Isomer differentiation by tri-osmium cluster complexation of substituted 1,3-cyclohexadienes

S.L. Ingham, B.F.G. Johnson [*,1], I.H. Sadler, J.G.M. Nairn

Department of Chemistry, University of Edinburgh, King's Buildings, West Main's Road, Edinburgh EH9 3JJ, UK

Abstract

A series of methyl- and dimethyl-substituted 1,3-cyclohexadienes have been prepared from their aromatic analogues via Birch reduction and subsequent isomerisation with $Fe(CO)_x$ fragments. These ligands were reacted with $[Os_3(CO)_{10}(CH_3CN)_2]$ to form tri-osmium decacarbonyl cluster compounds containing the η^4-coordinated substituted 1,3-cyclohexadienes. The various isomers of the substituted dienes show a dramatic difference in their reactivity towards the tri-osmium cluster and it is likely that this is due to the steric interactions between the methyl substituents and the cluster framework, with this effect being more marked for the di-substituted ligands.

Keywords: Cluster; Isomerism; Birch reduction; Methyl

1. Introduction

In 1985 the cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ (1) was prepared [1], in which the $[\mu_3\text{-}\eta^2\text{:-}\eta^2\text{:}\eta^2\text{-}C_6H_6]$ ligand demonstrated a striking resemblance to benzene adsorbed on Rh(III) [2] and Os(001) [3] single crystal surfaces. Since this initial investigation, a large number of ruthenium and osmium clusters have been prepared containing bound benzene ligands, either in the μ_3-face capping mode [4] as found in (1), or the more commonly observed η^6-terminal geometry [5]. To date, two main synthetic strategies have been employed in the formation of these arene-containing compounds. The first involves the ionic-coupling between a cationic mononuclear electrophile, such as $[(C_6H_6)Os(CH_3CN)_3]^{2+}$, and di-anionic cluster [6]. Whilst the second involves the direct reaction of an appropriate organic substrate (usually a diene) with a metal carbonyl cluster [7], resulting in coordination of the substrate. This latter method has been particularly successful with the ligands 1,3-cyclohexadiene and 1,4-cyclohexadiene, as these generally provide a simple synthetic pathway involving first the coordination of the diene moiety, followed by dehydrogenation to provide the cluster-bound arene [8]. However, it has been noted that 1,4-cyclohexadiene does not react with such a large variety of ruthenium and osmium clusters, in contrast to 1,3-cyclohexadiene. Furthermore, it has been observed that on reaction with $[Ru_6C(CO)_{17}]$ in the presence of $(CH_3)_3NO$ isomerisation of 1,4-cyclohexadiene to the 1,3-isomer occurs [9]. It is interesting to note that, to date, the only clusters isolated with the ligand 1,4-cyclohexadiene directly coordinated are those based on the pentanuclear ruthenium cluster $[Ru_5C(CO)_{15}]$, where it is apparent that the geometry of the cluster allows efficient coordination without isomerisation [10]. Whilst there has been a relatively thorough investigation of the reactivity of both 1,4- and 1,3-cyclohexadienes towards ruthenium and osmium clusters, this is in marked contrast to their substituted analogues, which to date have received little attention. In this paper we report the synthesis and characterisation of a series of tri-osmium clusters with bound mono- and di-substituted 1,3-cyclohexadiene ligands and discuss the effect that substitution has on the coordination ability of these ligands.

2. Results and discussion

Whilst substituted 1,4-cyclohexadienes may be prepared by Birch reduction [11], substituted 1,3-cyclohexadienes are not so readily available and in general

* Corresponding author.
[1] Present address: University Chemical Laboratory, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW.

