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Quantitative transfer of a methyl group from a methyl(hydrido)iridium complex to $SiRH_3$ (R = *n*-butyl, pentyl or hexyl) to give $SiR(Me)H_2$ and a dihydridoiridium complex

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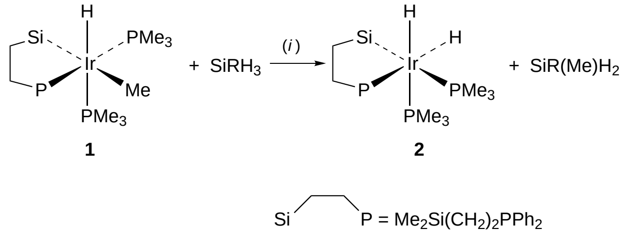
Thermal reaction of $[Ir(Me)(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ with $SiRH_3$ (R = *n*-butyl, pentyl or hexyl) resulted in silicon–carbon bond formation to give $SiR(Me)H_2$ and $[IrH_2\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$. Isolation of $Si(n\text{-}C_6H_{13})MeH_2$ was achieved by preparative gas chromatography.

Stoichiometric conversion of alkyl(hydrido) complexes into functionalised organic compounds can be an important preliminary to development of the transition-metal-catalysed alkane functionalisation reactions.[1] Only a very limited number of such conversions have been reported. In 1983, Janowicz and Bergman[2] found that treatment of $[IrR(H)(\eta\text{-}C_5Me_5)(PMe_3)]$ with bromoform followed by $HgCl_2$ led to the formation of $[IrBr(Cl)(\eta\text{-}C_5Me_5)(PMe_3)]$ and HgR(Cl), and the latter gave RBr by adding bromine. Baker and Field[3] reported that $[Fe(C_5H_{11})H(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) was transformed to 1-bromopentane by direct treatment with bromine. We report here a new reaction in which the methyl group of $[IrMe(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$[4] is stoichiometrically transferred to $SiRH_3$ (R = *n*-butyl, pentyl or hexyl) to give $SiR(Me)H_2$ and $[IrH_2\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$.

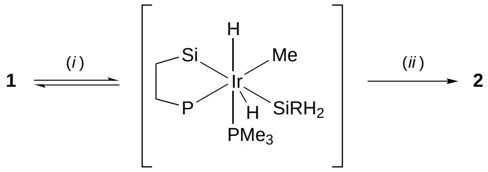
Results and Discussion

Treatment of $[IrMe(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **1** with 1 equivalent of $SiRH_3$ (R = *n*-butyl, pentyl or hexyl) in C_6D_6 at 45 °C led to the almost exclusive formation of $[IrH_2\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **2** and $SiR(Me)H_2$ within 1 h (Scheme 1). After removal of volatiles, recrystallisation from toluene–hexane afforded colourless crystals of **2** in 71% isolated yield. Complex **2** was independently synthesized by the reaction of $[IrCl(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ with $LiAlH_4$ in tetrahydrofuran (thf). The IrH signals appear in the ^1H NMR spectrum as two doublets of triplets at δ −11.70 [$J(HP_{trans}) = 114.0$, $J(HP_{cis}) = 16.5$] and −12.62 [$J(HP_{trans}) = 108.0$, $J(HP_{cis}) = 21.0$ Hz] split by P–H couplings. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits signals of three inequivalent mutually coupled phosphorus atoms with nearly identical *cis* P–P coupling constants, which establishes that **2** possesses three phosphorus atoms in a *fac* relationship. The IR, mass spectral and analytical data are also consistent with the composition shown in Scheme 1. Isolation of $Si(n\text{-}C_6H_{13})MeH_2$ in 52% yield was carried out by preparative gas chromatography. Characterisation of all the compounds of type $SiR(Me)H_2$ was based on comparison of the NMR spectra with the authentic samples synthesized by $LiAlH_4$ reduction of $SiR(Me)Cl_2$. Only recently, Aizenberg and Milstein[5] reported that when $[IrMe(H)(SiEt_3)(PMe_3)_3]$ was heated to 100 °C not only C–H but also Si–C reductive elimination occurred to give CH_4 and $SiMeEt_3$. The ratio of CH_4 to $SiMeEt_3$ was about 4 : 1. Our reaction in Scheme 1 is the first clean transformation of an alkyl(hydrido) complex into a silicon-containing organic product. Transition-metal-mediated Si–C bond formation reactions have attracted increasing attention in relation to the catalytic transformation of hydrosilane.[6]

