spectrum of this solution had two new bands at 1863 and 1788cm^{-1}, which compare favorably with the reported values for Bu_4N^+ Fp^- (lit. [19] 1865, 1788cm^{-1}). Upon addition of benzyl chloride, the solution lightened and from it Fp-benzyl could be isolated in 50% yield. The very rapid reaction of **1** with **2** demonstrated that the transition metal–silicon bond could be readily cleaved to generate Fp anion (**3**).

$$\underset{\mathbf{(1)}}{FpSiMe_3} + \underset{\mathbf{(2)}}{Bu_4N^+ \ F^-} \xrightarrow{THF} \underset{\mathbf{(3)}}{Bu_4N^+ \ Fp^-} + FSiMe_3 \qquad (4)$$

The driving force in the reaction can be seen in the strength of the fluorine–silicon bond [5]. Although an accurate bond energy for the organoiron–silicon bond is not known, a value of 70 kcal/mol is probably close [5,11]. The large net gain of ~ 60 kcal more than offsets any difference in anion stability between Fp anion and fluoride ion.

The apparent ready cleavage of **1** by **2** suggested that reaction 4 could be an efficient source of Fp^- to be used in other preparative reactions. We frequently need small amounts of **3** for related projects, and this procedure exhibited the potential to meet these needs. To determine how useful the procedure might be, a series of typical electrophiles were reacted with **3** generated via reaction 4.

If the desired result is to produce high yields of alkylated Fp compounds, then an improved procedure would result if the alkylating agent were present upon addition of fluoride ion. Any side reactions that would consume Fp anion would have to then compete with alkylation. Indeed, when benzyl chloride and **1** were dissolved in THF and **2** then added, an 80% isolated yield of $FpCH_2Ph$ was obtained along with 3% Fp_2. A similar result was found with 1-bromobutane as the alkylating agent. The prior generation method (Method A) produced a 45% yield of Fp-butyl while the in situ method (Method B) gave an 85% isolated yield. Method A involved use of a

$$\text{Method A:} \quad \mathbf{1} \xrightarrow[\text{2. RX}]{\text{1. } Bu_4N^+ F^-/THF} FpR \qquad (5)$$

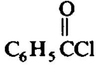
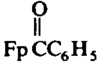
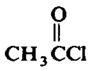
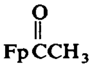
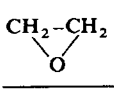
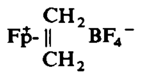
$$\text{Method B:} \quad \mathbf{1} \xrightarrow[\text{2. } Bu_4N^+ F^-]{\text{1. RX/THF}} FpR \qquad (6)$$

vacuum line to limit the possibility of contamination by air for these small scale reactions. For Method B, however, there was no difference in results between doing the reaction on the benchtop under a nitrogen atmosphere or on the vacuum line.

The in situ procedure (Method B) requires that **1** react faster with **2** than the alkylating agent. When Method B was attempted with CH_3I, a small amount of $FpCH_3$ was obtained and **1** could be reisolated. Apparently the competition of CH_3I

TABLE 1

REACTION OF RX AND $Bu_4N^+F^-$ WITH $Cp(CO)_2FeSi(CH_3)$ (**1**)

RX	$Bu_4N^+F^-$	FpR	Yield FpR (%)		Ref.
			Method A[a]	Method B[a]	
$PhCH_2Cl$	2	$FpCH_2Ph$	50[b]	80[b]	26
$PhCH_2Cl$	4	$FpCH_2Ph$	–	89[c]	26
$CH_3(CH_2)_3Br$	2	$Fp(CH_2)_3CH_3$	45[b]	85[b]	24
CH_3I	2	$FpCH_3$	88[c]	–	18a, p.151–152
$CH_2{=}C(CH_3)CH_2Cl$	2	$FpCH_2C(CH_3){=}CH_2$	63[c]	–	27
$C_6H_5CH{=}CHCH_2Cl$	2	$FpCH_2CH{=}CHC_6H_5$	89[c]	–	28
 $C_6H_5\overset{O}{\overset{\Vert}{C}}Cl$	2	 $Fp\overset{O}{\overset{\Vert}{C}}C_6H_5$	51[c]	–	29
 $CH_3\overset{O}{\overset{\Vert}{C}}Cl$	2	 $Fp\overset{O}{\overset{\Vert}{C}}CH_3$	47[c]	–	30
 [d]	2		–	78[b]	25

