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Journal of Organometallic Chemistry 673 (2003) 95–101
Journal of Organometallic Chemistry
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Dialkylaluminium complexes derived from 1,8-diphenyl-3,6-dimethylcarbazole: a new sterically hindered monodentate ligand system

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Received 10 February 2003; received in revised form 18 March 2003; accepted 19 March 2003

Abstract

A new type of sterically hindered, monodentate ligand system based on the carbazolide frame is introduced. (1,8-diphenyl-3,6-dimethylcarbazolide)AlR_2 (**4**, R = Me; **5**, R = Et) complexes have been prepared by N-lithiation of the carbazole, followed by reaction with the appropriate dialkylaluminium chloride. Treatment of the dialkyl complexes **4** and **5** with $B(C_6F_5)_3$ or $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ affords $[LAlR]^+$ species followed by products arising from alkyl/Ar^F exchange. The cationic alkylaluminium species are found to oligomerise ethylene to C_4–C_{10} olefinic products.

Keywords: Aluminium; Carbazole; Ethylene; Polymerisation

1. Introduction

Low-coordinate metal complexes are of great interest in coordination chemistry and catalysis for their ability to generate highly reactive metal centres capable of mediating unusual transformations. Recently a two-coordinate Al^I complex [1] and a three-coordinate Fe^{II} species [2] based on sterically demanding β-diketiminate ligands have been isolated and structurally characterised. These bulky ligands have also been successfully employed to stabilise three-coordinate Mg [3,4], Zn [5–7] and Sn [8] centres, and complexes of this type show remarkable activities in the polymerisation of lactide [7–10], methylmethacrylate [11] and for the co-polymerisation of CO_2 with epoxides [5].

We [12,13], and others [14–19], have been investigating the possible use of cationic alkylaluminium species in the polymerisation of olefins. To date, these studies have involved bi- and tri-dentate N-donor ligands, where the presumed active species involves three or four-coordinate cationic alkylaluminium centres, respectively. Their ethylene polymerisation activities, however, have proved to be relatively low [20], and recent computational studies by Budzelaar and co-workers have indicated that the barriers to ethylene insertion may be too high to allow efficient chain propagation [21–23]. We, therefore, decided to target aluminium pre-catalysts of the type R'_2NAlR_2 where the amide is a sterically hindered carbazolide ligand with the potential not only to stabilise mononuclear three-coordinate precatalysts but also two-coordinate cationic alkyl species of the type $[R'_2NAlR]^+$. Complexes of the type R'_2NAlR_2 generally form aggregates ranging from dimers to higher oligomers [24], but with bulky substituents R and/or R′, rare examples of monomeric complexes with three-coordinate aluminium centres have been isolated and structurally characterised [25–29]. A potentially useful additional facet of the diphenylcarbazole system is the positioning of phenyl substituents close to the metal centre, which may be able to lend stability to cationic species through weak Al···Ph interactions. Here we describe the synthesis of alumi-

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doi:10.1016/S0022-328X(03)00174-8

nium complexes bearing the novel sterically demanding 1,8-diphenyl-3,6-dimethylcarbazolide ligand, their reactivity towards Lewis and Brønsted acids and their potential as ethylene polymerisation catalysts.

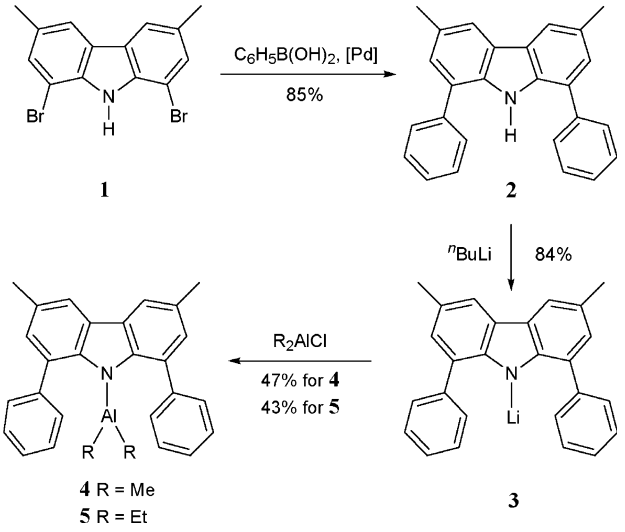
2. Results and discussion

2.1. Synthesis of diphenylcarbazolide Al complexes

1,8-Diphenyl-3,6-dimethylcarbazole (**2**) is readily prepared from the corresponding 1,8-dibromocarbazole **1** [30] via a Suzuki cross-coupling reaction using $Pd(PPh_3)_4$ as the catalyst under typical reaction conditions [31] (Scheme 1).

