Journal of Organometallic Chemistry, 462 (1993) 39–43

JOM 23698

Trimethylsilyl derivatives of cyclooctatetraene *

Nicholas C. Burton, F. Geoffrey N. Cloke, Stephen C.P. Joseph, Helen Karamallakis and Ausama A. Sameh

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

(Received March 5, 1993)

Abstract

An improved, large scale synthesis of 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene is described. The compound may be deprotonated with n-butyllithium/THF or n-butyllithium/TMEDA to afford stable dilithium salts of the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion, which may be oxidised with mercuric chloride to give free bis(trimethylsilyl)cyclooctatetraene as a mixture of the 1,4- and 1,6-isomers. Treatment of the bis(trimethylsilyl)cyclooctatetraenyl dianion with an excess of chlorotrimethylsilane gives 2,5,5,8-tetrakis(trimethylsilyl)cycloocta-1,3,6-triene.

1. Introduction

The strategy of employing bulky substituents on cyclic aromatic ligands to stabilise organometallic compounds in unusual oxidation states/coordination environments has ample precedent; for example, in pentamethylcyclopentadienyl complexes of p- [1] d- [2] and f-block [3] elements and tri-t-butylbenzene complexes of the lanthanides [4]. The use of trimethylsilyl substituents in this role is also well documented, and it is, of course, particularly appropriate to acknowledge Michael Lappert's significant contributions in the areas of trimethylsilyl-substituted alkyl [5], amide [6] and cyclopentadienyl [7] ligands. Apart from the steric influence and solubilising effect of alkylsilicon-based substituents, the reluctance of the latter to undergo rearrangements facilitates their introduction *via* nucleophilic substitution.

Syntheses of alkyl-substituted cyclooctatetraenes, *e.g.* 1,4-di-tert-butyl- [8] and 1,3,5,7-tetramethylcyclooctatetraene [9], have been described, but the procedures are lengthy and the resulting low yields limit their potential as ligands for metal complexes. Expecting that the introduction of trimethylsilyl substituents might prove more straightforward (*vide supra*), we set out to prepare trimethylsilyl derivatives of the cyclooctatetraene dianion for use as ligands for, in particular, organo-f-element complexes. Some of the results described herein have been briefly communicated [10].

2. Results and discussion

The synthesis of 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (**1**) in 35% yield, from lithium cyclooctatetraenide and chlorotrimethylsilane in diethyl ether, has been previously described [11]. In our hands, the related reaction using potassium cyclooctatetraenide and tetrahydrofuran as solvent afforded **1** in > 70% yield. A much more economical synthesis of **1** starts from cycloocta-1,5-diene: the latter may be reduced to the cyclooctatetraene dianion with n-butyllithium/tetramethylethylenediamine (as reported by Wilke [12]), which is then treated with chlorotrimethylsilane as before. This procedure provides a convenient, large (50 g) scale 'one pot' synthesis of **1** in high (70%) yield (see Scheme 1). Compound **1** may be isolated as a white crystalline solid, with spectroscopic properties consistent with those previously recorded [11], which is somewhat thermally sensitive, but may be stored indefinitely under nitrogen at −20°C.

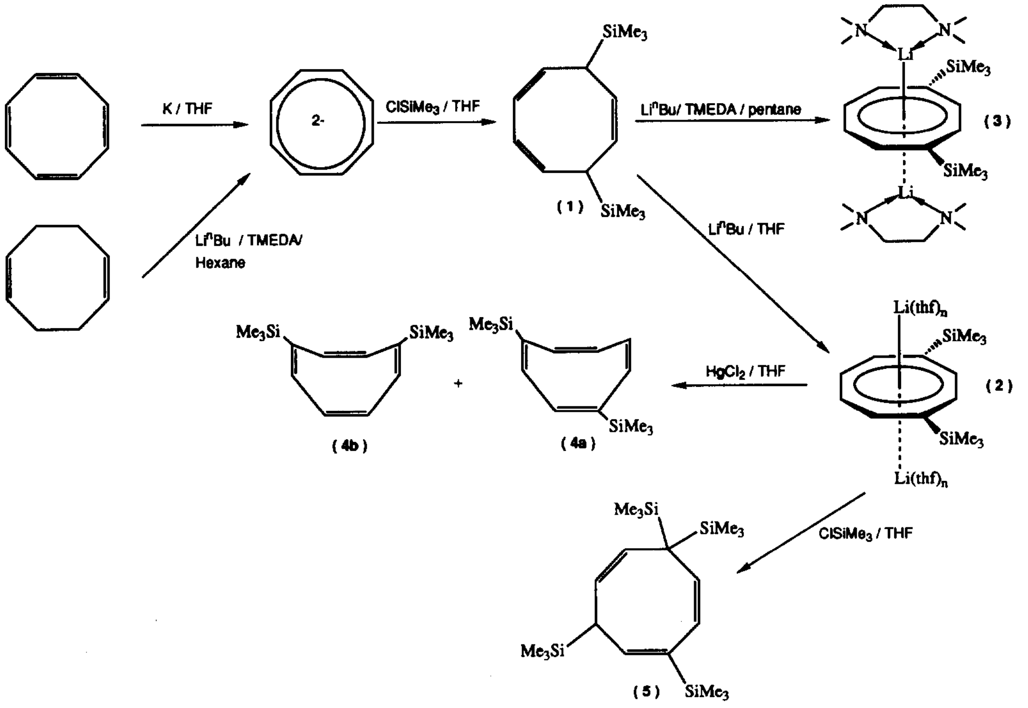
The acidity of the protons on the two carbons α to silicon in **1** allows the ready deprotonation of the latter