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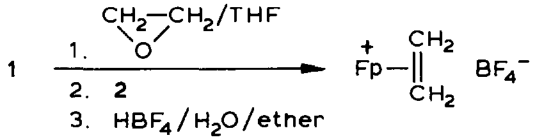
[a] See text for description of methods. [b] Isolated yield. [c] NMR yield. [d] HBF_4 (48%) added after reaction complete.

and **1** for **2** favors CH_3I. However, when Method A was applied to CH_3I on the vacuum line, an 88% yield of $FpCH_3$ was obtained (NMR determination). Results of the reactions of **3** generated from **1** and **2** are presented in Table 1.

The results in the Table indicate that the **1** plus **2** method of producing **3** gives Fp-alkyls, -allyls and -acyls in moderate to high yields. In cases where the yields are moderate, most of the remaining iron was present as Fp_2. It was felt that the main applications for this procedure would involve small scale reactions, therefore, these were all done on a 1–3 mmol scale using an excess of RX. The yields reported are representative for this scale, however, higher yields would be expected if the reactions were done on a larger scale.

A very useful reaction of **3** is the production of Fp-olefin cations via an epoxide [12]. When **2** was reacted with ethylene oxide and **1** on the vacuum line (Method B), then treated with tetrafluoroboric acid, a 78% yield of $Fp(C_2H_4)^+$ BF_4^- was obtained.



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After most of this work was completed using the commercial THF solution **2**, $Bu_4NF \cdot 3H_2O$ (**4**) became available as a white crystalline solid. When benzyl chloride was reacted with **1** and **4** an 89% yield of $FpCH_2Ph$ was obtained (NMR method). The reaction seemed to be cleaner with less Fp_2 being formed than when using **2**. Although not as convenient as **2**, **4** is useful in those cases where the extra water in **2** would be a problem.

The question arose as to whether the fluoride ion itself or hydroxide from the small amount of water present was the reactive agent. To clarify the point, the reaction was carried out on a vacuum line and the volatile products collected in a gas IR cell. Besides the anticipated THF bands, absorptions at 2965, 1267, 918, 855 and 758 cm^{-1} were the only other ones present and these are similar to those reported previously for $FSiMe_3$ [13a]. Further evidence was obtained for direct cleavage by fluoride through doing the reaction on the vacuum line with benzyl chloride present (Bu_4N^+ $F^- \cdot 3H_2O$ was used in this case). The volatiles were collected in an NMR tube and the major silicon compound was identified as $FSiMe_3$ [13b] produced in 63% yield as determined by NMR (CH_2Br_2 as internal standard). The NMR yield of Fp-benzyl for the reaction was 89%. An additional singlet at δ 0.06 ppm was assigned to $[(CH_3)_3Si]_2O$ which was produced in about 10% yield. The $[(CH_3)_3Si]_2O$ may have arisen from a secondary reaction of $FSi(CH_3)_3$ with water in the reaction flask since $FSi(CH_3)_3$ is known to produce $[(CH_3)_3Si]_2O$ in the presence of water and base [14].

We decided to check if hydroxide ion would cleave the iron-silicon bond in **1** under aprotic conditions [8b]. Tetrabutylammonium hydroxide (40% in H_2O) (**5**) when treated with **1** and benzyl chloride in THF produced a 46% yield of $FpCH_2Ph$ with 8% recovered **1**. The reaction with **5** was heterogeneous which may explain why the yield was low. The use of **5** in the generation of **3** would be limited to those cases not affected by the strong base present.