Several attempts were made to form metal complexes directly via the reaction of ligand precursor **2** with trialkylaluminium reagents. Reactions were carried out with **2** and one equivalent Me_3Al or $Me_3Al(CH_3CN)$ in C_6D_6, CD_3CN and d_8-toluene solutions in NMR tubes at elevated temperatures. In all cases no complexation was observed as indicated by the persistence of the resonance for the N–H proton in C_6D_6 and d_8-toluene solutions, even after several days. This was unexpected since aluminium alkyls generally react with amines and alcohols readily at ambient temperature with concomitant elimination of the corresponding alkane [13–15]. When the reaction of **2** with the $Me_3Al(CH_3CN)$ precursor was carried out in CD_3CN solution in a sealed NMR tube, the resonance for the N–H proton diminished in intensity but no signal attributable to an aluminium methyl species appeared. ^{2}H-NMR spectroscopy confirmed the formation of the N-deuterated carbazole, **2**-d_1, indicated by a resonance for the N-bound deuterium at 8.40 ppm (in CH_2Cl_2).

Deprotonation of **2** was achieved using ^{n}BuLi in heptane solution and the corresponding lithium salt **3** was isolated as a bright yellow, air and moisture sensitive solid, which is highly fluorescent in solution. Since the reaction was carried out in heptane no additional donor is coordinated to the Li atom, as confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy as well as by elemental analysis. Compound **3** is, therefore, tentatively formulated as a mononuclear base-free lithium species. Additional stabilisation of the one-coordinate lithium atom might be provided through interactions with the π-system of the phenyl rings. All attempts to obtain single crystals suitable for an X-ray analysis were unsuccessful.



Scheme 1. Synthesis of diphenylcarbazolide complexes **4** and **5**.

The lithium carbazolide species **3** is a useful precursor for the synthesis of the Al complexes **4** and **5** via salt metathesis using R_2AlCl (R = Et, Me). Both complexes were isolated in moderate yields as yellow, air sensitive solids. In the ^{1}H-NMR spectrum of **4** (Fig. 1), a singlet resonance for the aluminium bonded methyl protons (H_a) is found at −1.33 ppm, which is shifted upfield of the range (typically −0.23 to −0.99 ppm) usually observed for neutral $LAlMe_2$ complexes, e.g. those containing imino-amide [14], troponiminate [15], β-diketiminate [32] and amidinate [33] ligands. This is possibly due to a ring-current effect arising from the proximal phenyl substituents, which may lead to magnetic shielding of the Al–Me protons. The ^{13}C-NMR resonance for the Al–Me carbons, at −8.5 ppm, lies within the range typically found for $LAlMe_2$ complexes.

The ^{1}H-NMR spectrum of the diethylaluminium complex **5** is analogous to that for **4**. A quartet at −0.95 ppm is attributed to the aluminium-bonded methylene protons along with an associated triplet at 0.56 ppm due to the CH_3 protons of the ethyl unit. Both of these resonances are shifted considerably upfield compared with the usual chemical shift ranges found for the methyl (0.91–1.21 ppm) and methylene units (0.14–0.52 ppm) of diethylaluminium species [14,15,33]. Solution structures for **4** and **5** in which the phenyl substituents lie orthogonal to the carbazolide backbone and with the aluminium centres sandwiched between the aromatic groups, are proposed.

2.2. Reactivity towards Lewis and Brønsted acids

In earlier reports of ethylene polymerisation catalysts based on aluminium, the dialkyl precursors are converted into cationic alkyl complexes by alkyl abstraction or protonation with suitable Lewis or Brønsted acids such as $B(C_6F_5)_3$, $[CPh_3][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$ or $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ [12–16]. These cationic alkylaluminium complexes are readily characterised by ^{1}H-NMR and ^{19}F-NMR spectroscopy [17,18,33,34], and in rare cases the molecular structure has been determined by X-ray analysis [19].