---

Correspondence to: Dr. F.G.N. Cloke.

* Dedicated to Professor M.F. Lappert FRS on the occasion of his 65th birthday, with sincere thanks for his help and encouragement over the years.

0022-328X/93/$6.00

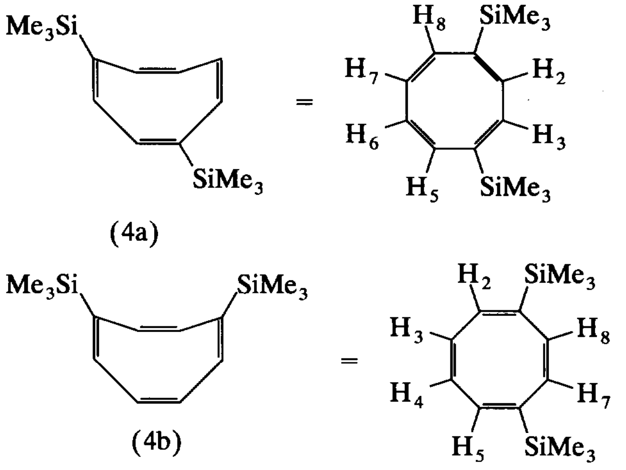


Scheme 1.

with n-butyllithium in tetrahydrofuran to afford the the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion as its dilithium salt **2**, solvated by tetrahydrofuran. The salt **2** is an extremely air-sensitive white solid, which shows reasonable solubility in hydrocarbon solvents, and indeed may be recrystallised from pentane, although the resulting crystals lose tetrahydrofuran very readily. Accordingly, the exact value of n in $[Li(thf)_n]_2[C_8H_6\{1,4\text{-}(SiMe_3)_2\}]$ (**2**) must be determined by ^1H NMR spectroscopy in $^2H_6$-benzene, and is typically 0.5–1.5. Deprotonation of **1** with n-butyllithium-tetramethylethylenediamine, however, afforded **3** in which each lithium counterion is coordinated by precisely one tetramethylethylenediamine ligand, as indicated by both NMR integration and microanalysis. The pale-yellow crystalline **3** is also extremely air- and moisture-sensitive, and is very soluble in saturated hydrocarbons. The ^7Li NMR spectra of both **2** and **3** exhibited singlets shifted to low frequency (δ −11.7 and δ −8.8 respectively), which is characteristic of lithium symmetrically bound to an aromatic π-system [13], and we therefore assume that **2** and **3** have the structures shown in Scheme 1. The ^1H NMR spectra of **2** and **3** showed the expected AA′BB′CC′ pattern for the six ring protons of the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion, and the $^{13}C\{^1H\}$ spectra were also entirely consistent with the proposed structures (see Experimental section).

The 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion in **2** (and presumably also **3**, although the attempt was not made in this case) can be readily oxidised with mercury(II) chloride in tetrahydrofuran to afford the free bis(trimethylsilyl)cyclooctatetraene (**4**) as a mixture of the 1,4 and 1,6 isomers, (**4a**) and **4b**) respectively, in high yield (see Scheme 1). Compound **4** is a white volatile crystalline solid that exhibits a parent ion in the mass spectrum, and is somewhat thermally sensitive and is slowly transformed into a viscous yellow oil on standing at room temperature. The ^1H NMR spectrum of **4** clearly shows the presence of the 1,4 and 1,6 isomers (see Fig. 1 for NMR labelling scheme).