The liberation of the olefins from Fp-olefin cations is a synthetically useful tool [12,15]. The most common methods for this purpose are iodide ion [12] or NaFp [15] which produce FpI and Fp_2 respectively. When **4** was reacted with Fp(styrene) cation (**6**) a 100% yield of styrene was obtained with a 56% yield of Fp_2. The question also arose as to whether the fluoride or hydroxide was doing the olefin cleavage. In fact, **5**, when treated with **6**, also gave a quantitative yield of styrene with a 28% yield of Fp_2.

$$\underset{(\mathbf{6})}{Fp(CH_2{=}CHPh)BF_4} + \mathbf{4} \rightarrow CH_2{=}CHPh + Fp_2 \tag{8}$$

$$\mathbf{6} + \mathbf{5} \rightarrow CH_2{=}CHPh + Fp_2 \tag{9}$$

It seems likely that **4** is acting as a source of hydroxide which then cleaves the olefin to produce Fp_2. However, there is the possibility that FpF [7c] is formed via direct attack of F^- on the metal complex, followed by reaction with base to give Fp_2. We [16] and others [17] have shown that FpCl reacts rapidly with hydroxide under phase transfer conditions to give Fp_2 in high yield. FpF could be formed in the reaction, but then rapidly transformed to Fp_2. Although the mechanisms are still unclear, reactions 8 and 9 complement the use of iodine ion in the liberation of olefins from Fp-olefin cations and are more convenient than using the air sensitive NaFp.

Conclusions

The cleavage of the iron–silicon bond in **1** with fluoride is a very efficient process as evidenced by the moderate to high yields of alkylated products listed in Table 1. This is the first clear example of the cleavage of a metal–silyl bond by fluoride. It is anticipated that other of the many organotransition metal silanes would be cleaved in a similar manner with **2** and studies are in progress to examine the scope of related reactions.

Since the production of **3** is so efficient one must compare the current procedure with previous methods for Fp^- generation. All of these start with Fp_2 which is then reacted with sodium amalgam [18], sodium/potassium alloy [19], trialkylborohydrides [20], potassium hydride [21], sodium dispersion [22], potassium plus benzophenone [23] or an alkali metal plus an aromatic hydrocarbon [24]. Of these procedures, the potassium plus benzophenone [23] has the most potential for large scale reactions. For small scale in situ methods the trialkylborohydride route requires the use of hexamethylphosphoric triamide as cosolvent and the product boranes present isolation problems. All of these methods require caution in using very reactive, hazardous and air sensitive materials. The starting material **1** can be prepared in large quantities in high yield by using **3** generated by one of these previous procedures. **1** is a waxy solid that is stable enough to accurately weigh in air which makes it useful in small scale reactions. Both **2** and **4** are commercially available and can be used directly in the generation of **3**. The only by-product in the anion preparation is $FSi(CH_3)_3$ which is volatile and easily removed. Since **1** must be prepared by one of the other methods for Fp^- generation, no advantage is seen for large scale reactions. However, when a small amount of **3** is required on an infrequent basis, the procedure described here may be the method of choice and deserves consideration.

Fp(olefin)$^+$ cations can be cleaved to liberate the olefins using **2**. This procedure complements the use of iodide in that Fp_2 is produced instead of FpI and is better than using NaFp which is air sensitive and difficult to use in small amounts.

Experimental

General. Infrared spectra were recorded on a Perkin–Elmer 298 or Beckman 4250 spectrometer. Nuclear magnetic resonance spectra were obtained on Varian T60, EM360A and XL-100 spectrometers. GLC analyses were performed on a Perkin–Elmer Lamba 3 instrument equipped with a flame-ionization detector.

1 was prepared by the literature procedure from sodium amalgam and $Cp_2(CO)_4Fe_2$ plus $(CH_3)_3SiCl$ [6]. $Cp(CO)_2Fe(CH_2{=}CHC_6H_5)BF_4$ was prepared via the epoxide route [12,25]. Tetrahydrofuran was predried over KOH and then distilled from sodium benzophenoneketyl immediately before use. Hexane and dichloromethane were distilled before use while other solvents were reagent grade and used as received.