In a NMR-scale experiment, equimolar quantities of **4** and $B(C_6F_5)_3$ were dissolved in CD_2Cl_2. Within 15 min a

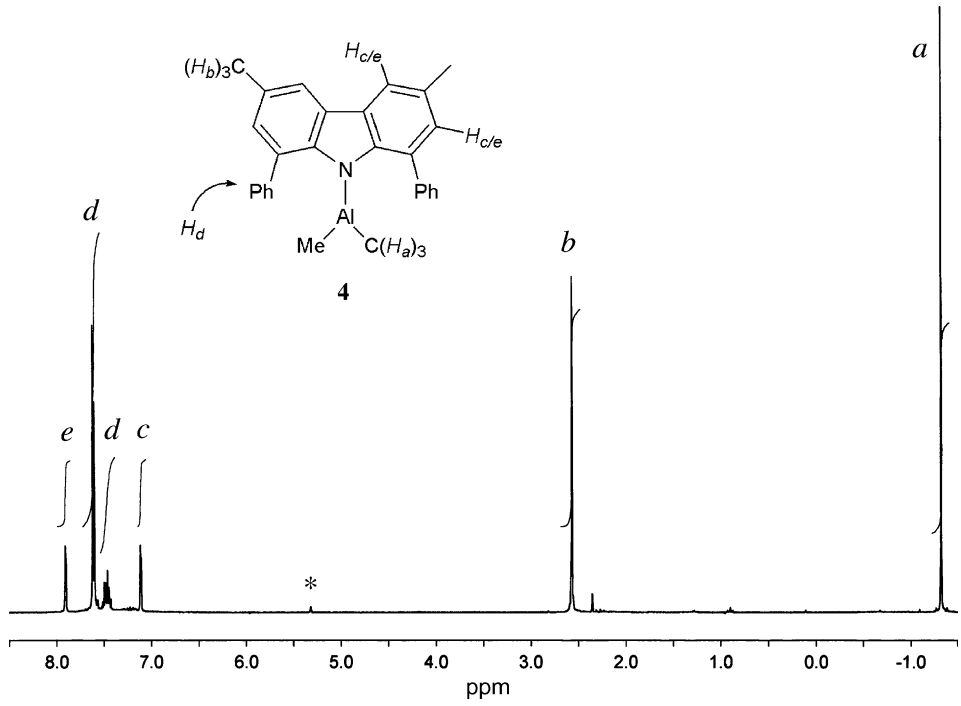


Fig. 1. ^{1}H-NMR spectrum of **4** in CD_2Cl_2 (*$CHDCl_2$).

broad singlet at 0.44 ppm was apparent along with resonances at −167.5, −164.8 and −133.5 ppm in the ^{19}F-NMR spectrum. These chemical shifts are consistent with the formation of a non-coordinated [$MeB(C_6F_5)_3$] anion rather than a contact ion pair [16,35]. In the ^{1}H-NMR spectrum, a singlet resonance at −1.11 ppm is attributed to the aluminium-bonded methyl group of the counter-cation [LAlMe]$^+$ present in **6**, while a resonance at 7.88 ppm is assigned to the aromatic protons of the carbazolide ligand. Monitoring the progress of the reaction over a period of 24 h revealed that the aluminium-bonded methyl protons of **4** slowly disappeared, but the signal corresponding to the non-coordinated anion [$MeB(C_6F_5)_3$] did not gain in intensity. The ^{1}H-NMR spectrum of the solution after 24 h (Fig. 2) reveals that a further reaction has taken place (the residual signals due to **6** are indicated by #) (Scheme 2).

The spectrum is consistent with $LAl(Me)C_6F_5$ (**7**) as the predominant product. Notably, the high-field triplet resonance at −1.02 ppm is characteristic of an Al–Me group (H_a) coupled to the two equivalents *ortho*-fluorines of a coordinated C_6F_5 unit. The $MeB(C_6F_5)_2$ side product of this reaction gives rise to a characteristic quintet at 1.68 ppm for the protons of the boron-bonded methyl group (H_b) coupled to four equivalents *ortho*-phenyl fluorines along with anticipated resonances in the ^{19}F-NMR spectrum [36–38]. These observations, together with the initial formation of the [$MeB(C_6F_5)_3$] anion, indicates a reaction pathway involving abstraction of an aluminium-bonded methyl group from **4** by $B(C_6F_5)_3$. The resultant coordinatively unsaturated cationic methylaluminium intermediate **6** is highly reactive and abstracts C_6F_5 from [$MeB(C_6F_5)_3$] to give **7** and $MeB(C_6F_5)_2$. Similar reactivity has been observed in the reaction of $B(C_6F_5)_3$ with dimethylaluminium complexes bearing amidinate [18,33], salicylaldimine [34] and β-diketiminate [39] ligands.

