ELSEVIER

Journal of Organometallic Chemistry 487 (1995) 167–171

Journal of Organometallic Chemistry

Some reactions of metal atoms with arenes illustrating the importance of half sandwich molecules, M(arene), as reaction intermediates

Andrew J. Seeley, Simon Hudson, Paul D. Sykes, W. Burkhard Weise, Peter L. Timms *

School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

Received 31 May 1994

Abstract

Reactions of chromium or molybdenum atoms with mixtures of bromobenzene and other arenes at -196°C have given several new sandwich compounds including $[Cr(C_6H_5Br)(C_6F_6)]$ and $[Mo(C_6H_5Br)(C_6F_6)]$. The work has led to the development of a theory for the mechanism of reaction of metal atoms with arenes which focuses on the redox properties of the coordinatively unsaturated half sandwich intermediate M(arene). The theory is then applied to explain the results of other new and known metal atom–arene reactions.

Keywords: Metal vapour synthesis; Arenes; Chromium; Molybdenum; Hexafluorobenzene; Bromobenzene

1. Introduction

The reaction of transition metal atoms with benzene and other arenes to form bisarenemetal complexes has been one of the most successful applications of metal atom synthetic techniques [1–4]. The mechanism of these reactions has not been studied in detail but there is evidence that they occur stepwise with immediate addition of one arene to give a half-sandwich species $M(\eta^6$-arene), which then adds a second arene ligand to form the final bisarenemetal product [5,6]. Not all metal atom/arene reactions give the desired product. For example, with chromium atoms fluoro- and chlorobenzene give excellent yields of bisarenechromium products, but the analogous reactions of bromobenzene or iodobenzene and chromium atoms do not take place, with oxidation of the chromium occuring instead [7].

We have been studying reactions of metal atoms with hexafluorobenzene [8,9] and other electron poor arenes. We now report some new synthetic work which has enabled us to propose and test a model for the successful preparation of sandwich complexes from metal atoms and arenes.

2. Results and discussion

2.1. New reactions with arenes under cocondensation conditions at -196°C

Cocondensation of chromium atoms and an at least ten-fold excess of bromobenzene and a monosubstituted arene, C_6H_5X ($X = F, CF_3$) on a liquid-nitrogen cooled surface followed by warm-up to room temperature gave mixtures of $[Cr(C_6H_5Br)(C_6H_5X)]$ and $[Cr(C_6H_5X)_2]$ ($X = F, CF_3$). Similarly, mixtures of $[Cr(C_6H_5Br)(C_6H_4X_2\text{-}1,3)]$ and $[Cr(C_6H_4X_2\text{-}1,3)_2]$ resulted from the cocondensation reactions of chromium atoms bromobenzene and the meta-disubstituted arenes, $C_6H_4X_2$ ($X = F, CF_3$). The similarity of the physical and chemical properties of these compounds precluded separation but the compounds were readily identified from their mass spectra. Meaningful NMR studies were hampered by the presence of traces of paramagnetic species which led to line broadening in the ^1H spectra of these mixtures.

Condensation of chromium atoms or molybdenum atoms at -196°C with mixtures of bromobenzene and

---

* Corresponding author.

SSDI 0022-328X(94)05104-6

hexafluorobenzene, followed by warm-up to room temperature, yielded $[Cr(C_6H_5Br)(C_6F_6)]$ or $[Mo(C_6H_5Br)(C_6F_6)]$, respectively, as the only organometallic products of the reactions, albeit in yields of $< 5\%$. Both compounds are yellow and air-stable, and were identified on the basis of their mass spectra and NMR spectra.

The above products are the first compounds containing coordinated bromobenzene to be made by metal atom synthesis. Confirming a previously reported result [7], we found that reactions of chromium or molybdenum atoms with pure bromobenzene did not give any organometallic products. The reaction of chromium atoms and a 1 : 1 mixture of bromobenzene and toluene gave only traces of bistoluenechromium, with no detectable product containing bromobenzene coordinated to chromium. Cocondensing molybdenum atoms and mixtures of bromobenzene with fluorobenzene or with 1,1,1-trifluorotoluene, also gave no bromobenzene-containing products.

