Palladium complexes of 6-aminofulvene-2-aldiminate (AFA) ligands†

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Bis(*N*,*N*′-2,6-diisopropylphenyl)-6-aminofulvene-2-aldimine (**4**) has been synthesised and characterised. The synthesis and characterisation of two zwitterionic Pd(II) complexes [(Ph_2AFA)Pd(Me)DMAP] (**1**) and [(Ph_2AFA)Pd(*N*,*N*-dimethylbenzylamine-2-C,N)] (**2**) are reported. Activation of **1** and **2** for ethene polymerisation with Lewis acids such as BF_3 and $B(C_6F_5)_3$ were not successful. Attempted synthesis of halide-bridged dimers of the form [(Ph_2AFA)Pd(μ-X)]$_2$ resulted in formation of bis-chelated complexes [(Cy_2AFA)$_2$Pd] (**3**) and [(^{t}Bu_2AFA)$_2$Pd] (**5**).

Introduction

The 6-aminofulvene-2-aldiminate (AFA) ligand[1] has the ability to coordinate to a wide range of metals through either the cyclopentadienyl or diimine donors, or both at the same time.[2] Moreover, a wide range of nitrogen substituents may be introduced to this ligand in order to precisely tune the steric and/or electronic properties.[3] The synthetic route also allows for two different nitrogen substituents to be introduced into the same ligand. The ligand displays facile tautomerism and an intramolecular hydrogen bond (Fig. 1).

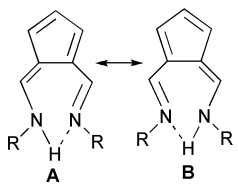

Fig. 1 Tautomeric forms of the 6-aminofulvene-2-aldimine system.

Once deprotonated, the ligand electronic structure may be represented as two resonance forms (**C** and **D**, Fig. 2). The characterisation of complexes in which this ligand displays symmetrical η^5-coordination of the cyclopentadienyl ring indicates that substantial negative charge is located here suggesting a predominant contribution from resonance form **D** in complexes.[2b,7]

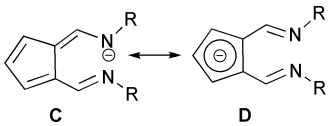

Fig. 2 Resonance forms of the 6-aminofulvene-2-aldiminate system.

This being so, the AFA ligand effectively provides a neutral bis-imine donor set and a negative charge localised in the C_5-ring; neutral metal complexes containing a κ^2-*N*,*N*-AFA ligand will therefore have zwitterionic character and may have significant positive charge at the metal centre (**F**, Fig. 3), which is a significant factor for activity in alkene polymerisation catalysts. Thus the AFA ligand system could in principle form zwitterionic, charge-neutral analogues of Brookhart-type[5] cationic alkene polymerisation catalysts containing 1,2-diimine ligands (**E**, Fig. 3).

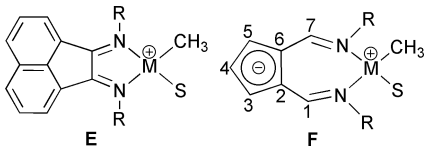

Fig. 3 1,2-Diimine ligand based group 10 alkene polymerisation catalysts (**E**) and its possible charge neutral zwitterionic analogue containing an AFA ligand (**F**). The numbering scheme of C/H atoms used in interpretation of NMR spectra of the AFA ligand and its complexes are also shown in **F**.

In comparison to the cationic Brookhart system, the charge-neutral zwitterionic catalysts should provide a range of benefits. (i) The absence of a counter anion would remove the limitations imposed by its occupation of the active site. (ii) These neutral systems are in principle single component catalysts which do not require a Lewis acid co-catalyst. This would significantly reduce the cost of these catalysts since the large quantities of MAO or other Lewis acid required in the conventional systems is often a limiting economic factor. (iii) The charge neutrality should increase solubility in non-polar solvents. (iv) The electronic structure of the AFA ligand provides a somewhat "softer" metal centre with a reduced positive charge due to contribution from the second ligand resonance form (**C**). The effect of this on the polymer microstructure is likely to be a reduction in the amount of branching by reducing the "chain walking" of the catalyst along the growing polymer chain. (v) The reduced metal electrophilicity may provide catalysts compatible with polar monomers and capable of alkene/polar co-monomer polymerisations.

Our earlier studies of the AFA ligand showed that the complex [(Ph_2AFA)Pd(Me)PPh_3] is indeed able to polymerise ethene when activated by [Ni(COD)$_2$] as phosphine scavenger, however the activity is exceptionally low.[2b] The reason is believed to be stronger coordination of PPh_3 by Pd than by Ni which results in an

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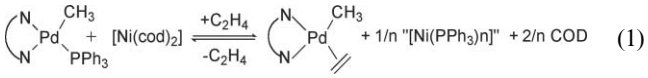
unfavourable activation equilibrium and low concentration of the phosphine-free active species (eqn (1)).



(1)

In order to assess the effect of replacing the phosphine in [(Ph_2AFA)Pd(Me)PPh_3] with an N-donor we have synthesised [(Ph_2AFA)Pd(Me)DMAP] (**1**) and [(Ph_2AFA)Pd(*N*,*N*-dimethylbenzylamine-2-C,N)] (**2**). Upon Lewis acid activation these complexes should provide zwitterionic polymerisation active species. The ideal phosphine-free catalyst precursor for palladium based system are the halide-bridged dimers of the form [(R_2AFA)Pd(μ-X)]$_2$, which could be converted into putative active species [(R_2AFA)Pd(Me)C_2H_4] by simple *in situ* alkylation in the presence of ethene monomer. Our efforts towards the synthesis of these dimers are also reported here.