A NMR tube containing a solution mixture of **6** and **7** was charged with ethylene (1 bar) and sealed. Over a period of several days, very slow conversion of ethylene to higher olefins was observed. A ^{1}H-NMR spectrum on the volatile products revealed multiplets centred at 0.90, 1.61 and 5.45 ppm, in a ratio of 2:28:5, respectively, consistent with internal olefins. This was confirmed by GC and GC–MS analysis of the NMR solution, which showed the presence of exclusively internal C_4–C_{10} olefins (all isomers). The mechanism of formation of internal olefins has not been elucidated, but initial formation of terminal olefins followed by an aluminium catalysed dimerisation or isomerisation process is probable. Olefin dimerisation reactions catalysed by aluminium compounds are well documented and they generally proceed at slow rates [40].

Reaction of the diethyl complex **5** with $B(C_6F_5)_3$ leads to similar results to those obtained with **4**, but the major reaction product **8** is less stable and partial decomposition of this species to unidentified products occurs as the reaction proceeds. Complex **8** gives rise to characteristic resonances for the aluminium-bonded ethyl unit (a quartet at −0.61 ppm and a triplet at 0.69 ppm), and the $EtB(C_6F_5)_2$ side product (a triplet at 1.13 ppm and a quartet at 2.10 ppm) is clearly evident [37,41]. There also

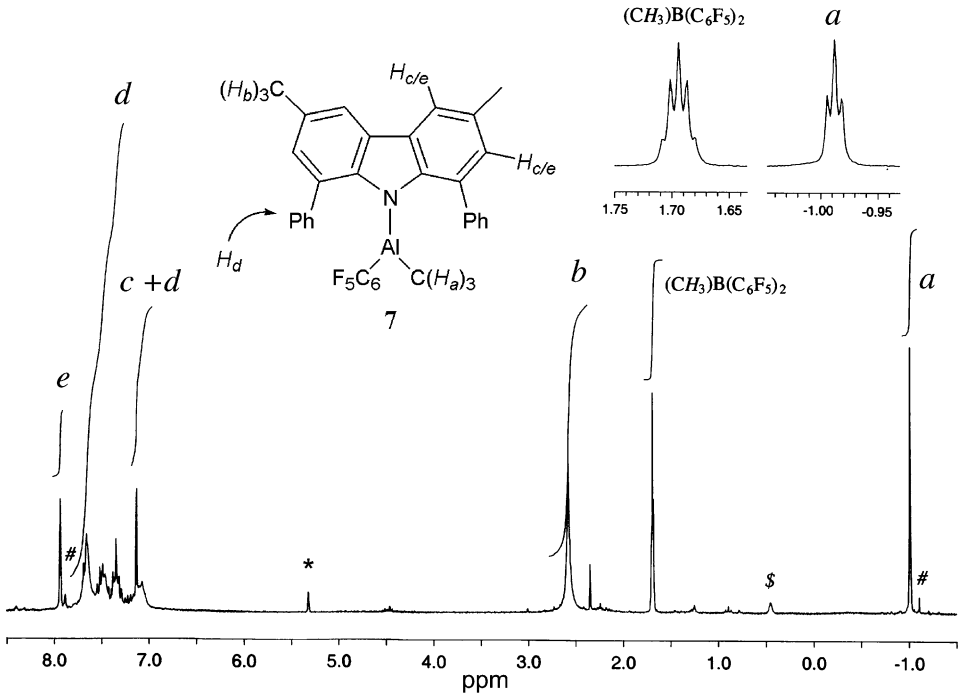
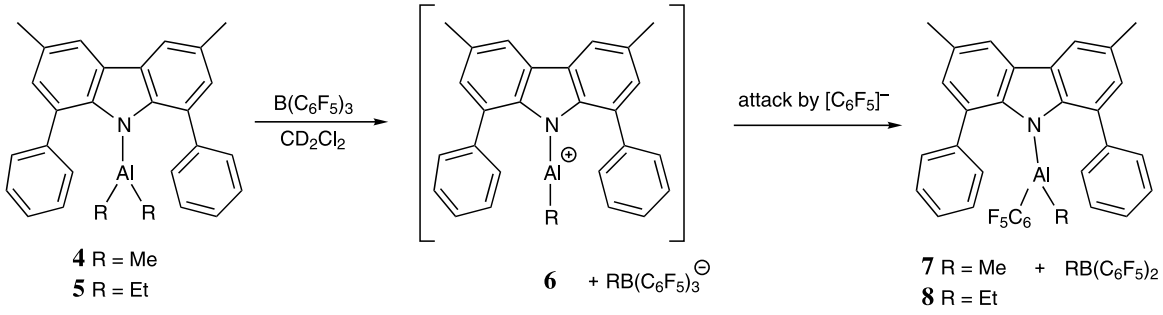