The signals from protons $H_{2,3}$ of **4a** and $H_{7,8}$ of **4b** appear as singlets and their relative integrations showed the isomeric ratio, **4a** : **4b**, to be 1.5 : 1, whereas in the related di-tert-butylcyclooctatetraene, the ratio of 1,4 to 1,6 isomer was found to be 2 : 1 [14]. The remaining protons of **4a** would be expected to show an AA′BB′ pattern, but the fine structure of the latter was not well resolved, and so it was treated as pseudo AB. Analysis of the spectrum yielded a value for the olefinic coupling constant $J_{5,6}(=J_{7,8})$ of 10.5 Hz, which compares well with value found for 1,4-di-tert-butylcyclooctatetraene of 10.4 Hz [14]. The expected AA′BB′ pattern for the remaining protons in **4b** was found to be not sufficiently well resolved for an analysis to be



(4a)

(4b)

Fig. 1. NMR labelling scheme for **4a** and **4b**.

attempted, but $J_{4,5}$ was estimated to be $\leqslant 1$ Hz, thus confirming **4b** as the 1,6 isomer. The $^{13}C\{^1H\}$ spectrum of **4** confirmed the presence of the isomers **4a** and **4b**, and the spectrum was further assigned by the use of $^{13}C\{^1H\}$ DEPT (see Experimental section).

We were interested in the possibility of preparing a tetrakis(trimethylsilyl)-substituted cyclooctatriene as a precursor to the corresponding highly substituted cyclooctatetraene dianion. Accordingly, **2** was treated with an excess of chlorotrimethylsilane and this resulted in the isolation of high yields of 2,5,5,8-tetrakis(trimethylsilyl)cycloocta-1,3,6-triene, **5**, see Scheme 1. **5** is a white, volatile crystalline solid, which may be purified by sublimation or low temperature recrystallisation from acetone, and which displays a strong parent ion peak in the electron-impact mass spectrum. The ^1H NMR spectrum of **5** is first order and confirms the proposed structure (see Fig. 2). The six multiplets arising from the ring protons (ABCDEF spin systems, see Experimental section for assignments) yielded the following coupling constants, which fall within accepted values for the proposed structure: $^3J_{af} = 8.7$, $^4J_{ac} = 0.7$, $^5J_{ae} = 0.7$, $^3J_{fb} = 8.7$, $^4J_{fd} = 1.3$, $^4J_{de} = 1.3$, $^3J_{db} = 10.5$, $^3J_{ce} = 12.8$.

Attempts to generate the cyclooctatretraenyl dianion derived from **5** by double deprotonation with either n-butyllithium-tetrahydrofuran or n-butyllithium-tetramethylethylenediamine were unsuccessful. This is not surprising in view of the fact that **5** only contains one proton (H_f) on a carbon α to silicon, and also clearly suggests the absence of an equilibrium concentration of an isomer of **5** containing two such protons that might arise from trimethylsilyl group migration.

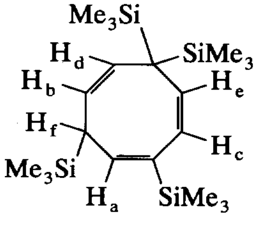


Fig. 2. NMR labelling scheme for **5**.

3. Experimental section

Unless otherwise stated, all operations were carried out under dinitrogen or argon by use of Schlenk line or drybox techniques. Tetrahydrofuran (thf) was pre-dried over sodium wire and freshly distilled from potassium under dinitrogen immediately prior to use. n-Pentane was freed from olefins by shaking with three portions of 1 : 1 conc. H_2SO_4/HNO_3, and was then thoroughly washed with water and dried over anhydrous $CaCl_2$, and, after pre-drying with sodium wire, freshly distilled from sodium-potassium alloy under dinitrogen immediately prior to use. Cyclooctatetraene was purified by vacuum transfer from a small amount of potassium metal, and cycloocta-1,5-diene was dried over freshly activated molecular sieves (4 Å) and then distilled. Chlorotrimethylsilane was freed from acidic impurities by standing over magnesium turnings, and then trap-to-trap vacuum transferred. N,N,N′,N′-Tetramethylethylenediamine (TMEDA) was dried over sodium-potassium alloy and then distilled. $^2H_6$-benzene was stored over freshly activated molecular sieves (4 Å) and freeze thaw degassed before use. Celite 545 filter aid was dried in an oven at 200°C. All other reagents were used as supplied.