must be prepared by isomerisation of the substituted 1,4-analogues. There have been several methods reported for the conversion of 1,4- to 1,3-cyclohexadienes [12]. However, in our hands we found that these methods are neither generally applicable nor reproducible. The method we chose for the preparation of the substituted 1,3-cyclohexadienes involved the coordination and concomitant isomerisation of the analogous 1,4-isomers with an $Fe(CO)_3$ fragment [13]. The uncoordinated substituted 1,3-cyclohexadienes were then obtained by oxidative removal of the iron moiety with Ce(IV) [14]. Using this synthetic strategy, 1,3-cyclohexadiene analogues of toluene, *ortho*-xylene, *meta*-xylene and *para*-xylene were prepared. This method of isomerisation results in the formation of a mixture of isomers, with the isomer distribution resulting from both the reduction of the arene to the 1,4-cyclohexadiene and on coordination to the $Fe(CO)_3$ fragment. The regiochemistry of Birch reduction of benzene derivatives has been thoroughly studied, with electron-donating substituents generally occupying a vinyl position in the product. This behaviour follows the 'Birch rule' [15], which states "electron-donating substituents direct reduction so that the major product has the maximum number of such groups attached to the residual double bonds, and a minimum of these groups are located at the allylic sites". This rule also applies to the isomerisation when isomerisation from 1,4- to 1,3-cyclohexadienes occurs on coordination to the $Fe(CO)_3$ unit. However, the degree of differentiation between possible isomers is not as significant. For example, it has been shown that Birch reduction of toluene yields only one product in any appreciable amount. In contrast, on coordination to an $Fe(CO)_3$ fragment, all possible isomeric derivatives are observed (Scheme 1) [16].

The $Fe(CO)_3$ unit may be readily removed by treatment of a pentane solution of the iron complex with an ammonium cerium(IV) nitrate solution. In this work no attempt has been made to isolate or purify the free ligand mixture, but these were generated in situ for subsequent reaction. An excess of the mixture of iso-
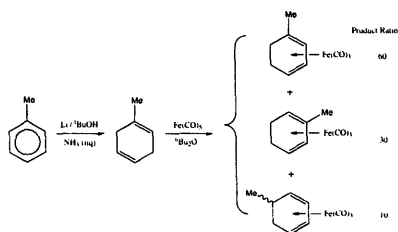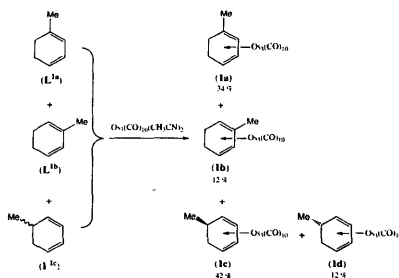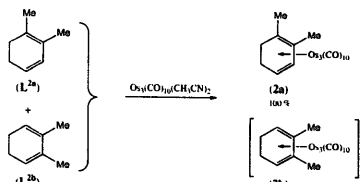
Scheme 2. Product distribution for reaction of 1,4-cyclohexadiene derivatives of toluene and $[Os_3(CO)_{10}(CH_3CN)_2]$.
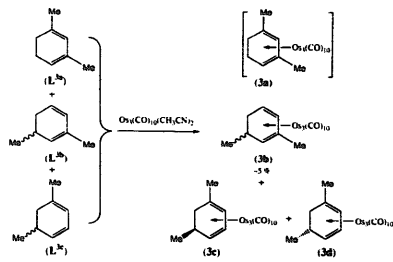
mers consisting of 1-methyl-1,3-cyclohexadiene (L^{1a}), 2-methyl-1,3-cyclohexadiene (L^{1b}) and 5-methyl-1,3-cyclohexadiene (L^{1c}), prepared from toluene in the above manner, reacts cleanly with $[Os_3(CO)_{10}(CH_3CN)_2]$, to yield after purification, a yellow solid $[Os_3(CO)_{10}(L^1)]$ (1) as the only isolable product. Spectroscopic evidence indicates that the ligand is coordinated in a η^4-fashion as previously reported for the unsubstituted 1,3-cyclohexadiene cluster $[Os_3(CO)_{10}(\eta^4-C_6H_8)]$ [17]. However, from the ^1H NMR spectrum of (1), it is apparent that the isolated solid contains a mixture of four isomers (1a–1d), which are present in the ratio 1.0:2.9:3.5:1.0. These four isomers, the structures depicted in Scheme 2, have been assigned on the basis of decoupling experiments and confirmed by selective nOe experiments. It is noteworthy that the relative amounts of the different isomers 1a–1d do not reflect the ratio of isomers observed for the uncoordinated ligands L^{1a}–L^{1c}. For example, 1-methyl-1,3-cyclohexadiene (L^{1a}) is formed in the largest amount, but on coordination, cluster 1a is observed as the lowest ratio isomer. In contrast, the ligand 5-methyl-1,3-cyclohexadiene (L^{1c}), formed as only 10% of the isomeric mixture of uncoordinated dienes, gives clusters 1c and 1d as the major components on coordination. The two compounds (1c and 1d) obtained on coordination of the racemic mixture of enantiomers of the ligand (L^{1c}) differ with the arrangement of the methyl substituent either *exo* or *endo* with respect to the cluster framework. The latter two isomers could not be unambiguously assigned, however, in view of the increased steric interactions that would be experienced between the methyl substituent of the ligand and the cluster framework for the *endo* isomer, it is reasonable to assign the predominant isomer to that of the *exo* product.