2.2. Proposed half sandwich theory

In an attempt to explain why some of the above atom reactions with arenes give the desired sandwich products while others do so only partially or not at all, we propose the following theory:

(i) The initial interaction of a metal atom with an arene is more likely to give a metal(arene) half sandwich molecule than to result in oxidative addition of the arene to the atom. This assumption is based on the results of various earlier spectroscopic studies of condensation of metal atoms at low temperatures with halogenated unsaturated ligands, in which coordination of the unsaturated ligand always occurs first at low temperatures and is followed in some cases by oxidative addition as a secondary process as the temperature is raised [10].

(ii) The rate of addition of the first arene molecule to a condensing metal atom to form a half-sandwich species is much greater than the rate of addition of a second arene to form the full sandwich species. This assumption is based on the facts, (a) that a free metal atom is a stronger acid (ligand acceptor) than the half sandwich molecule, and (b) that it is much more probable, for steric reasons, for one arene to η^6-coordinate to an atom than for the second arene to do so. The work of Kelly and Bonneau on the coordinately unsaturated species $[Cr(CO)_5]$ in cyclohexane solution shows that the vacant site is always coordinated, and the lifetime of the "naked" species is estimated to be only 25 picoseconds [11,12]. Essentially immediate "solvation" by arene molecules in the matrix is likely for both the condensing metal atom and the subsequently formed half sandwich molecule. There is a high probability that any one of the arene molecules which are loosely associated with the metal atom will move rapidly to η^6-coordination, displacing other solvating molecules. The addition of a second η^6-arene molecule is much less favourable as it has to displace further molecules from the coordination sphere within the steric constraints imposed by the first arene ligand.

(iii) It will always be easier to oxidatively add to a half-sandwich species than to the free transition metal atom as the half-sandwich is more electron rich. This assumption receives support from photoelectron spectra studies on bisarenemetal complexes which show that the ionisation energy for each complex, in which an electron is removed from a non-bonding orbital on the metal, is much lower than for the free metal atom [13]. It follows that thermodynamically it will often be easier to oxidise a bisarenemetal molecule than a half sandwich molecule as the latter will be less electron rich. However, the metal centre in a half sandwich will be far more accessible for reaction so that kinetically its oxidation is more favoured at low temperatures than oxidation of the full sandwich molecule.

(iv) The coordinated arene bestows certain electronic properties on the metal centre of the half sandwich molecule, according to the nature of the ligand. Thus, coordination of an electron rich arene to a metal atom results in the formation of an electron rich half sandwich. Conversely, the half sandwich molecule resulting from the coordination of a metal atom by an electron deficient arene will itself be electron deficient. The course of the subsequent reactions of the half sandwich molecule will be governed in part by its electronic properties.

Considering proposals (i)–(iv) first in relation to the reactions of monohalobenzenes and chromium atoms, we believe that the half-sandwich intermediates, $[Cr(C_6H_5F)]$ and $[Cr(C_6H_5Cl)]$, resist oxidative addition of fluoro- and chlorobenzene respectively, giving good yields of of the bisarenechromium complexes. The relative weakness of the C–Br bonds allows bromobenzene to oxidatively add to $[Cr(C_6H_5Br)]$, giving no bisarenechromium product. In a mixture of toluene and bromobenzene condensed with chromium atoms on a liquid nitrogen cooled surface, the bromobenzene destroys both types of half sandwich molecules, $[Cr(C_6H_5Br)]$ or $[Cr(C_6H_5CH_3)]$, at such a rate that no bisarenechromium product can be isolated. Oxidation of $[Cr(C_6H_5CH_3)_2]$ by bromobenzene does not occur at an appreciable rate below 0°C. With C_6H_5F or $C_6H_5CF_3$ as ligands, the half sandwich molecules $[Cr(C_6H_5F)]$ and $[Cr(C_6H_5CF_3)]$ now resist oxidative addition of bromobenzene, so that sandwich species containing bromobenzene can be isolated.

Bis(arene)molybdenum complexes are generally more easily oxidised than bis(arene)chromium complexes (e.g. bischlorobenzenechromium oxidises quite slowly in air while bischlorobenzenemolybdenum is pyrophoric) and it follows that (arene)molybdenum half sandwich intermediates will also be more susceptible to oxidation than their chromium analogues. So [$Mo(C_6H_5F)$] or [$Mo(C_6H_5CF_3)$] are oxidised by bromobenzene, whereas [$Mo(C_6F_6)$] resists oxidative addition of bromobenzene and [$Mo(C_6F_6)(C_6H_5Br)$] is formed. The low yield of this bis(arene)molybdenum compound reflects inefficient formation of [$Mo(C_6F_6)$] as C_6F_6 is a relatively poor donor ligand which does not inhibit aggregation of metal atoms as well as better donor ligands. The yield was, however, higher than that reported for [$Mo(C_6F_6)_2$] which is formed in < 1% yield upon cocondensation of molybdenum atoms and neat hexafluorobenzene [8]. It follows that the lack of formation of detectable amounts of [$Mo(C_6F_6)_2$] in the $Mo/C_6H_5Br/C_6F_6$ reaction is a result of the much higher rate of complexation of the electron poor half sandwich [$Mo(C_6F_6)$] by bromobenzene than by hexafluorobenzene.