Bis(dicarbonylcyclopentadienyliron) was purchased from Pressure Chemical Co. and recrystallized from acetone/hexane prior to use. The 1 *M* THF solution of $(C_4H_9)_4NF$ and solid $(C_4H_9)_4NF \cdot 3H_2O$ were purchased from Aldrich Chemical Co. and used as received. All reactions were carried out under an atmosphere of nitrogen or on a vacuum line.

Reaction of $Cp(CO)_2FeSi(CH_3)_3$ with $(C_4H_9)_4NF$ and RX

Method A. A 100 ml round bottom flask, equipped with a joint and a stopcock inlet plus a stirring bar was charged with **1** (1 mmol) and THF (5 ml) then attached to a vacuum line via the joint. The solution was degassed with liquid N_2 freeze-thaw cycles. A septum was placed on the stopcock inlet and **2** (1.1 mmol) added via syringe to the frozen solution. The flask was allowed to warm to room temperature and the volatiles collected in a liquid N_2 trap. The light yellow solution turned red on warming. After about one-half of the THF had distilled, the flask was cooled to liquid N_2 temperature and the alkyl halide transferred via vacuum-line distillation. When transfer was complete, the flask was sealed off and allowed to warm to room temperature with stirring. After 30 minutes at room temperature the THF was removed on a rotary evaporator and the residue filtered through a short column of alumina or silica gel with ether/hexane. The solvent was removed and in those cases where the product was analyzed by NMR, a standard was added and an NMR spectrum obtained. For those with isolated yields, a column was done using neutral alumina with hexane/ether and the yellow product band collected and weighed.

Method B. To a 100 ml round bottom sidearm flask was added **1** (1 mmol), an alkyl halide (1.5 mmol) and THF (5 ml). The flask was cooled to 0°C and **2** (1.1 mmol) added via syringe. After 10 min at 0°C the flask was warmed to room temperature and left stirring for 30 minutes. Workup and analysis were as in Method A.

Preparation of $Fp(CH_2{=}CH_2)BF_4$

To a 100 ml round bottom flask with sidearm were added **1** (0.25 g, 1.0 mmol) and THF (5 ml) which was then placed on the vacuum line and degassed. Ethylene oxide was transferred via vacuum line distillation to the flask cooled to liquid N_2 temperature. The **2** solution (1.0 ml, 1.0 mmol) was added via the sidearm using a septum and syringe. The flask was allowed to warm to room temperature and removed from the vacuum line. Nitrogen was introduced followed by HBF_4 (1 ml

48% in H_2O) in 50 ml ether. The resulting solid was collected and dissolved in acetone/CH_2Cl_2, filtered through celite and precipitated with ether to give $Fp(C_2H_4)BF_4$ (0.228 g, 0.78 mmol, 78%). In a separate experiment, no apparent reaction between **1** and ethylene oxide could be observed in the absence of **2** *.

Reaction of 1 with tetrabutylammonium hydroxide

Method B was followed using **1** (0.253 g, 1.09 mmol), benzyl chloride (0.189 g, 1.5 mmol) and THF (5 ml). To this was added $(C_4H_9)_4NOH$ (1.036 g, 40% in H_2O, 1.6 mmol) and the mixture stirred for 30 minutes at room temperature. The reaction was worked up as above and analyzed by NMR using dioxane as standard giving $FpCH_2C_6H_5$ (46%) and **1** (8%).