Fig. 2. ^{1}H-NMR spectrum (CD_2Cl_2) arising from reaction of **4** with $B(C_6F_5)_3$: *, residual protio impurity in CD_2Cl_2; $, signal corresponding to non-coordinated anion $[MeB(C_6F_5)_3]$; #, signals attributable to **6**.

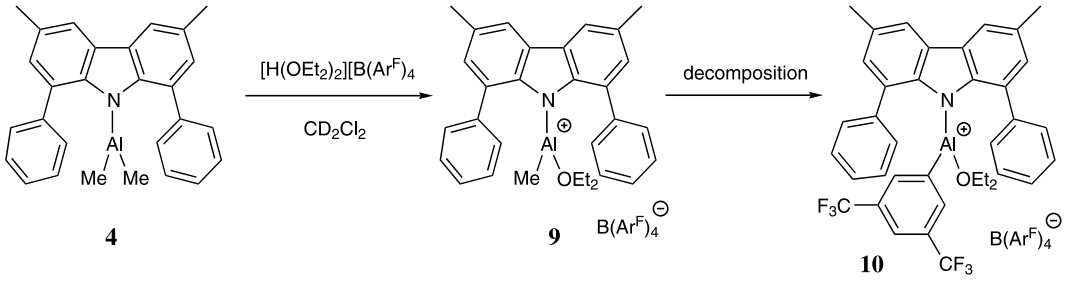
remains some unreacted $B(C_6F_5)_3$, as well as [(1,8-diphenyl-3,6-dimethylcarbazolide)AlEt][$EtB(C_6F_5)_3$] which, according to the ^{19}F-NMR spectrum (resonances at −167.7 −165.0 and −132.7 ppm), is present as a separated ion pair.

A mixture of several products is obtained upon reaction of **4** with one equivalent of $[CPh_3][B(C_6F_5)_4]$. None of the reaction products can be identified by ^{1}H-NMR spectroscopy, but several new signals in the chemical shift range 0 to −1.3 ppm indicate the formation of new methylaluminium species. Addition of ethylene (1 bar) to the product mixture in a NMR-tube sealed with a Young's tap results in the formation of oligomers at a rate and with a product distribution similar to those observed for **4**–$B(C_6F_5)_3$.

A much faster reaction is observed when equimolar amounts (0.05 mmol) of **4** and $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ are combined in CD_2Cl_2 at room temperature. The signal at −1.33 ppm in the ^{1}H-NMR spectrum corresponding to the $AlMe_2$ protons in **4** is replaced instantaneously by a new singlet at −1.02 ppm, along with a resonance at 0.21 ppm due to methane [42]. Resonances are also present corresponding to free and coordinated Et_2O [43], the latter showing characteristic quartet (4.60 ppm) and triplet (1.60 ppm) resonances [38]. These observations are consistent with the formation of an ether-stabilised cationic methyl species **9** (Scheme 3) arising by protonation of one of the methyl groups of **4** and elimination of methane [44]. This species is evidently not very stable and decomposes over a period of ca. 60 min, as indicated by the disappearance of the Al–Me resonance at −1.02 ppm. The decomposition product(s) show no high-field resonances for Al methyl protons, but signals corresponding to coordinated Et_2O remain in evidence. Given the propensity for Me–C_6F_5 exchange in cationic systems containing the diphenylcarbazolide ligand, it seems likely that the main decomposition product of **9** is the



Scheme 2. Reaction of the dialkylaluminium complexes **4** and **5** with $B(C_6F_5)_3$.