2.3. Reactions of metal atoms with cooled solutions of oxidising agents

We have also carried out some experiments involving reactions of metals atoms with cooled solutions of arene ligands in the presence of added oxidising agents which give results consistent with the ideas proposed above for metal atom reactions in solid matrices at −196°C.

It has long been known that bistoluenechromium is readily oxidised to the monocation by some dinuclear metal carbonyl species, e.g. [$Mn_2(CO)_{10}$], [$Fe(\eta\text{-}C_5H_5)(CO)_2]_2$, and [$Co_2(CO)_8$] at room temperature. However, cooling the solutions to −50°C completely suppresses these oxidation reactions. In a series of experiments, chromium atoms were condensed into toluene solutions of these metal carbonyl oxidising agents at −95°C in a rotary solution reactor [14].

The addition of chromium atoms to a solution of [$Co_2(CO)_8$] in toluene gave a precipitate of a dark solid which, after being filtered off from the cold solution and dissolved in THF, was identified as the known [$Cr(C_6H_5CH_3)_2$][$Co(CO)_4$]. We interpret this as an oxidative addition of [$Co_2(CO)_8$] to [$Cr(C_6H_5CH_3)$], to give an intermediate, possibly [$Cr\{Co(CO)_4\}_2(C_6H_5CH_3)$], in which the effective oxidation state of the chromium is still low enough to allow further reaction with toluene to give the observed final product. Similar results were obtained when [$Mn_2(CO)_{10}$] or [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2$] was used as oxidant, to give [$Cr(C_6H_5CH_3)_2$][$Mn(CO)_5$] or [$Cr(C_6H_5CH_3)_2$][$Fe(\eta\text{-}C_5H_5)(CO)_2$], respectively.

In the knowledge that dibromomethane also oxidises bistoluenechromium to the monocation at room temperature, but not at −50°C, we condensed chromium atoms into a 1% solution of dibromomethane in toluene at −95°C and then removed any residual dibromomethane by pumping at −50°C. No organo-chromium containing product could be isolated, but much of the CH_2Br_2 was converted in to $BrCH_2CH_2Br$. We interpret this as oxidative addition of CH_2Br_2 to [$Cr(C_6H_5CH_3)$] to give an unstable intermediate, possibly [$CrBr(CH_2Br)(C_6H_5CH_3)$], in which the effective oxidation state was too high to allow addition of further molecule of toluene and which decomposed to toluene, 1,4-dibromoethane and chromium bromides.

In a related experiment, condensation of iron atoms into a toluene solution of iodine at −95°C was found to give [$Fe(C_6H_5CH_3)_2$][I_3]$_2$ {subsequently converted into the known [$Fe(C_6H_5CH_3)_2$][PF_6]$_2$ [15] for characterisation}. This is similar to the reaction reported by Billups et al. for cocondensation of manganese atoms with toluene and iodine at −196°C, which gave a low yield of [$Mn(\eta\text{-}C_6H_5CH_3)_2$][$PF_6$] after work-up [16]. We believe that in both cases the mechanism involves initial formation of the half-sandwich intermediate, M(toluene) (M = Mn or Fe). The next step could involve formation of neutral bisarenemetal species {19e$^-$ [$Mn(C_6H_5CH_3)_2$] from manganese and 18e$^-$ [$Fe(\eta^6\text{-}C_6H_5CH_3)(\eta^4\text{-}C_6H_5CH_3)$] from iron} which are then oxidised by iodine. In the case of iron, it is possible that oxidative addition of I_2 to the half-sandwich to give [$FeI_2(\eta^6\text{-}C_6H_5CH_3)$] occurs, followed by addition of a second molecule of toluene (assisted by excess I_2 which complexes I atoms as [I_3]$^-$) to give the observed product. The reaction is unlikely to involve toluene addition to FeI_2 at low temperatures, as the known reaction between toluene and $FeCl_2$ requires elevated temperatures and the presence of $AlCl_3$ as a catalyst [15].