Results and discussion

Driven by the failure of Ni(COD)$_2$ to efficiently activate [(Ph_2AFA)Pd(Me)PPh_3], we have synthesised the complex in which the phosphine is replaced by 4-*N*,*N*′-dimethylaminopyridine (DMAP). The rationale for using DMAP being that Lewis acid coordination to the uncoordinated dimethylamino group would sufficiently weaken the coordination of the pyridine to allow its substitution by ethene to provide the catalytically active species [(Ph_2AFA)Pd(Me)C_2H_4]. The complex [(Ph_2AFA)Pd(Me)DMAP] (**1**) is prepared by treating [(COD)Pd(CH_3)(Cl)][6] with the lithiated ligand in the presence of DMAP in toluene solution. The ^{1}H NMR spectrum of **1** shows the coordination of both the DMAP and AFA ligands to the metal centre. A singlet at –0.1 ppm (3H) confirms the presence of a Pd bound CH_3 ligand. Upon coordination the original doublet originating from the proton attached to the imino carbon atoms, H–C=N (H1/H7, **F** Fig. 3) of the ligand split into two distinct singlets [8.37 ppm (H1) and 8.29 ppm (H7)] reflecting the absence of mirror-plane symmetry normal to the metal square plane. Upon coordination the H1 proton is shifted to higher frequency; however other ligand protons H3, H4 and H5, and the DMAP protons are shifted to lower frequency. The protons H3/H5 appear as two doublets of doublets due to mutual coupling in addition to coupling to H4.

The X-ray crystal structure of **1** (Fig. 4) shows that the N–Pd–N angle of 93.41(11)° is close to the ideal square-planar angle. However, the ligand itself is not planar, but greatly distorted. The plane of the C_5 ring is tilted by 61.6° from the metal square plane. The angle between the mean plane of the Pd coordination environment and the plane defined by the two N=C imine bonds (*θ*, Fig. 5) is 52.28° and the palladium centre is displaced 1.125 Å from this plane (ω, Fig. 5). The Pd–N bond *trans*- to the methyl ligand is substantially longer [2.160(3) Å] than that *trans*- to the DMAP ligand [2.041(3) Å], reflecting the greater *trans*-influence of the alkyl ligand. The Pd–N–C angles are close to 120°, consistent with sp^2 hybridization at N. All the C–C distances in the cyclopentadienyl ring are intermediate between the usual single and double bond values [range 1.393(5)–1.408(5) Å] suggesting electron delocalization in the C_5 ring and a substantial contribution from resonance form **D** to the ligand electronic structure. This view is also supported by the similarity of the two

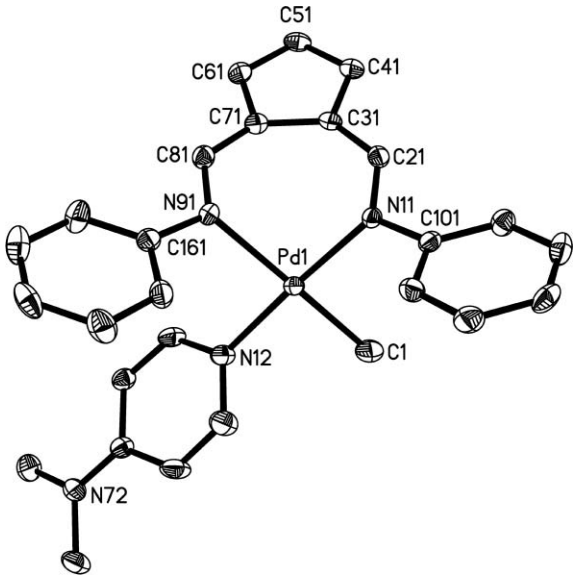


Fig. 4 Thermal ellipsoid drawing of [(Ph_2AFA)Pd(Me)(DMAP)] (**1**) (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond-lenghts (Å) and angles (°) are as follows: N(11)-Pd(1) 2.041(3), N(91)-Pd(1) 2.160(3), C(1)-Pd(1) 2.022(4), N(12)-Pd(1) 2.051(3), C(81)-N(91) 1.303(4), C(21)-N(11) 1.305(4), C(31)-C(71) 1.449(5), C(31)-C(41) 1.404(5), C(41)-C(51) 1.393(5), C(51)-C(61) 1.397(5), C(61)-C(71) 1.408(5), N(11)-Pd(1)-N(91) 93.42(11), C(1)-Pd(1)-N(12) 88.95(15), C(21)-N(11)-Pd(1) 121.4(3), C(81)-N(91)-Pd(1) 119.4(3).

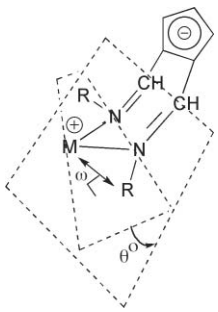


Fig. 5 Parametrization of the R_2AFA ligand coordination geometry. *θ* = the acute angle between plane defined by the metal and the two ligand nitrogen atoms and the mean plane defined by the two ligand C=N bonds; ω = the displacement of the metal from this plane.