Using the methodology outlines above, *ortho*-, *meta*- and *para*-xylene was converted to their respective 1,4-cyclohexadiene analogues. These were then further iso-

Scheme 3. Product distribution for reaction of 1,4-cyclohexadiene derivatives of *ortho*-xylene and [Os₃(CO)₁₀(CH₃CN)₂].

Scheme 4. Product distribution for reaction of 1,4-cyclohexadiene derivatives of *meta*-xylene and [Os₃(CO)₁₀(CH₃CN)₂].

merised on coordination to, and subsequent removal of, the Fe(CO)₃ fragment to give a complex mixtures of isomers as determined by NMR spectroscopy. An excess of these ligand mixtures reacted cleanly with [Os₃(CO)₁₀(CH₃CN)₂] to give a series of yellow compounds, formulated on the basis of IR and ¹H NMR spectroscopy as the derivatives [Os₃(CO)₁₀{μ⁴-1,3-diene}].

On reduction and isomerisation of *ortho*-xylene the major isomer obtained was 1,2-dimethyl-1,3-cyclohexadiene (L²ᵃ), with only small amounts of 2,3-dimethyl-1,3-cyclohexadiene (L²ᵇ) being formed. This isomer

Table 1
¹H NMR assignments for complexes **1a–1d** (600 MHz; CDCl₃)

	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
H^A	4.90	1H, d (3.8)	6.23	1H, d (6.8)
H^B	5.99	1H, ddd (7.1, 3.8, 1.2)	3.41	1H, dt (6.8, 2.7)
H^C	3.63–3.69 ᵈ	1H, m ᵈ	1.74–1.89 ᵈ	1H, m ᵈ
$H^{C'}$	--	--	1.74–1.89 ᵈ	1H, m ᵈ
$H^D/H^{D'}$	— ᵈ	— ᵈ	2.01–2.08	2H, m
H^E	— ᵈ	— ᵈ	3.80–3.82	1H, m
$H^{E'}$	— ᵈ	— ᵈ	—	—
H^F	2.32	3H, s	1.87	3H, s

	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
H^A	3.63–3.65	1H, m	3.55	1H, dt (6.8, 1.6)
H^B	5.58–5.59	1H, m	5.87–5.89	1H, m
H^C	5.55–5.57	1H, m	5.26–5.28	1H, m
H^D	3.66–3.69	1H, m	3.80–3.82	1H, m
$H^E/H^{E'}$	— ᵈ	— ᵈ	— ᵈ	— ᵈ
H^F	2.20–2.29	1H, m ᵈ	1.74–1.89	1H, m ᵈ
H^G	1.07	3H, d (6.6)	0.91	3H, d (6.8)

ᵈ Obscured by other resonances or too weak to measure accurately.
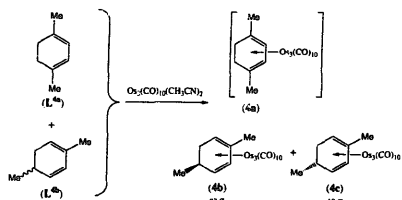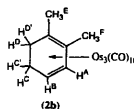
Scheme 5. Product distribution for reaction of 1,4-cyclohexadiene derivatives of *para*-xylene and [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$].