NMR spectra were recorded on Bruker WP80 or WM360 spectrometers at probe temperature. ^1H and ^{13}C spectra were referenced to the residual proton and carbon chemical shifts of the deuterated solvents, and ^7Li spectra were referenced to external 1M $LiNO_3/D_2O$.

Mass spectra were obtained on a MS 80 RF instrument equipped with a dedicated Kratos ion source.

Microanalyses were determined by Analytische Laboratorien, Gummersbach, Germany.

3.1. Preparation of 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (1)

3.1.1. From cyclooctatetraene

Potassium sand was prepared from potassium (15.6 g, 400 mmol) and paraffin oil (*ca.* 15 ml) in 500 ml round bottom flask equipped with an egg-shaped magnetic stirring bar: the mixture was heated until the potassium was molten, and then vigorously stirred to produce finely divided potassium. The resulting sand was then allowed to cool without any further stirring, the paraffin oil removed by cannula, and the sand washed several times with tetrahydrofuran. The flask was then charged with 100 ml of tetrahydrofuran then cooled to −10°C, and a solution of cyclooctatetraene (21 g, 200 mmol) in tetrahydrofuran (20 ml) was added dropwise *via* a cannula, with stirring. When the addition was complete, the red mixture was stirred at 0°C for 1 h and then cooled to −40°C. A solution of chlorotrimethylsilane (55 g, 500 mmol) in tetrahydrofuran (100 ml) was then added dropwise with vigorous stirring and, when the addition was complete, the mixture stirred at room temperature for 3 h. The subsequent manipulations were carried out in air, **although caution should be exercised with potentially pyrophoric potassium residues.** The reaction mixture was filtered through Celite on a glass frit, and the filter cake thoroughly washed with reagent grade diethyl ether. The combined filtrates were then evaporated to dryness on a rotary evaporator at room temperature, and the resulting pale yellow oily solid recrystallised from Analar (or equivalent) methanol at −30°C to afford white needle-like crystals of *5,8-bis(trimethylsilyl)-cycloocta-1,3,6-triene*, yield 40 g (80%).

3.1.2. From cycloocta-1,5-diene

To a stirred solution of cycloocta-1,5-diene (24.5 ml, 200 mmol) in pentane (200 ml) at 0°C, contained in a three necked round bottom flask equipped with a reflux condenser and argon bubbler was added dropwise a solution of n-butyllithium (2.5 M solution in hexane, 240 ml, 600 mmol).

After completion of this addition, TMEDA (90.5 ml, 600 mmol) was added dropwise to the stirred, yellow mixture. The resulting deep red solution was stirred at room temperature overnight during which time an orange precipitate separated. The mixture was then refluxed under argon for 24 h and cooled to −30°C. Chlorotrimethylsilane (90 ml, 350 mmol) was added dropwise with stirring, and the mixture then stirred overnight at room temperature. The dark brown solution was then cautiously hydrolysed by pouring it on to an ice water slush (500 g). The organic layer was separated, washed with water (6 × 250 ml) to remove the TMEDA, and dried over magnesium sulphate. The solvent was then removed on a rotary evaporator at room temperature and the residual pale yellow oily solid recrystallised from Analar (or equivalent) methanol at −30°C to afford white needle-like crystals of *5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene*, yield 35 g (70%).

Mass spectrum (EI): *m/z* 250 (M^+, 23%).

^{1}H NMR ($CDCl_3$, 80 MHz): δ 5.84–5.79 (2H, m, ring CH), 5.57–5.50 (4H, m, ring CH), 2.82 (2H, m, ring CHSiMe$_3$), 0.03 (18H, s, Si(CH_3)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 20.1 MHz): δ 128.7 (ring =CH), 125.2 (ring =CH), 124.6 (ring =CH), 33.8 (ring -CHSiMe$_3$), −2.60 (Si(CH$_3$)$_3$).