C–N bond distances [C81-N91 1.303(4) and C21-N11 1.305(4)] which are consistent with double bonds and the cyclopentadienyl-1,2-diimine (**D**, Fig. 2) rather than the 6-aminofulvene-2-aldimine (**C**, Fig. 2) electronic structure for the coordinated ligand.

The cyclometallated complex [(Ph_2AFA)Pd(*N*,*N*-dimethylbenzylamine-2-C,N)] (**2**) has been synthesised by reacting the dimer[8] [(*N*,*N*-dimethylbenzylamine-2-C,N)Pd(μ-Cl)]$_2$ with two equivalents of LiPh_2AFA in THF. The ^{1}H NMR spectrum of **2** shows that upon coordination the original doublet at *δ* 8.29 for the HC=N (H1/H7) protons in the free AFAH ligand is again split into two distinct singlets [8.65 (H1) and 8.61 ppm (H7)]. The H4 proton appears as a triplet at 6.40 ppm and the H3 and H5 protons of the C_5-ring appear as doublets of doublets at 6.86 and 6.87 ppm respectively. The N(CH_3)$_2$ protons appear as two distinct singlets at 2.30 and 2.53 ppm. The methylene protons appear as

two distinct doublets at 3.89 and 3.72 ppm with a geminal coupling constant of 13.54 Hz.

The X-ray crystal structure of **2** (Fig. 6) shows that the angle at Pd between the two AFA nitrogen donors (N151-Pd1-N71) is 89.01(14)°. The corresponding angle for the cyclometallated dimethylbenzylamine ligand (N82-Pd1-C12) angle is 81.96° reflecting the constrained geometry of the five-membered chelate ring. The angle between the mean plane of the Pd coordination environment and the plane defined by the two N=C imine bonds (θ, Fig. 5) is 68° and the palladium centre is displaced 1.33 Å from this plane (ω, Fig. 5). The C_5 ring of the ligand is planar; however, it is tilted by 75.39° to the metal plane. The C(81)-N(71)-Pd angle is 114° which is significantly less than the expected sp^2 hybridization at nitrogen. As found in **1**, all the bond lengths in the C_5-ring of **2** are intermediate between those typical for single and double bonds and the imine C–N bond distances are consistent with double bonds.

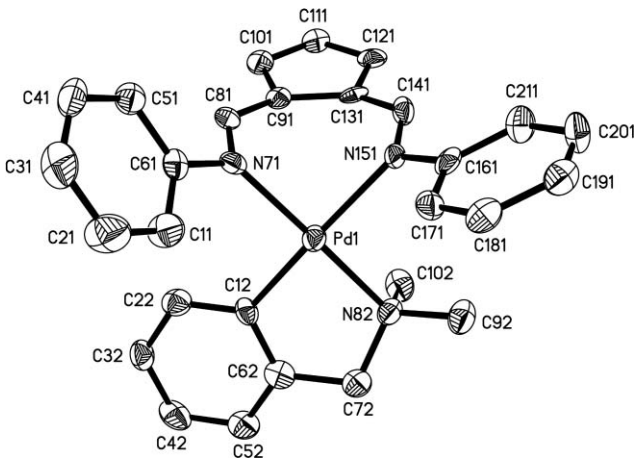
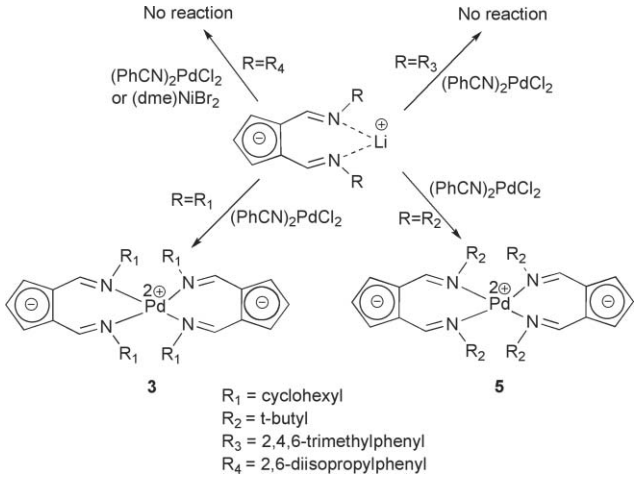


Fig. 6 Thermal ellipsoid drawing of [(Ph_2AFA)(*N*,*N*-dimethylbenzylamine-2-C,N)-Pd] (**2**) (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond-lengths (Å) and angles (°) are as follows: C(131)-C(91) 1.454(6), C(91)-C(101) 1.407(6), C(101)-C(111) 1.386(6), C(111)-C(121) 1.394(6), C(121)-C(131) 1.414(6), C(141)-N(151) 1.301(5), C(81)-N(71) 1.272(5), N(151)-Pd(1) 2.145(4), N(71)-Pd(1) 2.045(4), Pd(1)-N(82) 2.104(4), Pd(1)-C(12) 2.001(4), N(151)-Pd(1)-N(71) 89.01(14), N(82)-Pd(1)-C(12) 81.96(17), C(141)-N(151)-Pd(1) 114.7(3), C(81)-N(71)-Pd(1) 114.9(3), C(72)-N(82)-Pd(1) 108.6(3).