differentiation was also observed on coordination to the osmium cluster, with no evidence found for the formation of the other expected isomer [Os$_3$(CO)$_{10}$(L^{2b})] (**2b**), even in trace amounts (Scheme 3). A mixture of the three possible isomers (L^{3a}–L^{3c}) was obtained on reduction and isomerisation of *meta*-xylene. Subsequent reaction of the ligand mixture with [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] gave as predominant products the *endo* (**3c**) and *exo* (**3d**) isomers, obtained from the coordination of the racemic ligand 1,5-dimethyl-1,3-cyclohexadiene (L^{3c}) as depicted in Scheme 4. In addition there were trace amounts of the cluster (**3b**) which was obtained from the coordination of the racemic ligand 2,6-dimethyl-1,3-cyclohexadiene (L^{3b}). On reduction and isomerisation of *para*-xylene the major product obtained was 1,4-dimethyl-1,3-cyclohexadiene (L^{4a}) with only trace amounts of 2,5-dimethyl-1,3-cyclohexadiene (L^{4b}) observed. Therefore, it is surprising that the subsequent reaction with [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$], gave no product from the coordination of L^{4a} with the tri-osmium cluster (Scheme 5). The isolated product was in fact a mixture of the *exo*

and *endo* isomers **4b** and **4c** formed by the coordination of the enantiomers of L^{4b}, with the *exo* isomer the major product.

The absence of **2b**, may be due in part to the small amount of this isomer present in the uncoordinated ligand mixture. However, as no evidence was obtained for the coordination of the ligands L^{3a} and L^{4a}, despite these being present in significant amounts, it seems likely that steric factors also play a major role in the complexation of the isomer mixtures. There was also significant selectivity between the two enantiomers of L^{3c} and L^{4b} on coordination to the tri-osmium cluster, with the ratio between the *exo* and *endo* products in both cases being 4.6:1.0. The di-substituted 1,3-cyclohexadienes obtained from the reduction and isomerisation *ortho*-, *meta*- and *para*-xylene, showed a greater degree of isomer differentiation than the mono-substituted 1,3-cyclohexadienes obtained from toluene.
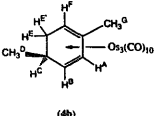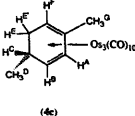
Table 2
^{1}H NMR assignments for complex **2b** (250 MHz; CDCl$_3$)

	δ (ppm)	J (Hz)
H^A	6.11	1H, d (6.8)
H^B	3.35	1H, dt (6.8, 2.5)
H^E	2.33	3H, s
H^D/H$^{D'}$	1.90–2.11	2H, m
H^F	1.87	3H, s
H^C/H$^{C'}$	1.66–1.78	2H, m

Table 3
^{1}H NMR assignments for complex **3b–3d** (250 MHz; CDCl$_3$)
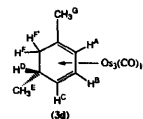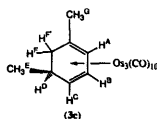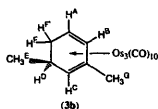
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
H^A	3.28	1H, dt (6.7, ~ 1.5 ^{a})	4.92	1H, dd (3.7, 1.6)	4.89	1H, dd (3.7, ~ 1.6 ^{a})
H^B	6.19	1H, dd (6.7, ~ 1.5 ^{a})	5.96	1H, dd (6.9, 3.7)	6.07	1H, dd (6.9, 3.7)
H^C	3.73	1H, dd (2.5, ~ 1.5 ^{a})	3.55	1H, dt (6.9, 1.6)	3.47	1H, dt (6.9, ~ 1.6 ^{a})
H^D	— ^{a}		2.14–2.26	1H, m	— ^{a}	
H^E	1.16	3H, d (6.8)	0.97	3H, d (6.6)	0.88	3H, d (6.6)
H^F	— ^{a}	— ^{a}	1.55	1H, dd (14.2, 4.1)	— ^{a}	— ^{a}
H^F	— ^{a}	— ^{a}	2.34	1H, dd (14.2, 3.8)	— ^{a}	— ^{a}
H^G	1.86	3H, s	1.81	3H, s	1.42	3H, s

^{a} Obscured by other resonances or too weak to measure accurately.

Table 4
^{1}H NMR assignments for complex **4b** and **4c** (250 MHz; CDCl$_3$)

(4b)   **(4c)**

	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
H^A	6.20	1H, dd (6.7, 1.5)	6.27	1H, dd (6.6, ~ 1.5 [a])
H^B	3.30	1H, dd (6.7,2.5)	3.26	1H, dd (6.6, ~ 2.0 [a])
H^C	1.97–2.09	1H, m	1.68–1.73	1H, m
H^D	0.96	3H, d (6.7)	0.79	3H, d (6.7)
H^E	2.37	1H, td (14.3, 3.9)	2.17–2.28	1H, m
H$^{E'}$	1.54	1H, dd (14.3, 4.0, 1.6)	~ 1.45–1.55 [a]	1H, m
H^F	3.68	1H, dt (3.9, 1.5)	3.80	1H, dt (3.0, ~ 1.5 [a])
H^G	2.35	3H, s	2.28	3H, s

[a] Obscured by other resonances or too weak to measure accurately.