3.2. Preparation of 1,4-bis(trimethylsilyl)cyclooctatetraenide dilithium-tetrahydrofuran adduct (2)

To a stirred solution of 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (5 g, 20 mmol) in tetrahydrofuran (100 ml), cooled to −80°C was added dropwise a solution of n-butyllithium (1.6 M solution in hexane, 25 ml, 40 mmol) (during the addition the initially colourless solution turned green). The mixture was then stirred at room temperature for 2 h and the volatiles were removed *in vacuo*. The residual extremely air-sensitive pale yellow solid was washed with pentane (3 × 25 ml) and dried *in vacuo* to afford the product as a white solid. The combined pentane washings afforded a further crop white crystals after concentration to *ca.* 30 ml and cooling to −30°C. Total yield 6.1 g, 85%.

^{1}H NMR (C_6D_6, 80 MHz): δ 6.46 (2H, m, ring CH), 6.33 (4H, m, ring CH), 2.80 (m, *thf*), 1.03 (m, *thf*), 0.71 (18 H, s, Si(CH_3)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 90.54 MHz): δ 95.90 (ring CH), 94.99 (ring CH), 89.54 (ring CH), 86.66 (ring CSiMe$_3$), 68.22 (*thf*), 26.39 (*thf*), 2.28 (Si(CH$_3$).

^{7}Li NMR (C_6D_6, 139.9 MHz): δ −11.70.

3.3. Preparation of 1,4-bis(trimethylsilyl)cyclooctatetraenide dilithium-bis(N,N,N′,N′-tetramethylethylenediamine) adduct (3)

To a stirred solution of 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (1.0 g, 4 mmol) in pentane (30 ml), cooled to −80°C, was added dropwise a solution containing n-butyllithium (1.6 M solution in hexane, 5 ml, 8 mmol) and TMEDA (0.975 g, 8.4 mmol) in pentane (20 ml). The brick-red reaction mixture was then stirred at room temperature for 4 h, filtered, concentrated *in vacuo* to *ca.* 5 ml, and cooled to −30°C. The resulting pale yellow crystals of the product were isolated, washed with pentane (2 × 10 ml) at −80°C, and dried *in vacuo*. Yield 1.1 g, 56%.

Microanalysis; found: C, 61.95; H 11.56; N 10.92. $C_{26}H_{56}N_4Li_2Si_2$ requires: C, 63.11; H, 11.41; N, 11.33%.

^{1}H NMR (C_6D_6, 80 MHz): δ 6.86 (2H, m, ring CH), 6.32 (4H, m, ring CH), 1.57 (24H, s, CH_3 of TMEDA), 1.20 (8H, s, CH_2 of TMEDA), 0.70 (18H, s, Si(CH_3)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 90.54 MHz): δ 96.86 (ring CH), 93.68 (ring CH), 88.29 (ring CH), 86.24 (ring CSiMe$_3$), 55.95 (CH$_2$ of TMEDA), 44.63 (CH$_3$ of TMEDA), 2.77 (Si(CH$_3$)$_3$).

^{7}Li NMR (C_6D_6, 139.9 MHz): δ −8.80.

3.4. Preparation of 1,6- and 1,4-bis(trimethylsilyl)cyclooctatetraene (4a and 4b)

To a stirred solution of $[Li(thf)_{1.3}]_2[C_8H_6\{1,4-(SiMe_3)_2\}]$ (0.90 g, 2.65 mmol) in thf (40 ml) cooled to 0°C was added solid mercuric chloride (0.720 g, 2.66 mmol) in small portions. The mixture was allowed to warm to room temperature and stirred for a further 30 min. Volatiles were removed *in vacuo* at room temperature and the residual oily grey solid extracted with pentane (3 × 25 ml). The extract was filtered through Celite on a frit, the yellow filtrate pumped to dryness, and the residue sublimed *in vacuo* (10^{-2} mbar/70°C) on to a dry ice cooled probe to afford a mixture of 1,4- and 1,6-bis(trimethylsilyl)cyclooctatetraene as white crystals. Yield 0.45 g, 68%.

Mass spectrum (EI): m/z 248 (M^+, 45%).

^1H NMR ($CDCl_3$, 360 MHz), **4a**: δ 6.17 (2H, s, ring $CH_{2,3}$), 5.95–5.75 (4H, m, ring $CH_{5,6,7,8}$), 0.10 (18H, s, $Si(CH_3)_3$).