A conventional mechanism for the reaction in Scheme 1 involving oxidative addition/reductive elimination can be considered, as shown in Scheme 2. According to Scheme 2, carbon–silicon reductive elimination has to occur preferentially over carbon– or hydrogen–hydrogen reductive elimination. This assumption is in contradiction to the usual tendency of reductive elimination,[7] although we cannot rule out this mechanism.



Scheme 1 R = *n*-butyl, pentyl or hexyl. (*i*) C_6D_6, 1 h, 45 °C

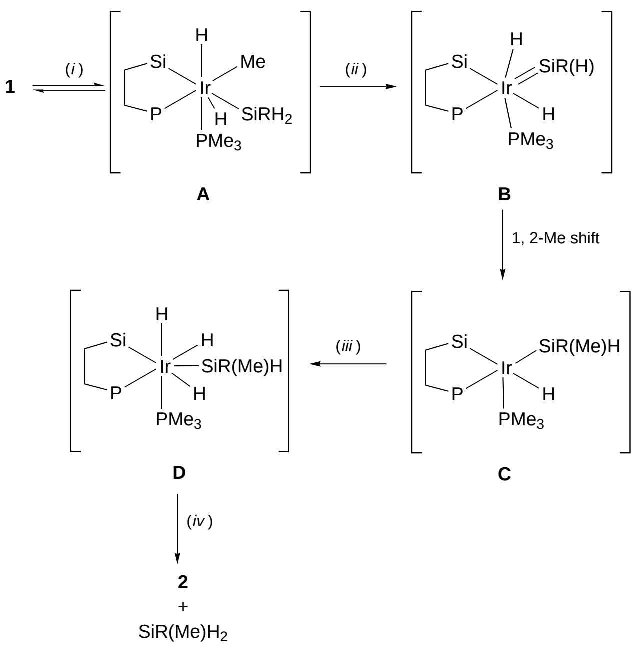


Scheme 2 R = *n*-butyl, pentyl or hexyl. (*i*) $+SiRH_3$, $-PMe_3$; (*ii*) $+PMe_3$, $-SiR(Me)H_2$

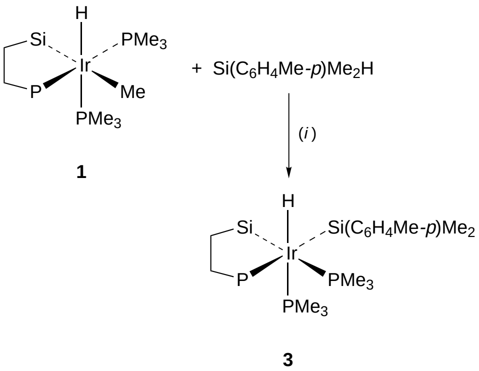
An alternative mechanism is illustrated in Scheme 3. This involves the initial generation of a seven-co-ordinate iridium(V) intermediate **A** by dissociation of a PMe_3 ligand and subsequent Si–H oxidative addition. Similar seven-co-ordinate trihydridobis(silyl)-iridium(V)[8] and -rhodium(V)[9] complexes have been reported recently. The intermediate **A** eliminates dihydrogen to give a methylsilylene intermediate **B**.[10] Intermediate **B** undergoes a 1,2 shift of the Me ligand to the silylene silicon atom to give a hydrido(methylsilyl)iridium(III) complex **C**.[11] Berry *et al.*[12] reported facile migration of a silyl ligand from tantalum to an alkylidene at −10 °C. Oxidative addition of H_2 to **C** gives a seven-co-ordinate iridium(V) species **D**, which subsequently eliminates $SiR(Me)H_2$ and binds a PMe_3 to give **2**.