For *ortho*-xylene only one product isomer was obtained (**2a**), whereas for *meta*- and *para*-xylene the isomers **3c** and **4b** were 78% and 82% of the respective isomer mixtures. This relative increase in the degree of differentiation between the possible isomers is most likely due to the greater steric congestion of the di-substituted ligands on coordination to the metal cluster.

The relevant ^{1}H NMR have been assigned on the basis of decoupling and nOe experiments and are tabulated in Tables 1–4. The chemical shift values of the resonances attributable to the diene protons were found to be particularly sensitive to substitution, with the protons in the 1- and 4- positions found in the range 4.89–6.27 ppm and those in the 2- and 3- positions in the range 3.28–3.82 ppm.

However, no obvious correlation could be made between the position of substituents and chemical shift values.

In conclusion we have shown the synthetic use of reversibly adding Fe(CO)$_3$ fragments to effect the isomerisation of substituted 1,4- to 1,3-cyclohexadiene isomerisations. This methodology has been used in the formation of a series of tri-osmium decacarbonyl cluster compounds containing substituted η^4-coordinated 1,3-cyclohexadienes. The various isomers of the substituted dienes show a dramatic difference in their reactivity towards the tri-osmium cluster and it is likely that this is due to the steric interactions between the methyl substituents and the cluster framework, with this effect being more marked for the di-substituted ligands.

3. Experimental

All reactions were performed under an atmosphere of purified dinitrogen by standard Schlenk and vacuum

line techniques [18]. Solvents used were distilled from appropriate drying agents under dinitrogen. Routine separations of products were performed by thin layer chromatography using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 PF$_{254}$. IR spectra were recorded as *n*-pentane solutions on a Perkin–Elmer 1710 Fourier Transform spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-250 or Varian UNITY-600 spectrometer and referenced to tetramethylsilane. Mass spectral data were obtained by the method of fast atom bombardment on a Kratos MS-50 mass spectrometer. The synthesis of the cluster [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] and the substituted 1,3-cyclohexadienes were performed according to published procedures [14,16,19,20].

A typical synthesis of the clusters of general formula [Os$_3$(CO)$_{10}$(η^4-1,3-diene)] was as follows.

To the yellow solution obtained by dissolving 93.3 mg (0.10 mmol) [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] in 50 ml dichloromethane, was added approximately 1 ml (excess) of the appropriate isomer mixture of substituted 1,3-cyclohexadiene. The reaction mixture was stirred at room temperature for 1 h, the solvent and unreacted ligand were then removed at reduced pressure and the yellow residue obtained was purified by thin layer chromatography eluting with a 15% CH$_2$Cl$_2$/*n*-hexane mixture. For each of the respective ligand mixtures, only one isolable product was obtained and characterised by spectroscopic techniques as [Os$_3$(CO)$_{10}$(η^4-1,3-diene)]. The relevant ^{1}H NMR data are tabulated in Table 1, with IR and mass spectral data (calculated M$^+$ based on ^{192}Os) listed: [Os$_3$(CO)$_{10}$(L^1)]; IR {v(CO), cm^{-1}, pentane} 2111(m), 2062(vs), 2032(vs), 2023(vs), 2009(s), 1990(w), 1982(m), 1973(w), 1937(w); mass spectrum {$^+$ve FAB} observed 950 (calculated 950); [Os$_3$(CO)$_{10}$(L^2)]; IR {v(CO), cm^{-1}, pentane} 2110(m),

2062(vs), 2032(vs), 2023(vs), 2010(s), 1991(w), 1982(m), 1967(w), 1929(w); mass spectrum {$^+$ve FAB} observed 964 (calculated 964); [Os$_3$(CO)^{10}(L^3)]; IR {v(CO), cm^{-1}, pentane} 2110(m), 2062(vs), 2031(vs), 2022(vs), 2007(s), 1990(w), 1981(m), 1971(w), 1934(w); mass spectrum {$^+$ve FAB} observed 965 (calculated 964); [Os$_3$(CO)$_{10}$(L^4)]; IR {v(CO), cm^{-1}, pentane} 2111(m), 2062(vs), 2032(vs), 2023(vs), 2011(s), 1991 (w), 1982(m), 1970(w), 1932(w); mass spectrum {$^+$ve FAB} observed 964 (calculated 964).