Scheme 3. Reaction of **4** with $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$.

$LAl[C_6H_3(CF_3)_2](Et_2O)$ (**10**) (Scheme 3). However, decomposition of **9** via C–H activation involving the phenyl substituents with concomitant formation of methane can not be excluded.

2.3. Conclusions

A new type of monodentate, anionic ligand derived from 1,8-disubstituted carbazole has been described. 1,8-Diphenyl-3,6-dimethylcarbazole offers very good steric protection of the carbazole N–H proton as demonstrated by its reluctance to react with alkylaluminium reagents via N–H deprotonation. Deprotonation can be achieved using ^{n}BuLi as a base and dialkylaluminium complexes are readily obtained via salt metathesis reactions using R_2AlCl compounds. The dialkylaluminium products can be converted to cationic species of the type $[LAlR]^+$ which readily abstract Ar^F from the counter-anion. $[LAlR]^+$ species show low activities for the oligomerisation of ethylene to low molecular weight (C_4–C_{10}) olefinic products.

3. Experimental

3.1. General considerations

All manipulations of water and/or moisture sensitive compounds were performed using standard Schlenk and cannula techniques. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-250 spectrometer. Infrared spectra were obtained as KBr discs using a Perkin–Elmer 1760X FTIR spectrometer. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the microanalytical services of the Chemistry Departments of the University of North London and University College London.

3.2. Solvents and reagents

Solvents were purified by standard methods. The following compounds were prepared according to published procedures: 1,8-dibromo-3,6-dimethyl-9*H*-carbazole (**1**) [30], $Me_3Al(CH_3CN)$ [45], $B(C_6F_5)_3$ [46,47] and $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ [48]. All other reagents are commercially available and were used without further purification.

3.3. 1,8-Diphenyl-3,6-dimethyl-9H-carbazole (*2*)

To a solution of 310 mg (0.88 mmol) 1,8-dibromo-3,6-dimethyl-9*H*-carbazole (**1**) and 100 mg (0.09 mmol) $Pd(PPh_3)_4$ in 50 ml toluene was added a solution of 1.52 g (12.5 mmol) phenylboronic acid in 30 ml ethanol, followed by 9 ml 1 M aqueous Na_2CO_3 solution. The resulting yellow suspension was degassed in a stream of nitrogen and stirred at 80 °C for 16 h. The reaction mixture was filtered hot and the filtrate was washed with 2×30 ml 1 M aqueous NaOH and 2×30 ml H_2O, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The crude product was purified by recrystallisation from hot ethanol–hexane to afford an off-white solid. Yield: 260 mg (85%). M.p. 160–161 °C. R_F (SiO_2, hexane–EtOAc 10:1) 0.40. ^{1}H-NMR (250 MHz, $CDCl_3$, room temperature (r.t.)): δ (ppm) 2.57 (s, 6H, C*H*$_3$), 7.25 (s, 2H, Ar-*H*), 7.37 (m, 2H, Ph-*H*), 7.49 (m, 4H, Ph-*H*), 7.64 (m, 4H, Ph-*H*), 7.86 (s, 2H, Ar-*H*), 8.32 (br, 1H, N*H*). ^{13}C{^{1}H}-NMR (63 MHz, $CDCl_3$, r.t.): δ (ppm) 21.4 (*C*H$_3$), 119.5, 124.1, 124.6, 127, 127.4, 128.1, 129.2, 135.7, 139.1, 139.9 (all Ar-*C*). IR (KBr): 3482 (w, ν(N–H)) cm^{-1}. EIMS (*m*/*e*): 347 $[M]^+$. Anal. Calc. for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03. Found: C, 89.81; H, 5.99; N, 3.91%.