Reaction of $Fp(CH_2{=}CHC_6H_5)BF_4$ with 4

To a 100 ml sidearm flask was added $Fp(CH_2{=}CHC_6H_5)BF_4$ (0.180 g, 0.503 mmol), THF (4 ml), cumene (0.00273 g, GC standard) followed by solid **4** (0.3921 g, 1.2 mmol). The yellow solution turned dark immediately. After 5 minutes a 0.2 ml sample was removed and analyzed by GC (3% Carbowax, 6 ft. by 2 mm column, 100°C, 30 ml/min) to give styrene as the only volatile product (0.050 g, 0.50 mmol, 100%). The remainder of the reaction was worked up by removal of solvent, filtration through celite with ether and removal of solvent. The residue was dissolved in $CDCl_3$ and dioxane added (0.035 g). The only product observed by NMR was $Cp_2(CO)_4Fe_2$(0.14 mmol, 56%). A similar result was obtained using **2** instead of **4**.

Reaction of $Fp(CH_2{=}CHC_6H_5)BF_4$ with tetrabutylammonium hydroxide

The styrene complex (0.181 g, 0.50 mmol) and THF (5 ml) were placed in a flask and tetrabutylammonium hydroxide (0.532 g, 40% in H_2O, 0.82 mmol) added. Workup and analysis as above gave styrene (0.50 g, 100%) and $Cp_2(CO)_4Fe_2$ (0.07 mmol, 28%).

Characterization of $(CH_3)_3SiF$

To the flask on the vacuum line at −196°C containing **1** (0.732 g, 2.9 mmol), benzyl chloride (0.418 g, 3.3 mmol) and 5 ml THF was added **2** (3.3 ml, 3.3 mmol). The flask was allowed to warm to room temperature and volatiles collected. The reaction flask was removed and the trapped material allowed to expand into a gas IR cell until a 4.8 mmHg pressure was obtained. The IR spectrum showed a mixture of THF and $(CH_3)_3SiF$ [13a].

A second experiment was done using **4**. The solid **4** (0.095 g, 0.3 mmol) was added to the frozen THF solution of **1** (0.050 g, 0.2 mmol) and benzyl chloride (0.055 g, 0.43 mmol), then placed on the vacuum line and evacuated. The flask was warmed and the volatiles collected in an NMR tube. Methylene bromide (20 μl, 0.285 mmol) was added to the NMR tube as a standard. The NMR spectrum showed THF and a doublet at δ0.20, J 7.2 Hz (lit. [13b] δ 0.21 ppm, J 7.5 Hz) (0.125 mmol, 63%). A singlet at δ 0.06 ppm was assigned to $[(CH_3)_3Si]_2O$ [14] (10%). Fp-benzyl was isolated as in Method A and the NMR yield was 89%.

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* We wish to thank a referee for suggesting this experiment which supports the necessity of **2** while ruling out the possibility of a direct reaction of **1** with ethylene oxide to produce $FpCH_2CH_2OSi(CH_3)_3$, in the production of the ethylene cation complex.