References

[1] M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby and A.H. Wright, J. Chem. Soc. Chem. Commun., (1985) 1682.

[2] M.A. Van Hove, R.F. Lin and G.A. Somorjai, J. Am. Chem. Soc., 108 (1986) 2532.

[3] F.P. Netzer, H.H. Green, H. Kuhlenbeck and M. Neumann, Chem. Phys. Lett., 133 (1987) 49.

[4] (a) B.F.G. Johnson, J. Lewis, M. Martinelli, A.H. Wright, D. Braga and F. Grepioni, J. Chem. Soc. Chem. Commun., (1990) 364. (b) M.A. Gallop, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1987) 1809. (c) P.J. Bailey, D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, J. Lewis and P. Sabatino, J. Chem. Soc. Chem. Commun., (1992) 177.

[5] (a) B.F.G. Johnson, R.D. Johnston and J. Lewis, J. Chem. Soc. Chem. Commun., (1967) 1057. (b) R. Mason and W.R. Robinson, J. Chem. Soc. Chem. Commun., (1968) 468. (c) L.J. Farrugia, Acta Crystallogr. Sect. C:, 44 (1988) 997. (d) D. Braga, F. Grepioni, B.F.G. Johnson, H. Chen and J. Lewis, J.

Chem. Soc. Dalton Trans., (1991) 2559. (e) R. Adams and W. Wu, Polyhedron, 11 (1992) 2123.

[6] (a) A.T. Brooker, P.A. Jackson, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1991) 707. (b) J. Lewis, C.-K. Li, M.R.A. Al-Mandhary and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1993) 1915.

[7] (a) B.F.G. Johnson, R.D. Johnston and J. Lewis, J. Chem. Soc., 4 (1968) 2865. (b) D. Braga, F. Grepioni, E. Parisini, P.J. Dyson, A.J. Blake and B.F.G. Johnson, J. Chem. Soc. Dalton Trans., (1993) 2951.

[8] (a) H. Chen, B.F.G. Johnson, J. Lewis, D. Braga, F. Grepioni and E. Parisini, J. Chem. Soc. Dalton Trans., (1991) 21. (b) D. Braga, F. Grepioni, P. Sabatino, P.J. Dyson, B.F.G. Johnson, J. Lewis, P.J. Bailey, P.R. Raithby and D. Stalke, J. Chem. Soc. Dalton Trans., (1993) 985.

[9] P.J. Dyson, B.F.G. Johnson, D. Reed, D. Braga, F. Grepioni and E. Parisini, J. Chem Soc. Dalton Trans., (1993) 2817.

[10] P.J. Dyson, B.F.G. Johnson, J. Lewis, D. Braga and P. Sabatino, J. Chem. Soc. Chem. Commun., (1993) 301.

[11] (a) K.G. Harvey, Synthesis, 4 (1970) 161. (b) P.W. Rabideau and Z. Marcinow, Org. React., 42 (1992) 1.

[12] (a) A.J. Pearson, Acc. Chem. Res., 13 (1980) 463. (b) A.J. Birch and G.S.R. Subba Rao, Tetrahedron Lett., 35 (1968) 3797.

[13] B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1958) 642.

[14] D.F. Shriver, H. Fitton and J. Lewis, J. Chem. Soc. Perkin Trans. I:, (1973) 2051.

[15] A.J. Birch, Q. Rev. Chem. Soc., 4 (1950) 69.

[16] A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, J. Chem. Soc. A:, (1968) 332.

[17] E.G. Bryan, B.F.G. Johnson, J.W. Kelland, J. Lewis and M. McPartlin, J. Chem Soc. Chem. Commun., (1976) 254.

[18] D.F. Shriver, Manipulation of Air-Sensitive Compounds, Mc-Graw-Hill, New York, 1969.

[19] S.R. Drake and R. Khattar, Organomet. Synth., 4 (1988) 234.

[20] D.N. Butler and R. Milburn, Can. J. Chem., 50 (1972) 1249.