Finally, we believe that the reactivity of half sandwich molecules provide a reasonable explanation for some other published results such as the formation of products from scandium atoms [17], from rhenium atoms [18] and from osmium atoms [19] in which there are C–H oxidative-additions to the metals as well as coordination of arenes. These oxidation-additions will occur to the initially formed (arene)metal half-sandwich followed by stabilisation on further addition of an arene (for scandium) or by metal–metal bond formation (for rhenium or osmium). The fact that dibenzenetantalum but no other bisarenetantalum compound has been isolated from condensation of tantalum atoms with arenes may be because the C–H bonds of benzene are less readily involved in oxidative addition than the C–H bonds of alkyl substituents or any other substituent on benzene [20].

These ideas on redox properties of half-sandwich molecules can provide a rational basis for understanding the behaviour of metal atom/arene systems. As a result, it should now be possible to predict the course of reactions with greater accuracy.

3. Experimental section

Chromium and iron atoms were formed by evaporating the metals from resistively heated crucibles and molybdenum and ruthenium atoms were formed by evaporating the metals by electron bombardment.

Mass spectra were recorded using AEI MS902 and VG AutoSpec instruments. Reported m/z and ion intensity values are for ^{52}Cr, ^{92}Mo and ^{79}Br. Proton NMR spectra were recorded at 270 MHz using a Jeol GX270 spectrometer in sealed tubes in C_6D_6. Spectra were referenced against characteristic solvent resonances. Fluorine spectra were recorded on a Jeol FX90Q at 90 MHz, also in sealed tubes, with an external $CFCl_3$ reference.

3.1. Reaction of chromium atoms with mixtures of bromobenzene and fluorinated ligands

3.1.1. $Cr + C_6H_5Br + C_6H_5F$, $C_6H_5CF_3$, $C_6H_4F_2$ or $C_6H_4(CF_3)_2$

In a typical reaction, 1 g (19 mmol) of chromium vapour was condensed at −196°C with 20 g of an equimolar mixture of C_6H_5Br and C_6H_5F, $C_6H_5CF_3$, $C_6H_4F_2$ or $C_6H_4(CF_3)_2$. The residual arene was pumped away and the soluble organometallic products washed out of the reactor in 100 cm^3 of hexane at room temperature. The solvent was evaporated and the products sublimed under high vacuum.

Parent ions and appropriate fragments were seen in the low resolution mass spectra of the mixtures isolated from the reactions described. Thus for the general case of a mixture containing Cr(arene′)(arene″) and Cr(arene″)$_2$, the mass spectra showed the ions M_1^+, $(M_1\text{-arene}')^+$, $(M_1\text{-arene}'')^+$, M_2^+, $(M_2\text{-arene}'')^+$ where arene′ = C_6H_5Br and arene″ = C_6H_5X or $C_6H_4X_2$ (X = F, CF_3). Following this pattern of ionisation, the mass spectra of the mixtures obtained were as follows: C_6H_5F product; m/z (relative intensity) 304 {7%, $[Cr(C_6H_5Br)(C_6H_5F)]^+$}, 244 {61%, $[Cr(C_6H_5F)_2]^+$}, 208 {8%, $[Cr(C_6H_5Br)]^+$}, 148 {48%, $[Cr(C_6H_5F)]^+$}, 96 (16%, $C_6H_5F^+$), 52 (100%, Cr^+). $C_6H_5CF_3$ product; m/z 354 {12%, $[Cr(C_6H_5Br)(C_6H_5CF_3)]^+$}, 344 {32%, $[Cr(C_6H_5CF_3)_2]^+$}, 208 {6%, $[Cr(C_6H_5Br)]^+$}, 198 {38%, $[Cr(C_6H_5CF_3)]^+$}, 127 (100%, $C_6H_5CF_2^+$), 108 (13%, $C_6H_5CF^+$), 89 (14%, $C_6H_5C^+$), 77 (18%, $C_6H_5^+$), 52 (24%, Cr^+). $C_6H_4F_2$ product; m/z 322 {13%, $[Cr(C_6H_5Br)(C_6H_4F_2)]^+$}, 280 {69%, $[Cr(C_6H_4F_2)_2]^+$}, 208 {19%, $[Cr(C_6H_5Br)]^+$}, 166 {32%, $[Cr(C_6H_4F_2)]^+$}, 156 (19%, $C_6H_5Br^+$), 154 (12%, $C_{12}H_{10}^+$), 114 (29%, $C_6H_4F_2^+$), 95 (8%, $C_6H_4F^+$), 52 (100%, Cr^+). $C_6H_4(CF_3)_2$ product; m/z 422 {17%, $[Cr(C_6H_5Br)(C_6H_4(CF_3)_2]^+$}, 420 {22%, $[Cr(C_6H_4\{CF_3\}_2)_2]^+$}, 247 {7%, $[Cr\{C_6H_4(CF_3)(CF_2)\}]^+$}, 214 (15%, $C_8H_4F_6^+$), 195 (54%, $C_8H_4F_5^+$), 176 (20%, $C_8H_4F_4^+$), 154 (36%, $C_{12}H_{10}^+$), 145 (19%, $C_7H_4F_3^+$), 126 (15%, $C_7H_4F_2^+$), 52 (100%, Cr^+).