The ideal catalyst precursors are the halide-bridged dimers of the form [(Ph_2AFA)Pd(μ-X)]$_2$.[12] These could be methylated (MeLi) in presence of a donor solvent (S) to provide [(Ph_2AFA)Pd(Me)S], or potentially [(Ph_2AFA)Pd(Me)C_2H_4] in the presence of ethene. In our previous attempts to obtain such species [$PdCl_2$(NCPh)$_2$] was treated with LiPh_2AFA; however, this reaction resulted in the bis-chelate complex [(Ph_2AFA)$_2$Pd].[2b] This observation has lead us to introduce more bulky cyclohexyl substituents in the AFA ligand in order to hinder the formation of a complex containing two of the AFA ligands. However, the reaction of LiCy_2AFA with [$PdCl_2$(NCPh)$_2$] again leads to the formation of a bis-chelated complex [(Cy_2AFA)$_2$Pd] (**3**) (Scheme 1). Metal coordination of the ligand is confirmed by a singlet at 7.71 ppm for H1/H7, which appear as a doublet in the free ligand Cy_2AFAH due to coupling to the N–H proton. The protons H3 and H5



Scheme 1 Attempted syntheses of halide-bridged complexes [(R_2AFA)Pd(μ-Cl)]$_2$.

appear as a doublet at 6.54 ppm, and the H4 proton as a triplet at 6.30 ppm.

The X-ray crystal structure of **3** (Fig. 7) shows that the complex is centrosymmetric and that the two ligands are therefore equivalent. The geometry of the complex is square-planar with an intraligand N–Pd–N angle of 92.90(7)°. As was observed in the [(Ph_2AFA)$_2$Pd] complex,[2b] coordination induces the usual distortion of the ligand, with the mean plane of the ligand atoms being tilted toward an axial position relative to the square-planar environment of the metal. The acute angle between the PdN_4 plane and the mean plane defined by the two N=C imine bonds (θ, Fig. 5) is 50.80° and the displacement of the metal from this plane (ω, Fig. 5) is 1.091 Å. The corresponding values of θ and

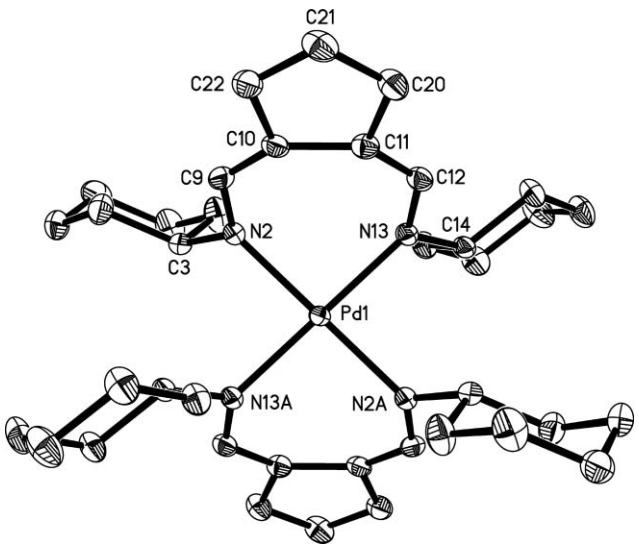


Fig. 7 Thermal ellipsoid drawing of [(Cy_2AFA)$_2$Pd] (**3**) (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond-lenghts (Å) and angles (°) are as follows: Pd(1)-N(2) 2.036(18), Pd(1)-N(13) 2.049(17), N(2)-C(9) 1.300(3), N(13)-C(12) 1.300(3), C(10)-C(11) 1.442(3), C(10)-C(22) 1.419(3), C(22)-C(21) 1.389(3), C(21)-C(20) 1.394(3), C(20)-C(11) 1.414(3), N(2)-Pd(1)-N(13) 92.90(7), Pd(1)-N(13)-C(12) 121.49(15), Pd(1)-N(2)-C(9) 121.82(15), N(2)-C(9)-C(10) 129.00(2), N(13)-C(12)-C(11) 128.90(2).

ω in [$(Ph_2AFA)_2Pd$] are 53.6° and 1.127 Å respectively. Thus it seems that the introduction of cyclohexyl substituents into the ligand surprisingly causes 2.8° less distortion towards an axial position relative to the PdN_4 plane in comparison to the complex containing the Ph_2AFA ligand. This is unexpected as cyclohexyl nitrogen substituents are undoubtedly more sterically demanding than phenyl and yet the distortion observed in **3** is less severe than in [$(Ph_2AFA)_2Pd$]. This points to an electronic contribution to the distortion observed in these complexes, in addition to the fact that as θ approaches zero the *cis*-nitrogen substituents increasingly occupy the same space.

As expected the Pd–N–C angles in **3** are close to 120° consistent with sp^2 hybridization at N. The C_5 ring of the ligand is planar; however, the imine CH carbon atoms lie 0.249 Å (C12) and 0.262 Å (C9) above this plane, while the nitrogen atoms are 0.153 Å (N13) and 0.161 Å (N2) above this plane. The plane of the C_5 ring is tilted by 55.19° out of the metal square plane.

In order to introduce further steric bulk into the AFA ligand we have also synthesised the *N*,*N*′-bis(2,6-diisopropylphenyl)-6-aminofulvene-2-aldimine ligand (**4**) by reacting 6-dimethylaminofulvene-2-*N*,*N*′-dimethylaldimmonium chloride with two molar equivalents of 2,6-diisopropylaniline. The ^{1}H NMR spectrum of this ligand shows a characteristic triplet at 6.56 ppm for H4 and doublets at 7.97 and 7.13 ppm for H1/H7 and H3/H5 respectively. The presence of the isopropyl groups is indicated by doublet and septet signals at 1.23 and 3.27 ppm respectively. Mass spectrometry of **4** (EI and +FAB) showed molecular ion peaks at *m*/*z* 440.3 and 439.52 (M – H) consistent with the formulation.