Reaction of compound **1** with $Si(n\text{-}C_5H_{11})H_3$ in the presence of PMe_3 (5 equivalents) was carried out. The Si–C bond formation was completely inhibited. This means that the reaction in Scheme 1 requires the initial dissociation of a PMe_3 ligand.

We carried out the thermal reaction of compound **1** with a monohydrosilane $Si(C_6H_4Me\text{-}p)Me_2H$ from which it is impossible to generate a silylene moiety *via* dehydrogenation as illustrated in Scheme 3. In contrast to the reaction with trihydrosilanes in Scheme 1 (at 45 °C, 1 h) the reaction with $Si(C_6H_4Me\text{-}p)Me_2H$ was extremely slow at 45 °C. At 55 °C it proceeded almost quantitatively to give $[IrH\{Si(C_6H_4Me\text{-}p)\text{-}$



Scheme 3 R = *n*-butyl, pentyl or hexyl. (*i*) $+SiRH_3$, $-PMe_3$; (*ii*) $-H_2$; (*iii*) $+H_2$; (*iv*) $+PMe_3$



Scheme 4 (*i*) C_6D_6, 6 h, 55 °C, −MeH

$Me_2\}\{\eta^2-Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **3** within 6 h (Scheme 4). Crystallisation from toluene–hexane gave colourless crystals in 82% isolated yield. The formation of methane was confirmed by ^1H NMR spectroscopy (δ 0.15 in C_6D_6). The Si–C bond formation product $Si(C_6H_4Me$-*p*$)Me_3$ and **2** were not detected spectroscopically. These results indicate that the rate-determining step of the reaction needs a condition slightly more drastic than that in Scheme 1, but even under the conditions 55 °C, 6 h Si–C reductive elimination does not occur at all. These observations favour the mechanism in Scheme 3 involving the silylene intermediate for the metal-mediated silicon–carbon bond formation reaction in Scheme 1.

We are now trying to apply this stoichiometric reaction to the transition-metal catalysed hydrosilane–alkane dehydrogenative coupling reactions.

Experimental

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade toluene, hexane and thf were distilled from sodium–benzophenone immediately before use. $[^2H_6]$Benzene was dried over a potassium mirror and transferred to NMR tubes under vacuum. The compounds $SiRH_3$ (R = *n*-C_4H_9, C_5H_{11} or C_6H_{13}), $SiR(Me)H_2$ (R = *n*-C_4H_9, C_5H_{11} or C_6H_{13}) and $Si(C_6H_4Me$-*p*$)Me_2H$ were prepared by $LiAlH_4$ reduction of the appropriate chlorosilane. Other chemicals were from Wako Pure Chemical Industries, used as received. All NMR spectra were recorded on a Bruker ARX-300 spectrometer, ^1H referenced to residual internal C_6D_5H at δ 7.15, ^{29}Si by the distortionless enhancement of polarisation transfer (DEPT) pulse sequence, and chemical shifts were measured relative to internal tetramethylsilane. In ^{31}P NMR spectra the chemical shifts were relative to external 85% H_3PO_4 with downfield values reported as positive. The IR spectra were recorded on a Bruker IFS66v spectrometer.