3.1.2. $Cr + C_6H_5Br + C_6F_6$

Condensation of 1.2 g (23 mmol) of chromium vapour with 20 g of a equimolar mixture of C_6H_5Br and C_6F_6 at −196°C, followed by removal of the residual ligand, extraction with hexane, purification on a silica gel column, and high vacuum sublimation gave an air stable yellow solid $[Cr(C_6H_5Br)(C_6F_6)]$ (ca. 0.23 g, 0.58 mmol, 2.5% yield). Mass spectrum: high resolution, calcd for $C_{12}H_5BrCrF_6$ m/z 383.888, found m/z 383.890; low resolution m/z 394 (M^+, 43%), 244 ($C_{12}H_5F_5^+$, 29%), 208 (M-C_6F_6, 42%), 186 ($C_6F_6^+$, 6%), 154 ($C_{12}H_{10}^+$, 100%). NMR spectra; ^{1}H(ppm) 4.82 (m, 2H, H_{ortho}), 4.42 {spt (J(H–F) 1.5 Hz), 1H, H_{para}), 4.21 (m, 2H, H_{meta}); ^{19}F(ppm) −193.6 (sxt, J(H–F) = 1.5Hz). Anal. Calc. for $C_{12}H_5BrCrF_6$, C 36.46%, H 1.28%. Found, C 37.20%, H 1.26%.

3.1.3. $Mo + C_6H_5Br + C_6F_6$

Condensation of 0.8 g (8.3 mmol) of molybdenum vapour with 15 g of an equimolar mixture of bromobenzene and hexafluorobenzene at −196°C, followed by removal of the residual ligand, extraction with 180 cm^3 hexane, evaporation of the solvent and vacuum sublimation, gave 140 mg (0.32 mmol, 4% yield) of yellow, fairly air stable $[Mo(C_6H_5Br)(C_6F_6)]$ contaminated with traces of biphenyl. Mass spectrum: high resolution; Calc. for $C_{12}H_5BrF_6Mo$ 433.8546, Found m/z 433.8498: low resolution; 434 (M^+, 56%), 248 ($M - C_6F_6$, 100%), 310 ($C_{12}H_8Br_2^+$, 26%), 232 ($C_{12}H_9Br^+$, 28%), 168 (MoF_4^+, 40%). NMR spectra: ^{1}H(ppm) 4.92 (m, 2H, H_{ortho}) 4.47 (m, 1H, H_{para}) 4.26 (m, 2H, H_{meta}); ^{19}F(ppm) −176.0 (sxt, J(H–F) = 1.9 Hz)].

3.2. Reactions of metal atoms with solutions of metal carbonyls in toluene

Typically, 0.5–1.0 g of the vapour of the metal was condensed into a solution containing about 3 g of the metal carbonyl in 200 cm^3 of toluene cooled to < −90°C and under a pressure of < 0.05 Pa. The bistoluenechromium salt formed was insoluble in toluene at room temperature but was extracted from the solid residue with tetrahydrofuran.