The X-ray crystal structure of the ligand **4** (Fig. 8) shows that the C_5 ring is planar. However, as expected, the phenyl rings deviate substantially from this plane (by 56.06°) in order to minimise the steric interaction between the isopropyl groups on each. Also reflecting this are the dihedral angles C13-C8-N7-C6 (58.29°) and C23-C22-N21-C20 (59.34°). The carbon-carbon and carbon-nitrogen distances are intermediate between the usual single and double bonds. The bond angles C1-C6-N7 and C2-C20-N21 are 126.30(16)° and 125.59(16)° respectively, consistent with sp^2 hybridization at the imine carbon atoms. An N21-H-N7 intramolecular hydrogen bond exists in **4**. The hydrogen atom is bonded to N21 atom. The donor (N21)-acceptor (N7) distance is 2.680(2) Å which compares with the value of 2.79 Å in Ph_2AFAH.[4]

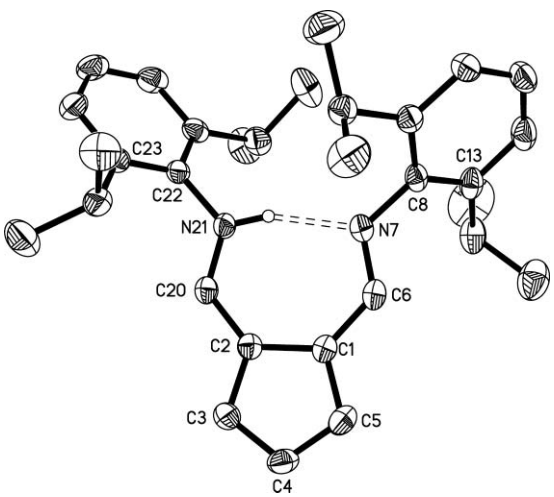


Fig. 8 Thermal ellipsoid drawing of [(2,6-diipropylphenyl)$_2$AFAH] (**4**) (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond-lenghts (Å) and angles (°) are as follows: C(1)-C(2) 1.461(2), C(1)-C(5) 1.402(2), C(5)-C(4) 1.393(3), C(4)-C(3) 1.391(3), C(3)-C(2) 1.411(2), C(6)-N(7) 1.302(2), C(20)-N(21) 1.305(2), N(7)-C(8) 1.424(2), N(21)-C(22) 1.419(2), C1-C6-N7 126.30(16), C2-C20-N21 125.59(16), C6-N7-C8 121.41(14), C20-N21-C22 123.03(14).

All attempts at synthesis of a halide-bridged complex with the ligand **4** have been unsuccessful. And furthermore, none of the bis-chelate complex, which are formed by treatment of all other AFA ligands with [$PdCl_2(NCPh)_2$], is formed in this case. Only unreacted ligand could be isolated from the reaction mixture. It is therefore clear that the presence of the 2,6-diisopropylphenyl substituents in **4** not only prevents the coordination of two ligands to the same metal, but precludes complexation all together.

It is apparent from the above results that, if there is a steric regime which will permit the formation of our desired species, [(AFA)Pd(μ-Cl)]$_2$, by hindering the formation of the apparently preferred bis-chelate complex while still permitting the coordination of one ligand, it lies somewhere between the Cy_2AFA and $(dipp)_2AFA$ ligands. Two further ligands have been prepared to explore this space containing mesityl and *tert*-butyl[3] nitrogen substituents. Unfortunately these two ligands lie on either side of the divide with $(mesityl)_2AFA$ failing to coordinate to Pd and $^tBu_2AFA$ forming the bis-chelate complex **5** only. The ^{1}H NMR spectrum of the complex **5** shows that upon coordination the original doublet at δ 7.95 for the HC=N protons in the free ligand appear as a sharp singlet at δ 7.78 (H1/H7). The protons H3/H5 are also shifted to lower frequency and appear as a doublet at 6.55 ppm. The H4 proton is shifted to higher frequency and appears as a triplet at 6.46 ppm and the methyl protons of the ^{t}Butyl groups appear as a singlet at 1.38 ppm. The complex **5** contains a trace amount of free ligand which could not be removed due to high solubility of both the complex and ligand in all organic solvents.

Ethene polymerisation

We have tested complexes **1** and **2** toward ethene polymerisation at 5 bar and 50 °C. Activation of both complexes with Lewis acids such as BF_3 and $B(C_6F_5)_3$ was also explored. Unfortunately none of the complexes were active for ethene polymerisation. An aliquot of the mother liquor was also analyzed by EI-MS to detect formation of oligomers. However, ethene oligomers were not observed either. An ^{1}H NMR study of the Lewis acid treatment of **1** shows that $B(C_6F_5)_3$ abstracts the Pd-bound CH_3 group instead of abstracting DMAP, forming $[CH_3B(C_6F_5)_3]^-$ species (δ_H 1.18, s, br). This is not surprising as $B(C_6F_5)_3$ is known to activate Brookhart type Pd dimethyl complexes [(diimine)$PdMe_2$] and metallocene precatalysts by methyl abstraction.[5,13]

Conclusions

In summary, it can be concluded that formation of halide-bridged complexes using R_2AFA ligands is not solely dependent on steric factors. Electronic factors are also playing an important role. Introduction of bulky N-substituents in the AFA ligand

did not afford any halide-bridged dimeric complexes; instead the bis-chelated complexes are formed, *e.g.* [($Cy_2AFA)_2Pd$] and [($^tBu_2AFA)_2Pd$].