3.4. (1,8-Diphenyl-3,6-dimethylcarbazolide)Li (*3*)

4.3 ml (10.8 mmol) ^{n}BuLi (2.5 M in hexane) was added at r.t. to a solution of 3.06 g (8.8 mmol) 1,8-diphenyl-3,6-dimethyl-9*H*-carbazole (**2**) in 200 ml heptane. The resulting yellow suspension was stirred for 3 h and then concentrated to 40 ml. The supernatant solution was separated by filtration and the residue washed with 3×40 ml pentane. After drying in vacuo the product was obtained as a bright yellow, amorphous solid. Yield: 2.6 g (84%). ^{1}H-NMR (250 MHz, CD_2Cl_2, r.t.): δ (ppm) 2.47 (s, 6H, C*H*$_3$), 6.97 (s, 2H, Ar-*H*), 7.27 (m, 2H, Ph-*H*), 7.41 (m, 4H, Ph-*H*), 7.63 (m, 4H, Ph-

H), 7.68 (s, 2H, Ar-*H*). $^{13}C\{^1H\}$-NMR (63 MHz, CD_2Cl_2, r.t.): δ (ppm) 21.5 (CH_3), 119.8, 124.3, 125.1, 127.6, 127.8, 128.4, 129.6, 136.1, 138.7, 139.4 (all Ar-*C*). Anal. Calc. for $C_{26}H_{20}LiN$: C, 88.37; H, 5.70; N, 3.96. Found: C, 88.26; H, 5.69; N, 3.80%.

3.5. (1,8-Diphenyl-3,6-dimethylcarbazolide)$AlMe_2$ (**4**)

606 mg (1.80 mmol) 1,8-diphenyl-3,6-dimethylcarbazolide)Li (**3**) were suspended in 50 ml toluene and 1.8 ml (1.8 mmol) Me_2AlCl (1.0 M in hexane) was added at 0 °C. The resulting orange solution was stirred at r.t. for 3 h after which the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2. This CH_2Cl_2 solution was concentrated to 10 ml and the product precipitated by the addition of 50 ml pentane. The supernatant solution was separated by filtration and, after drying in vacuo, the product obtained as a yellow, amorphous solid. Yield: 480 mg (47%). ^1H-NMR (250 MHz, CD_2Cl_2, r.t.): δ (ppm) −1.33 (s, 6H, $AlCH_3$), 2.56 (s, 6H, CH_3), 7.10 (s, 2H, Ar-*H*), 7.45 (m, 2H, Ph-*H*), 7.60 (m, 8H, Ph-*H*), 7.90 (s, 2H, Ar-*H*). $^{13}C\{^1H\}$-NMR (63 MHz, CD_2Cl_2, r.t.): δ (ppm) −8.5 ($AlCH_3$), 21.3 (CH_3), 119.8, 126.3, 126.4, 127.1, 127.2, 128.1, 129.3, 136.7, 144.4, 145.3 (all Ar-*C*). Anal. Calc. for $C_{28}H_{26}AlN$: C, 83.35; H, 6.49; N, 3.47. Found: C, 83.27; H, 6.57; N, 3.37%.

3.6. (1,8-diphenyl-3,6-dimethylcarbazolide)$AlEt_2$ (**5**)

340 mg (0.96 mmol) 1,8-diphenyl-3,6-dimethylcarbazolide)Li (**3**) were suspended in 30 ml toluene and 560 μl (1.01 mmol) Et_2AlCl (1.8 M in toluene) was added at −78 °C. The resulting orange solution was stirred at r.t. for 2 h after which the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2. After evaporation of the solvent the residue was washed with cold (−78 °C) pentane. After drying in vacuo the product was obtained as a yellow, amorphous solid. Yield: 178 mg (43%). ^1H-NMR (250 MHz, CD_2Cl_2, r.t.): δ (ppm) −0.95 (q, 4H, $^3J(HH) = 7.9$ Hz, $AlCH_2CH_3$), 0.56 (t, 6H, $^3J(HH) = 7.9$ Hz, $AlCH_2CH_3$), 2.56 (s, 6H, CH_3), 7.10 (m, 2H, Ar-*H*), 7.47 (m, 2H, Ph-*H*), 7.63 (m, 8H, Ph-*H*), 7.89 (m, 2H, Ar-*H*). $^{13}C\{^1H\}$-NMR (63 MHz, CD_2Cl_2, r.t.): δ (ppm) 0.9 ($AlCH_2CH_3$), 9.1 ($AlCH_2CH_3$), 21.3 (CH_3), 119.8, 126.3, 126.4, 126.8, 127.2, 128.1, 129.2, 133.3, 144.6, 145.2 (all Ar-*C*). Accurate elemental analysis could not be obtained due to the extreme air and moisture sensitivity of the compound.