Reaction of $[IrMe(H)\{\eta^2-Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ 1 with $Si(n-C_6H_{13})H_3$

A Pyrex NMR tube (5 mm outside diameter) was charged with compound **1** (7.0 mg, 0.011 mmol) and $Si(n-C_6H_{13})H_3$ (1.7 µl, 0.011 mmol) and C_6D_6 (0.7 cm^3) was introduced to the tube under high vacuum by the trap-to-trap transfer technique. The tube was flame-sealed. The sample was placed in an oil-bath, where it was kept at 45 °C. The reaction was monitored by ^1H, ^{31}P and ^{29}Si NMR spectroscopy. After 1 h at 45 °C the clean formation of $[IrH_2\{\eta^2-Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **2** and $Si(n-C_6H_{13})MeH_2$ was confirmed spectroscopically. Isolation of **2** was carried out as follows. A Pyrex tube (10 mm outside diameter) was charged with **1** (320 mg, 0.506 mmol) and $Si(n-C_6H_{13})H_3$ (60 mg, 0.516 mmol), and benzene (0.8 cm^3) was introduced under high vacuum by the trap-to-trap transfer technique. This tube was flame-sealed. The sample was placed in an oil-bath, where it was kept at 45 °C for 1 h. The tube was opened in a glove-bag, and the solution concentrated under high vacuum. Crystallisation of the residue from toluene–hexane afforded colourless crystals of **2** (222 mg, 0.36 mmol, 71%) (Found: C, 43.78; H, 6.26. $C_{22}H_{52}IrP_3Si\cdot0.125C_6H_5CH_3$ requires C, 43.66; H, 6.57%). The molar ratio of the complex **2** to the associated toluene was confirmed by ^1H NMR data: *m/z* 618 (M^+, 10) and 616 ($M - 2$ H, 100%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 2021, 1996 (IrH); δ_H(300 MHz, C_6D_6) 7.74–7.67, 7.56–7.50, 7.16–6.94 (10 H, m, aryl), 2.59, 1.86 (1 H × 2, m, PCH_2), 1.32 [9 H, d, *J*(HP) 7.4, PMe_3], 1.08 [3 H, d, *J*(HP) 1.5, SiMe], 1.10, 0.73 (1 H × 2, m, $SiCH_2$), 1.02 [9 H, d, *J*(HP) 8.0, PMe_3], 0.75 [3 H, d, *J*(HP) 4.8, SiMe], −11.70 [1 H, dt, $J(HP_{trans})$ 114.0, $J(HP_{cis})$ 16.5, IrH] and −12.62 [1 H, dt, $J(HP_{trans})$ 108.0, $J(HP_{cis})$ 21.0, IrH]; δ_C(75.5 MHz, C_6D_6) 141.4, 140.0, 132.7, 132.0, 128.9, 128.2, 127.8, 127.7 (aryl), 36.6 [dd, *J*(CP) 37.7, 11.2, PCH_2], 26.4 [dt, *J*(CP) 24.8, 3.5, PMe_3], 23.5 [ddd, *J*(CP) 28.2, 5.7, 3.5, PMe_3], 21.1 [dd, *J*(CP) 23.3, 6.1, $SiCH_2$], 14.5 [ddd, *J*(CP) 8.8, 6.0, 1.3, SiMe] and 7.2 [ddd, *J*(CP) 8.5, 3.2, 2.0, SiMe]; δ_P(121.5 Hz, C_6D_6) −62.3 [dd, $J(PP_{cis})$ 23.1, 17.0, PMe_3 (*trans* to IrSi)], −57.0 [dd, $J(PP_{cis})$ 23.1, 20.7, PMe_3 (*trans* to IrH)], 35.1 [dd, $J(PP_{cis})$ 17.0, 20.7, PPh_2]; δ_{Si}(59.6 MHz, C_6D_6) 14.7 [ddd, $J(SiP_{trans})$ 120.8, $J(SiP_{cis})$ 9.6, 6.7 Hz].

Reaction of compound 1 with $Si(n-C_4H_9)H_3$ or $Si(n-C_5H_{11})H_3$

The procedure was the same as that with $Si(n-C_6H_{13})H_3$ described above. The quantitative formation of compound **2** and the corresponding methyldihydrosilanes were also confirmed spectroscopically.