Experimental

All reactions and manipulations of moisture- and air-sensitive compounds were carried out in an atmosphere of dry nitrogen using Schlenk techniques or in a conventional nitrogen-filled glovebox (Saffron Scientific), fitted with oxygen and water scavenging columns. All the solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. Toluene, THF, diethyl ether, and hexane were all distilled from Na/benzophenone under a nitrogen atmosphere. NMR solvents were degassed using freeze-thaw cycles and stored over 4 Å molecular sieves. All solvents and reagents were purchased from Sigma-Aldrich, Fischer or Acros and used as received unless otherwise stated. NMR spectra were recorded on Bruker AC 250 and 360 MHz spectrometers operating at room temperature. ^1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity and the ^{13}C resonances respectively. Multiplicities and peak types are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m; broad, br; aromatic, ar. Mass spectra were recorded on a Kratos MS50TC spectrometer (FAB-MS). Elemental analyses were performed using a Perkin Elmer 2400 CHN Elemental Analyser.

Synthesis of [(Ph_2AFA)Pd(CH_3)(DMAP)] (1)

To a solution of Ph_2AFAH (0.538 g, 1.98 mmol) in toluene (40 cm^3), 1.24 cm^3 (1.98 mmol) of ^{n}BuLi (1.6 M in hexane) were added and the mixture was stirred for 1 h. To a solution of [(COD)Pd(CH_3)(Cl)] (0.524 g, 1.98 mmol) in toluene (20 cm^3), DMAP (0.241 g, 1.98 mmol) was added and the resulting brown suspension was transferred into the solution of the deprotonated ligand. The colour of the reaction mixture immediately became dark red. The mixture was stirred overnight at room temperature. After filtration through celite, the volume of the solvent was reduced to *ca.* 2/3 under vacuum. Upon storage at -10 °C, the red product precipitated. Suitable crystals for X-ray analysis were obtained by slow diffusion of hexane into a dichloromethane solution of the product. Yield: 0.30 g (44%). ^1H NMR ($CDCl_3$, 250 MHz, 25 °C): δ 8.37 (s, 1H, H1), 8.29 (s, 1H, H7), 7.81 (d, 2H, DMAP, $J = 7$ Hz), 7.66-6.89 (m, 10H, C_6H_5), 6.83 (dd, 1H, H5, $J = 5.28$, 2.31 Hz), 6.80 (dd, 1H, H3, $J = 5.6$, 2.31 Hz), 6.35 (t, 1H, H4, $J = 3.63$ Hz), 6.12 (d, 2H, DMAP, $J = 7.26$ Hz), 2.92 (s, 6H, DMAP), -0.1 (s, 3H, CH_3–Pd);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 163.74 (C1), 160.34 (C7), 154.06, 153.92, 152.87, 150.95 (C, DMAP), 133.02, 132.62, 128.79, 128.68, 124.78, 124.15, 123.94, 122.55, 117.98, 117.81, 117.54, 107.21 (C, DMAP), 39.40 (*N*-CH_3), 1.37 (Pd-CH_3); MS (FAB, *m/z*): 515 (M^+). Anal. Calcd for $C_{27}H_{28}N_4Pd$: C, 62.97; H, 5.48; N, 10.88. Found: C, 63.54; H, 5.56; N, 10.52.

Synthesis of [(Ph_2AFA)(*N*,*N*-dimethylbenzylamine-2-C,N)-Pd(II)] (2)

To a solution of Ph_2AFAH (0.224 g, 0.822 mmol) in THF (15 cm^3) was added ^{n}BuLi (0.56 cm^3, 1.6M in hexane, 0.91 mmol) at -78 °C. The mixture was stirred for 1.5 h, and then allowed to warm to -40 °C. The colour of the solution turned from yellow-orange to dark orange. A solution of di-μ-chloro-bis(*N*,*N*-dimethylbenzylamine-2-C,N)dipalladium (0.227 g, 0.411 mmol) in THF (15 cm^3) was added at -40 °C. The colour of the reaction mixture turned to dark red. The mixture was stirred overnight at room temperature. The solvent was removed *in vacuo* and the crude product was washed with a solvent mixture of toluene–hexane (2 : 1) and the residue was subsequently dissolved in a CH_2Cl_2–hexane mixture (8 : 1) and filtered through celite to remove LiCl. The solvent was removed *in vacuo* and the resulting residue washed with hexane which yielded pure product. Yield: 0.012 g (3%). Crystals suitable for X-ray analysis were obtained from slow diffusion of hexane into a concentrated solution of the product in CH_2Cl_2. ^1H NMR ($CDCl_3$, 250 MHz, 25 °C): δ 2.30 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 3.72 (d, 1H, $J = 13.54$ Hz), 3.89 (d, 1H, $J = 13.54$ Hz), 6.40 (t, 1H, H4, $J = 3.63$ Hz), 6.58-6.85 & 6.89-7.87 (m, 14H, Ar), 6.86 (dd, 1H, H3, $J = 3.63$, 1.65 Hz), 6.87 (dd, 1H, H5, $J = 3.30$, 1.32 Hz), 8.61 (s, 1H, H7), 8.65 (s, 1H, H1); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 158.83 (C1), 158.40 (C7), 149.82, 148.54, 146.88, 146.55, 134.67, 132.47, 131.96, 129.30, 128.79, 124.79, 124.72, 124.60, 123.99, 123.72, 121.55, 121.51, 121.06, 119.37, 119.06 (C4), 73.66 (C, CH_2), 52.13 (C, NCH_3), 51.42 (C, NCH_3); MS (EI, *m/z*): 511(M^+). Anal. Calcd for $C_{28}H_{27}PdN_3$: C, 65.69; H, 5.32; N, 8.21 Found: C, 65.29; H, 5.41; N, 8.31.