3.7. Reaction of **4** with $B(C_6F_5)_3$ and ethylene

14.9 mg, 0.037 mmol (1,8-diphenyl-3,6-dimethylcarbazolide)$AlMe_2$ (**4**) and 18.9 mg (0.037 mmol) $B(C_6F_5)_3$ were placed into a NMR-tube sealed with a Young's tap and CD_2Cl_2 was added. This resulted in the formation of a dark orange solution. The reaction mixture was kept at r.t. over a period of 24 h and was monitored by ^1H- and ^{19}F-NMR spectroscopy. ^1H-NMR (250 MHz, CD_2Cl_2, r.t.) for (1,8-diphenyl-3,6-dimethylcarbazolide)$AlMe(C_6F_5)$ (**7**): δ (ppm) −1.02 (t, 3H, $^5J(FH) = 1.6$ Hz, $AlCH_3$), 2.57 (s, 6H, CH_3), 7.12 (s, 2H, Ar-*H*), 7.06–7.68 (m, 10H, Ph-*H*), 7.93 (s, 2H, Ar-*H*). ^{19}F-NMR (235 MHz, CD_2Cl_2, r.t.) for **7**: δ (ppm) −162.8 (2F, *m*-C_6F_5), −154.2 (1F, *p*-C_6F_5), −123.2 (2F, *o*-C_6F_5). ^1H-NMR (250 MHz, CD_2Cl_2, r.t.) for $MeB(C_6F_5)_2$: δ (ppm) 1.68 (quint, 3H, $^5J(FH) = 1.8$ Hz, BCH_3). ^{19}F-NMR (235 MHz, CD_2Cl_2, r.t.) for $MeB(C_6F_5)_2$: δ (ppm) −161.9 (4F, *m*-C_6F_5), −147.9 (2F, *p*-C_6F_5), −129.6 (4F, *o*-C_6F_5).

The atmosphere in the NMR-tube was replaced after 24 h with ethylene (1 bar). Over a period of 7 days the formation of internal olefins could be observed, although not all ethylene was consumed. All volatiles were then vacum-transferred into another NMR-tube. ^1H-NMR (250 MHz, CD_2Cl_2, r.t.): δ (ppm) 0.90 (m, 2H), 1.61 (m, 28H), 5.45 (m, 5H).

3.8. Reaction of **5** with $B(C_6F_5)$

27.7 mg (0.064 mmol) (1,8-diphenyl-3,6-dimethylcarbazolide)$AlEt_2$ (**5**) and 32.9 mg (0.064 mmol) $B(C_6F_5)_3$ were placed into a NMR-tube sealed with a Young's tap and CD_2Cl_2 was added. This resulted in the formation of a dark orange solution. The reaction mixture was kept at r.t. over a period of 9 h and was monitored by ^1H- and ^{19}F-NMR spectroscopy. ^1H-NMR (250 MHz, CD_2Cl_2, r.t.) for (1,8-diphenyl-3,6-dimethylcarbazolide)$AlEt(C_6F_5)$ (**8**): δ (ppm) −0.61 (q, 2H, $^3J(HH) = 8.0$ Hz, $AlCH_2CH_3$), 0.69 (t, 3H, $^3J(HH) = 8.0$ Hz, $AlCH_2CH_3$), 2.58 (s, 6H, CH_3). ^{19}F-NMR (235 MHz, CD_2Cl_2, r.t.) for **8**: δ (ppm) −162.7 (2F, *m*-C_6F_5), −154.2 (1F, *p*-C_6F_5), −122.6 (2F, *o*-C_6F_5). ^1H-NMR (250 MHz, CD_2Cl_2, r.t.) for $EtB(C_6F_5)_2$: δ (ppm) 1.13 (t, 3H, $^3J(HH) = 7.5$ Hz, BCH_2CH_3), 2.10 (q, 2H, $^3J(HH) = 7.5$ Hz, BCH_2CH_3). ^{19}F-NMR (235 MHz, CD_2Cl_2, r.t.) for $EtB(C_6F_5)_2$: δ (ppm) −161.8 (4F, *m*-C_6F_5), −148.7 (2F, *p*-C_6F_5), −130.3 (4F, *o*-C_6F_5).

Acknowledgements

The authors are grateful to BP Chemicals Ltd. for financial support of this work.

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