Purification of $Si(n-C_6H_{13})MeH_2$ produced in the reaction of compound 1 with $Si(n-C_6H_{13})H_3$

A Pyrex tube (10 mm outside diameter) was charged with compound **1** (320 mg, 0.506 mmol) and $Si(n-C_6H_{13})H_3$ (60 mg, 0.516 mmol) and benzene (0.8 cm^3) introduced under high vacuum by the trap-to-trap transfer technique. The tube was flame-sealed. The sample was placed in an oil-bath, where it was kept at 45 °C for 1 h. The tube was opened in a glove-bag, and the solution passed through a short silica gel column to remove the iridium complex. The filtrate was injected into a preparative gas chromatograph to give pure $Si(n-C_6H_{13})MeH_2$. Yield 34 mg (52%).

Synthesis of $[IrH_2\{\eta^2-Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ 2

Tetrahydrofuran (50 cm^3) was added to $[IrCl(H)\{\eta^2$-

Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$][4] (0.20 g, 0.31 mmol) and LiAlH$_4$ (0.12 g, 3.4 mmol) at −48 °C, and the mixture was slowly warmed to room temperature. It was stirred at room temperature for 2 h. Volatile materials were removed under reduced pressure, and the residue was extracted by toluene–hexane (2 : 1). The extract was filtered through an alumina column and the solvent removed from the filtrate under reduced pressure. Recrystallisation of the residue from toluene–hexane afforded [IrH$_2${η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$] **2** (0.11 g, 0.18 mmol, 58% yield) as colourless crystals.

Reaction of compound 1 with Si(n-C$_5$H$_{11}$)H$_3$ in the presence of PMe$_3$

A Pyrex NMR tube (5 mm outside diameter) was charged with compound **1** (10.0 mg, 0.0158 mmol), Si(n-C$_5$H$_{11}$)H$_3$ (3 mg, 0.029 mmol) and PMe$_3$ (8.2 μl, 0.079 mmol) and C$_6$D$_6$ (0.7 cm^3) was introduced under high vacuum by the trap-to-trap transfer technique. The NMR tube was flame-sealed. The sample was warmed up to 45 °C in an oil-bath and kept for 1 h. No change was observed in ^{1}H and ^{31}P-{^{1}H} NMR spectra.