^1H NMR ($CDCl_3$, 360 MHz), **4b**: δ 6.00–5.85 (4H, m, ring $CH_{2,3,4,5}$), 5.92 (2H, s, ring $CH_{7,8}$), 0.08 (18H, s, $Si(CH_3)_3$.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.54 MHz), **4a** and **4b**: δ 149 (ring C–$SiMe_3$), 148 (ring C–$SiMe_3$), 140 (ring CH), 139 (ring CH), 135 (ring CH), 133 (ring CH), 132 (ring CH), 129 (ring CH), −1.5 ($Si(CH_3)_3$), −1.7 ($Si(CH_3)_3$).

3.5. Preparation of 2,5,5,8-tetrakis(trimethylsilyl)cycloocta-1,3,6-triene (5)

To a stirred solution of [Li(thf)0.75]2$[C_8H_6\{1,4-(SiMe_3)_2\}]$ (0.50 g, 1.58 mmol) in thf (30 ml) cooled to −30°C was added dropwise a solution of chlorotrimethylsilane (1.03 g, 9.5 mmol) in thf (10 ml). The mixture was allowed to warm to room temperature and stirred for a further 2 h. Volatiles were removed *in vacuo* at room temperature and the residue sublimed *in vacuo* (10^{-2} mbar/80°C) on to a dry ice-cooled probe to afford 2,5,5,8-tetrakis(trimethylsilyl)cycloocta-1,3,6-triene as white crystals. Yield 0.44 g, 70%.

Mass spectrum (EI): m/z 394 (M^+, 24%). M.Pt. 95°C.

^1H NMR (C_6D_6, 360 MHz): δ 6.39 (1H, dt, ring CH_a), 5.62 (1H, dd, ring CH_b), 5.52 (1H, dd, ring CH_c), 5.30 (1H, dt, ring CH_d), 5.22 (1H, dq, ring CH_e), 4.53 (1H, td, ring CH_f), 0.20 (9H, s, $Si(CH_3)_3$), 0.17 (9H, s, $Si(CH_3)_3$), 0.15 (9H, s, $Si(CH_3)_3$), 0.05 (9H, s, $Si(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (C_6D_6, 90.54 MHz): δ 145.9 (ring CH), 143.6 (ring C–$SiMe_3$), 133.4 (ring CH), 131.3 (ring CH), 129.3 (ring CH), 126.6 (ring CH), 37.6 (ring C–$(SiMe_3)_2$), 30.33 (ring CH), −1.22 ($Si(CH_3)_3$, −1.29 ($Si(CH_3)_3$), −1.32 ($Si(CH_3)_3$, −3.05 ($Si(CH_3)_3$).

Acknowledgments

We thank SERC (NCB, SCPJ), BP (SCPJ) and the Iraqi Government (AAS) for support.

References

1 P. Jutzi, D. Kanne and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, *25* (1986) 164.

2 J.E. Bercaw, *J. Am. Chem. Soc.*, *96* (1974) 5087; F.G.N. Cloke and J.P. Day, *J. Chem. Soc., Chem. Commun.*, (1985) 967.

3 W.J. Evans, L.A. Hughes and T.P. Hanusa, *J. Am. Chem. Soc.*, *106* (1984) 4270; T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, *19* (1980) 2999; J.M. Manriquez, P.J. Fagan and T.J. Marks, *J. Am. Chem. Soc.*, *100* (1978) 3939.

4 J.G. Brennan, F.G.N. Cloke, A.A. Sameh and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, (1987) 1668.

5 P.B. Hitchcock, M.F. Lappert, R.G. Smith, R.A. Bartlett and P.P. Power, *J. Chem. Soc., Chem. Commun.*, (1988) 1007.

6 M.S.J. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Riviere and M. Riviere-Bandet, *J. Chem. Soc., Dalton Trans.*, (1977) 2004.

7 M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Chem. Commun.*, (1981) 1190 and 1191.

8 M.J. Miller, M.H. Lyttle and A. Streitweiser, *J. Org. Chem.*, *46* (1981) 1977.

9 P. de Mayo and R.W. Yip, *Proc. Chem. Soc.*, (1964) 84.

10 N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos and A.A. Sameh, *J. Chem. Soc., Chem. Commun.*, (1989) 1463.

11 J.M. Bellama and J.B. Davison, *J. Organomet. Chem.*, *86* (1975) 69.

12 W. Gausing and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, *17* (1978) 371.

13 R.H. Cox, H.W. Terry and L.W. Harrison, *J. Am. Chem. Soc.*, *93* (1971) 3297.

14 M.H. Lyttle, A. Streitweiser and R.Q. Kluttz, *J. Am. Chem. Soc.*, *103* (1981) 3232.