Synthesis of [($Cy_2AFA)_2Pd$] (3)

To a red solution of Cy_2AFAH (0.311 g, 1.097 mmol) in toluene (25 cm^3), 0.822 cm^3 (1.316 mmol) of CH_3Li (1.6 M in diethyl ether) were added and the mixture was stirred at RT for 1 h. A pale red solution of $(PhCN)_2PdCl_2$ (0.421 g, 1.097 mmol) in toluene (50 cm^3) was stirred at 50 °C for 1 h and then transferred to the deprotonated ligand. The dark red reaction mixture was stirred at room temperature over night. After filtration through celite, the volume of the solvent was reduced to *ca.* 2/3 under vacuum and then acetonitrile was added to precipitate the product from the unreacted ligand. The solution was decanted and the solid orange product was dried under vacuum. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in a mixture of toluene and acetonitrile solvents under nitrogen. Yield: 0.07 g (10%). ^1H NMR ($CDCl_3$, 250 MHz, 25 °C): δ 7.71 (s, 2H, H1/H7), 6.54 (d, 2H, H3/H5, $J = 3.30$ Hz), 6.3 (t, 1H, H4, $J =$ 3.30 Hz), 3.11 (2H, *ipso*-CyH), 0.96-1.81(m, 20H, CyH);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 160.97 (C1/C7), 127.27 (C3/C5), 116.89 (C4), 115.54 (C2/C6), 65.31 (*ipso*-C, Cy), 37.02 (C, Cy), 32.79 (C, Cy), 26.24 (C, Cy); MS (EI, *m/z*): 672.4 (M^+). Anal. Calcd for $C_{38}H_{54}N_4Pd$: C, 67.79; H, 8.08; N, 8.32. Found: C, 67.09; H, 7.98; N, 8.11.

Synthesis of N,N′-bis(2,6-diisopropylphenyl)-6-aminofulvene-2-aldimine (4)

A solution of 6-dimethylaminofulvene-2-*N*,*N*′-dimethylaldimmonium chloride (2.01 g, 9.45 mmol) in dry ethanol (35 cm^3) was refluxed with 2,6-diisopropylaniline (3.54 cm^3, 18.80 mmol) for 12 h. The solvent and volatiles were removed *in vacuo*. The resulting solid was then refluxed in hexane (150 cm^3)

with activated charcoal (5 g) for 1.5 h. The mixture was filtered through celite while still hot and 3 portions of hot hexane (15 cm^3) were used to extract more products from the solid residue. The solutions were combined and the volume was reduced. The product was purified by column chromotography on silica using hexane and ethyl acetate (20 : 1) as an eluent. Crystals suitable for X-ray analysis were obtained on cooling at -30 °C in hexane. Yield: 1.548 g (37%). ^{1}H NMR ($CDCl_3$, 360 MHz, 25 °C): δ 14.55 (br, NH), 7.97 (d, 2H, H1/H7, J = 6.78 Hz), 7.18-7.34 (m, 6H, C_6H_5), 7.13 (d, 2H, H3/H5, J = 3.65 Hz), 6.56 (t, 1H, H4, J = 3.65 Hz), 3.27 (sept, 4H, ^{i}PrCH, J = 6.78 Hz), 1.23 (d, 24H, ^{i}PrCH_3, J = 6.78 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 90.6 MHz, 25 °C) 157.42 (C1/C7), 142.15 (C, *ipso*-Ar), 142.09 (*o*-C, Ar), 133.40 (C3/C5), 126.28 (C4), 123.44 (*m*-C, Ar), 120.80 (C2/C6), 119.43 (*p*-C, Ar), 28.19 (C, ^{i}Pr-CH), 23.94 (C, ^{i}Pr-CH_3); MS (EI, *m/z*): 440.3 (M^+). Anal. Calcd for $C_{31}H_{40}N_2$: C, 84.49; H, 9.15; N, 6.36. Found: C, 84.40; H, 9.21; N 6.56.