Reaction of compound 1 with Si(C$_6$H$_4$Me-p)Me$_2$H

A Pyrex NMR tube was charged with compound **1** (10.0 mg, 0.0158 mmol) and Si(C$_6$H$_4$Me-p)Me$_2$H (2 equivalents, 5 mg) and C$_6$D$_6$ (0.7 cm^3) was introduced into the tube under high vacuum by the trap-to-trap transfer technique. The NMR tube was flame-sealed. The thermal reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy (45 to 55 °C). No change was observed spectroscopically at 45 °C for 1 h. At 55 °C for 6 h the clean formation of [IrH{Si(C$_6$H$_4$Me-p)Me$_2$}{η^2-Me$_2$Si(CH$_2$)$_2$-PPh$_2$}(PMe$_3$)$_2$] **3** was observed. It was isolated as follows. A Pyrex tube (10 mm outside diameter) was charged with **1** (0.25 g, 0.40 mmol) and Si(C$_6$H$_4$Me-p)Me$_2$ (60 mg, 0.40 mmol) and toluene (3 cm^3) was introduced by the trap-to-trap transfer technique. The sample was placed in an oil-bath, where it was kept at 55 °C for 6 h. The tube was opened in a glove-box. Removal of volatiles under reduced pressure resulted in a colourless oily residue. Recrystallisation of the residue from toluene–hexane gave **3** (0.25 g, 0.33 mmol, 82% yield) as colourless crystals (Found: C, 48.61; H, 6.95. C$_{31}$H$_{52}$IrP$_3$Si$_2$ requires C, 48.60; H, 6.84%); m/z 766 ($M^+ - 2$) and 616 [M − Si(C$_6$H$_4$-Me-p)Me$_2$H, 100%]; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2031 (IrH); δ_H(300 MHz, C$_6$D$_6$) 8.25–8.21, 7.66–7.57, 7.30–7.27, 7.12–6.89 (14 H, m, aryl), 2.27 (3 H, s, C$_6$H$_4$CH_3), 2.20, 1.95 (1 H × 2, m, PCH$_2$), 1.13 [3 H, d, J(HP) 1.8, SiMe], 1.10 [9 H, d, J(HP) 7.4, PMe$_3$], 1.06 [3 H, d, J(HP) 1.9, SiMe], 1.05, 0.70 (1 H × 2, m, SiCH$_2$), 0.97 [3 H, d, J(HP) 2.0, SiMe], 0.96 [9 H, d, J(HP) 7.3, PMe$_3$], 0.69 [3 H, d, J(HP) 2.2, SiMe] and −12.41 [1 H, dt, J(HP$_{trans}$) 101.2, J(HP$_{cis}$) 17.0, IrH]; δ_C(75.5 MHz, C$_6$D$_6$) 148.3, 141.3, 136.7, 135.8, 135.7, 133.6, 132.2, 129.9, 129.1, 128.5, 128.2, 128.1 (aryl), 35.0 [dd, J(CP) 35.5, 10.4, PCH$_2$], 24.9 [ddd, J(CP) 24.8, 4.5, 2.6, PMe$_3$], 23.2 [dt, J(CP) 27.8, 4.6, PMe$_3$], 21.5 [dd, J(CP) 28.5, 5.4, SiCH$_2$], 21.4 (s, C$_6$H$_4$$CH_3$), 13.2 [t, J(CP) 5.0 Hz, SiMe], 12.3 [t, J(CP) 6.0, SiMe], 11.5 [ddd, J(CP) 8.9, 6.9, 3.2, SiMe] and 7.2 [dd, J(CP) 7.6, 3.5, SiMe]; δ_P(121.5 MHz, C$_6$D$_6$) 27.7 [dd, J(PP$_{cis}$) 25.5, 19.4, PPh$_2$], −70.8 [dd, J(PP$_{cis}$) 25.5, 24.3, PMe$_3$ (*trans* to Si)] and −62.4 [dd, J(PP$_{cis}$) 19.4, 24.3, PMe$_3$ (*trans* to IrH)]; δ_{Si}(59.6 MHz, C$_6$D$_6$) 9.7 [ddd, J(SiP$_{trans}$) 114.4, J(SiP$_{cis}$) 10.7, 7.2] and −16.1 [ddd, J(SiP$_{trans}$) 122.8, J(SiP$_{cis}$) 14.3, 10.1 Hz].

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References

1 B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154.
2 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929.
3 M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1987, **109**, 2825.
4 M. Okazaki, H. Tobita and H. Ogino, *Organometallics*, 1996, **15**, 2790.
5 M. Aizenberg and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 6456.
6 P. Braunstein and M. Knorr, *J. Organomet. Chem.*, 1995, **500**, 21.
7 S. Sakaki and M. Ieki, *J. Am. Chem. Soc.*, 1993, **115**, 2373.
8 M. Loza, J. W. Faller and R. H. Crabtree, *Inorg. Chem.*, 1995, **34**, 2937.
9 H. Nagashima, K. Tatebe, T. Ishibashi, A. Nakaoka, J. Sakakibara and K. Itoh, *Organometallics*, 1995, **14**, 2868.
10 H. Handwerker, C. Leis, R. Probst, P. Bissinger, A. Grohman, P. Kiprof, E. Herdtweck, J. Blümel, N. Auner and C. Zybill, *Organometallics*, 1993, **12**, 2162; B. P. S. Chauhan, R. J. P. Corriu, G. F. Lanneau and C. Priou, *Organometallics*, 1995, **14**, 1657.
11 H. Sharma and K. H. Pannell, *Chem. Rev.*, 1995, **95**, 1351.
12 D. H. Berry, T. S. Koloski and P. J. Carroll, *Organometallics*, 1990, **9**, 2952.

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