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References

1 E.W. Colvin, Silicon in Organic Synthesis, Butherworths, New York, 1981.
2 I. Fleming, Organic Silicon Compounds in D. Barton and W.D. Ollis (Eds.), Comprehensive Organic Chemistry, vol. 3 (1979) 541-686.
3 E.J. Corey and A. Venkateswarlu, J. Am. Chem. Soc., 94 (1972) 6190.
4 Some recent applications: (a) Y. Ito, S. Miyata, M. Nakatsuka and T. Saegusa, J. Org. Chem., 46 (1981) 1043; (b) Y. Ito, M. Nakatsuka and T. Saegusa, J. Am. Chem. Soc., 102 (1980) 863; (c) I. Kuwajima, E. Nakamura and M. Shimizu, J. Am. Chem. Soc., 104 (1982) 1025.
5 D_{298}^{0}(F-Si) 129 kcal/mole. CRC Hankbook of Chemistry and Physics, 57th ed., 1976.
6 T.S. Piper, D. Lemal and G. Wilkinson, Naturwissenschaften, 43 (1956) 129.
7 (a) R.E. Bichler, H.C. Clark, B.K. Hunter and A.T. Rake, J. Organomet. Chem., 69 (1974) 367; (b) R.E. Bichler, M.R. Booth and H.C. Clark, ibid., 24 (1970) 145; (c) W. Malisch and P. Panster, Chem. Ber., 108 (1975) 2554; (d) J.R. Chipperfield, J. Ford, A.C. Hayter and D.E. Webster, J. Chem. Soc., Dalton, (1976) 360; (e) J.R. Chipperfield, A.C. Hayter and D.E. Webster, ibid., (1977) 921; (f) R. Gompper and E. Bartmann, Angew. Chem. Int. Ed. Engl., 17 (1978) 456.
8 (a) W.J. Malisch, J. Organomet. Chem., 61 (1973) C15; (b) M.A. Nasta and A.G. MacDiarmid, ibid., 18 (1969) P11; (c) W.J. Malisch and M. Kuhn, Angew. Chem. Int. Ed. Engl., 13 (1974) 84; (d) S.R. Berryhill and B. Sharenow, J. Organomet. Chem., 221 (1981) 143.
9 J.H. Clark, Chem. Rev., 80 (1980) 429.
10 H. Alper and L.C. Damude, Organometallics, 1 (1982) 579.
11 C. Windus, S. Sujishi and W.P. Giering, J. Organomet. Chem., 101 (1979) 279.
12 (a) M. Rosenblum, Accounts Chem. Research, 7 (1974) 122; (b) W.P. Giering, M. Rosenblum and J. Tancrede, J. Am. Chem. Soc., 94 (1972) 7170; (c) K.M. Nicholas, ibid., 97 (1975) 3254.
13 (a) V.H. Kriegsmann, Z. Anorg. Allg. Chem., 294 (1958) 113: 2968, 1262, 912, 858, 760 cm^{-1}; (b) H. Schmidbaur, J. Am. Chem. Soc., 85 (1963) 2336.
14 A.F. Janzen, J.A. Gibson and D.G. Ibbott, Inorg. Chem., 11 (1972) 2853.
15 (a) B. Foxman, D. Marten, A. Rosan, S. Raghu and M. Rosenblum, J. Am. Chem. Soc., 99 (1977) 2160; (b) D.F. Marten, J. Org. Chem., 46 (1981) 5422.
16 D.F. Marten and D.H. Hanlon, unpublished results.
17 D.H. Gibson, W.-L. Hsu and F.U. Ahmed, J. Organomet. Chem., 215 (1981) 379.
18 (a) R.B. King, Organometallic Syntheses, Academic Press, New York, Vol. 1 (1965); (b) J.M. Burlitch, M.E. Leonowicz, R.B. Petersen and R.E. Hughes, Inorg. Chem., 18 (1979) 1097.
19 J.E. Ellis and E.A. Flow, J. Organomet. Chem., 99 (1975) 263.
20 J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker and J.C. Selover, Inorg. Chem., 18 (1979) 553.
21 K. Inkrott, R. Goetze and S.G. Shore, J. Organomet. Chem., 154 (1978) 337.
22 D.L. Reger, D.J. Fauth and M.D. Dukes, Synth. React. Inorg. Met.-Org. Chem., 7 (1977) 151.
23 J.S. Plotkin and S.G. Shore, Inorg. Chem., 20 (1981) 284.
24 R. Gompper and E. Bartmann, Liebigs Ann. Chem., (1979) 229.
25 R.C. Kerber and D. Ehntholt, J. Am. Chem. Soc., 95 (1973) 2927.
26 J.P. Bibler and A. Wojcicki, J. Am. Chem. Soc., 88 (1966) 4862.
27 J.-Y. Merour and P. Cadiot, C. R. Acad. Sci., Ser. C, 271 (1970) 83.
28 A. Cutler, D. Ehnholt, P. Lennon, K. Nicholas, D. Marten, M. Madhavarao, S. Raghu, A. Rosan and M. Rosenblum, J. Am. Chem. Soc., 97 (1975) 3149.
29 R.B. King and M.B. Bisnette, J. Organomet. Chem., 2 (1964) 15.
30 R.B. King, J. Am. Chem. Soc., 84 (1963) 1918.