For each of the products, an infra red spectrum was recorded from a thin film prepared on the KBr window of an airtight cell by evaporation in a nitrogen stream of the tetrahydrofuran solvent from a concentrated solution. The spectra shown are characteristic of $[Cr(C_6H_5CH_3)]^+$ salts, with additional strong peaks in the carbonyl region appropriate for each of the anions $[M(CO)_x]^-$: $[Cr(C_6H_5CH_3)][Mn(CO)_5]$; 3070sh, 3045sbr, 2969mbr, 2910mbr, 2872mbr, 1900vsbr, 1887vsbr, 1862vsbr, 1850vsbr, 1444mbr, 1385sh, 1374m, 487sh, 466sbr, 452sh, 420s cm^{-1}. $[Cr(C_6H_5CH_3)]$-$[FeCp(CO)_2]$; 3059w, 3040s, 2962m, 2918mbr, 2861mbr, 1889vs, 1445mbr, 1374m, 489sh, 468s, 450s cm^{-1}. $[Cr(C_6H_5CH_3)][Co(CO)_4]$; 3080s, 3062s, 2952mbr, 2910mbr, 2848mbr, 1870vsbr, 1502w, 1447s, 1388m, 472s, 442s, 420sbr cm^{-1}.

3.3. Reaction of iron atoms with iodine in toluene

1.0 g (18 mmol) of iron vapour was condensed during 40 min into a solution containing 8.1 g of iodine in 200 cm^3 toluene cooled at −95°C. A portion of the purple, crystalline product, $[Fe(C_6H_5CH_3)_2][I_3]_2$, sufficient for IR spectroscopic analysis, was recovered in crude form by filtering a little of the the toluene solution at room temperature. The bulk of the toluene solution was extracted with aqueous $Na_2S_2O_3$ to give, after filtration, a clear yellow solution of $[Fe(C_6H_5CH_3)_2]I_2$, from which $[Fe(C_6H_5CH_3)_2][PF_6]_2$ (0.92 g, 1.75 mmol) was precipitated and identified spectroscopically.

Acknowledgement

We thank SERC for a research grant and a studentship to A.J.S.

References

[1] K.J. Klabunde, *Chemistry Of Free Atoms And Particles*, Academic Press, 1980.
[2] M.L.H. Green, *J. Organomet. Chem.*, 200 (1980) 119.
[3] P.L. Timms, *Proc. Royal. Soc. Lond. Ser. A*, 396 (1984) 1.
[4] U. Zenneck, *Chemie in unserer Zeit*, 1993, p. 208.
[5] M.P. Andrews, H.X. Huber, S.M. Mattar, D.F. McIntosh and G.A. Ozin, *J. Am. Chem. Soc.*, 105 (1983) 6170.
[6] M.P. Andrews, S.M. Mattar and G.A. Ozin, *J. Phys. Chem.* 90 (1986) 744.
[7] V. Graves and J.J. Lagowski, *Inorg. Chem.* 15 (1976) 577
[8] J.J. Barker, A.G. Orpen, A.J. Seeley and P.L. Timms, *J. Chem. Soc. Dalton. Trans.*, (1993) 3097.
[9] A. Martin, A.G. Orpen, A.J. Seeley and P.L. Timms, *J. Chem. Soc. Dalton. Trans.*, (1994) 2251.
[10] G.A. Ozin and W.J. Power, *Inorg. Chem.* , 17 (1978) 2386.
[11] J.M. Kelly and R. Bonneau, *J. Am. Chem. Soc.*, 102 (1980) 1220.
[12] J.A. Welch, K.S. Peters and V. Vaida, *J. Phys. Chem.* 86 (1982) 1941.
[13] J.C. Green, *Struct. Bonding*, 43 (1981) 37.
[14] R. Mackenzie and P.L. Timms, *J. Chem. Soc., Chem. Commun.*, (1974) 650.
[15] J.F. Helling, S.L. Rice, D.M. Braitsh and T. Mayer *J. Chem. Soc., Chem. Commun.*, (1971) 930.
[16] W.E. Billups, A.W. Moorehead, P-J. Ko, J.L. Margrave and J.P. Bell, *Organometallics*, (1988) 2230.
[17] F.G.N. Cloke, K. Kahn and R.N. Perutz, *J. Chem. Soc., Chem. Commun.*, (1991) 1372.
[18] (a) M.L.H. Green and D. O'Hare, *J. Chem. Soc., Dalton. Trans.*, (1986) 2469; (b) J.C. Green, M.L.H. Green, D. O'Hare, R.R. Watson and J.A. Bandy, *J. Chem. Soc., Dalton. Trans.* (1987) 391.
[19] J.A. Bandy, M.L.H. Green and D. O'Hare, *J. Chem. Soc., Dalton. Trans.*, (1986) 2477.
[20] F.G.N. Cloke and M.L.H. Green, *J. Chem. Soc., Dalton. Trans.* (1981) 1938.