Synthesis of [(^{t}Bu$_2$AFA)$_2$Pd] (5)

To a yellow solution of ^{t}Bu$_2$AFAH (0.10 g, 0.43 mmol)[3] in toluene (15 cm^3), 0.4 cm^3 (0.64 mmol) of CH_3Li (1.6 M in diethyl ether) were added and the mixture was stirred at RT for 1 h. A pale red solution of $(PhCN)_2PdCl_2$ (0.165 g, 0.43 mmol) in toluene (30 cm^3) was stirred at 50 °C for 1 h and then slowly transferred to the deprotonated ligand. The brown reaction mixture was stirred at room temperature over night. After filtration through celite, the solvent was removed under vacuum and the unreacted ligand was partly removed by washing with hexane. The brown solid product contains traces amount of ligand. Yield: 0.10 g (41%). Suitable crystals for X-ray analysis were not obtained. Slow diffusion of hexane into a toluene solution of the product yielded only brown powder. ^{1}H NMR ($CDCl_3$, 360 MHz, 25 °C): δ 7.78 (s, 2H, H1/H7), 6.55 (d, 2H, H3/H5, J = 3.30 Hz), 6.46 (t, 1H, H4, J = 3.30 Hz), 1.38 (s, 18H, ^{t}Bu-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 90.6 MHz, 25 °C) δ 164.83 (C1/C7), 151.74 (C2/C6), 124.15 (C3/C5), 118.38 (C4), 59.95 (C-$_{quaternary}$, ^{t}Bu), 32.66 (C, ^{t}Bu-CH_3); MS(EI, *m/z*): 568.2. NMR (^{1}H and ^{13}C) spectra showed the presence of small amounts of the free ligand which resulted in elemental analysis results being unsatisfactory. The ^{13}C nmr spectrum is available as electronic supplementary information.†

Procedure of ethene polymerisation test

Büchi glass autoclave was heated at 80 °C under vacuum for 3 h and then cooled to room temperature under an ethene pressure. The autoclave was charged with 20 cm^3 of toluene and the ethene pressure and temperature was set to 5 bar and 50 °C respectively. After releasing the pressure, a solution of **1** or **2** (75 μmol in 5 cm^3 of toluene) and tris(pentaflurophenyl)borane, $B(C_6F_5)_3$ or boron trifluoride, BF_3 (150 μmol in 5 cm^3 of toluene) were added *via* syringe. The reactor was sealed and pressurized with ethene to 5 bar. The reaction mixture was stirred under constant pressure for 6 h, after which time the pressure was released and acidified methanol was added to quench the catalyst. An aliquot of the mother liquor was also analyzed by EI-MS to detect formation of oligomers.

X-ray crystallography†

Data were collected with Mo-Kα radiation at 150 K on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device. Multi-scan absorption corrections were applied using the programs SADABS[14] (**1**, **3** and **4**) or TWINABS[14] (**2**). The structures were solved with direct (SIR92)[15] or Patterson methods (DIRDIF)[9] and refined using SHELXL (**2**) or Crystals **1**, **3** and **4**).[10,11]

Crystal data for 1. $C_{27}H_{28}N_4Pd$, M = 514.95, monoclinic, a = 10.5970(3) Å, b = 16.3536(5) Å, c = 13.4978(4) Å, β = 94.160 (2)°, V = 2332.99(12) Å^3, space group $P2_1/n$, Z = 4, 19454 reflections measured, 6128 unique (R_{int} = 0.053) which were used in all calculations. The final conventional R factor [based on F and 4650 data with $F > 4\sigma(F)$] was 0.048, and wR_2 (based on F^2 and all data) was 0.0995. The final ΔF synthesis extremes were 0.93 and –0.88 e Å^{-3}.

Crystal data for 2. $C_{28}H_{27}N_3Pd$, M = 511.93, triclinic, a = 11.2909(6) Å, b = 13.9873(8) Å, c = 15.0483(8) Å, α = 87.193 (4)°, β = 87.521 (4)°, γ = 76.180 (4)°, V = 2303.8(2) Å^3, space group $P\bar{1}$, Z = 4, 41311 reflections measured, 13456 unique (R_{int} = 0.075) which were used in all calculations. The crystal was a twinned *via* a two-fold rotation about [-1 1 0] (CELL_NOW).[16] Data from both domains were harvested simultaneously during integration, but only data involving the principal domain were used in refinement. The twin scale factor was 0.4369(8). The final conventional R factor [based on F and 5654 data with $F > 4\sigma(F)$] was 0.047, and wR_2 (based on F^2 and all data) 0.080. The final ΔF synthesis extremes were 1.36 and –1.07 e Å^{-3}.

Crystal data for 3. $C_{38}H_{54}N_4Pd$, M = 673.24, monoclinic, a = 9.4867(2) Å, b = 16.9336(3) Å, c = 10.6112(2) Å, β = 101.6900(10)°, V = 1669.27(6) Å^3, space group $P2_1/c$, Z = 2, 21684 reflections measured, 4918 unique (R_{int} = 0.042) which were used in all calculations. The final conventional R factor [based on F and 3757 data with $F > 4\sigma(F)$] was 0.035, and wR_2 (based on F^2 and all data) was 0.079. The final ΔF synthesis extremes were 0.72 and –0.61 e Å^{-3}.

Crystal data for 4. $C_{31}H_{40}N_2$, M = 440.67, triclinic, a = 10.4988(2) Å, b = 13.5676(3) Å, c = 19.0281(4) Å, α = 89.809(1)°, β = 83.736(1)°, γ = 87.957(1)°, V = 2692.53(10) Å^3, space group $P\bar{1}$, Z = 4, 52192 reflections measured, 15537 unique (R_{int} = 0.047) which were used in all calculations. The final conventional R factor [based on F and 9712 data with $F > 4\sigma(F)$] was 0.069, and wR_2 (based on F^2 and all data) was 0.178. The final ΔF synthesis extremes were 0.52 and –0.40 e Å^{-3}.

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