Preparation of a *super* bulky silver *N*-heterocyclic carbene complex†

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The preparation of a 1,3-bis(2,6-terphenyl)imidazolium salt and the first coordination complex containing a 1,3-bis(2,6-terphenyl)-imidazol-2-ylidene NHC (IDitop) is reported; comparison of the steric parameters of IDitop with commonly used *bulky* NHCs such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDip) indicates a significantly greater cone angle for the former, and the molecular structures of [AgCl(IDitop)], the parent diazabutadiene of IDitop and the 1,3-bis(2-phenylphenyl)imidazol-2-ylidene (IBp) complex [AgCl(IBp)] are reported.

The use of super bulky aryl substituents to kinetically stabilise unusual or unprecedented chemical functionalities is a common feature of contemporary organometallic chemistry.[1] Two landmark examples are Yoshifuji's preparation of a diphosphene in 1981[2] and Robinson's report of $Na_2[Ar^*GaGaAr^*]$ (Ar* = Tripp = 2,6-($^i Pr_3C_6H_2)_2C_6H_3$, see Fig. 1) in 1997 that was controversially described as containing a 'gallyne' metal–metal triple bond.[3] Compounds such as these have inspired many research ensembles to incorporate super bulk into a variety of ligand classes, such as cyclopentadienyls,[4] *N*,*N*′-disubstituted amidinates[5] and β-diketiminates,[6] in order to quantitatively evaluate the impact of 'steric engineering' on their chemistry.[7]

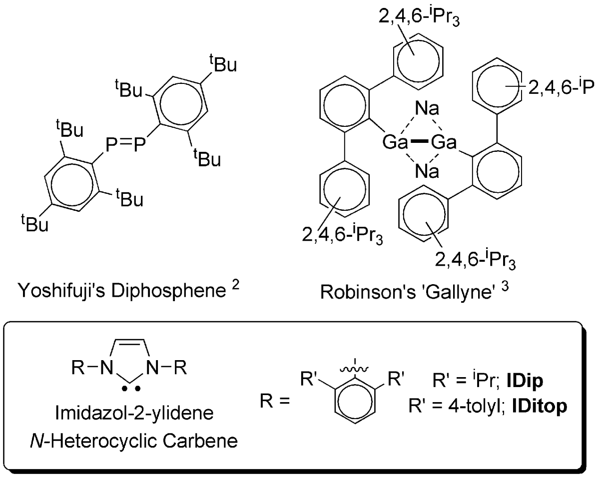
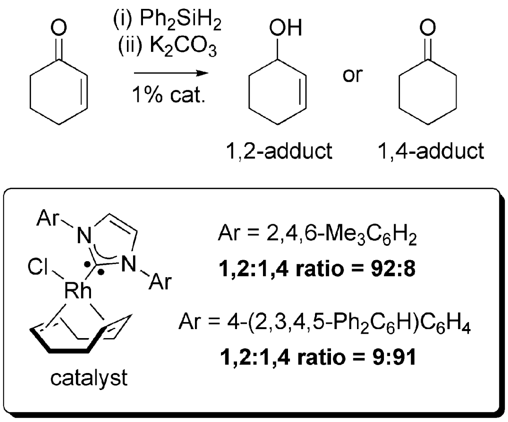


Fig. 1 Example main group species stabilised by aryl *super* bulk and the underlying structural scaffold for 1,3-disubstituted imidazol-2-ylidene NHCs.

Of the aryl substituents employed, the 2,6-terphenyl based Tripp, Dipp (2,6-bis(2,6-diisopropylphenyl)phenyl) and Dmp (2,6-dimesitylphenyl, mesityl = 2,4,6-$Me_3C_6H_2$) aryls, in which the 2,6-aryls are positioned orthogonal to the primary aryl plane, have been particularly effective due to their spatial shielding of substituents at the *ipso*-carbon.[1]

Considering the wide application of 2,6-terphenyls[1] it is perhaps surprising that they have not yet been incorporated into 1,3-disubstituted imidazol-2-ylidene *N*-heterocyclic carbenes (NHCs) (Fig. 1), one of the most studied ligand classes in modern organometallic chemistry.[8] As recently reviewed by Hahn and Jahnke,[9] imidazol-2-ylidenes have been successfully incorporated into dendrimer frameworks,[10] solid-state scaffolds[11] and even porphyrin based constructs;[12] however, 1,3-substitution of these NHCs by 2,6-terphenyl groups has not been accomplished. To our knowledge, only 3,5-terphenyls have been applied in this regard.[13] The most commonly utilised bulky NHC at this time is IDip (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (Fig. 1), first prepared by Nolan and co-workers.[14] In view of the unusual reaction of palladium *N*,*N*′-bis(3,5-terphenyl)imidazol-2-ylidene complexes with carbon dioxide, which affords carbonate under aerobic conditions,[13] and the distinct hydrosilylation selectivities reported for monovalent rhodium catalysts supported by dendrimeric polyaryl NHCs (Scheme 1),[10] it is our contention that *N*,*N*′-bis(2,6-terphenyl)imidazol-2-ylidenes will generate metal complexes with unique reactivities relative to less bulky counterparts. Herein we report the preparation of the first *N*,*N*′-bis(2,6-terphenyl)imidazolium salt, IDitop·HCl (Fig. 1), from its parent diazabutadiene, and the preparation of its silver(I) chloride coordination



Scheme 1 Example hydrosilylation catalysts that highlight selectivities based on the *N*-aryl bulk of the catalyst NHC ligand.[10]

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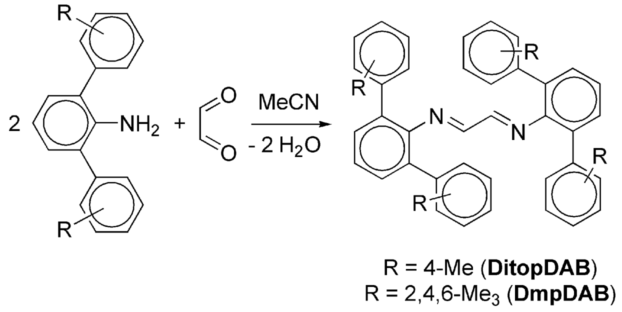


Scheme 2 Preparation to the first *N*-2,6-terphenyl α-dialdimines.

complex. We also report the preparation of the *N*,*N*′-bis-(2-phenylphenyl)imidazolium (IBpH$^+$) and imidazol-2-ylidene (IBp) congeners. The spatial bulk of IDitop and IBp is discussed relative to existing bulky NHCs like IDip using the molecular structure of their silver(I) chloride complexes as a basis for calculation.

The bulky NHC precursors DmpDAB (DAB = *N*,*N*′-disubstituted-1,4-diazabutadiene) and DitopDAB (Ditop = 2,6-bis(4-tolyl)phenyl) were prepared in moderate yield by condensation of the respective anilines, DmpNH$_2$ and DitopNH$_2$, with half an equivalent of glyoxal in acetonitrile (Scheme 2).

Although this preparation has previously been used to access several *N*,*N*′-bis(2,6-terphenyl)-α-diketimines, which have found utility in late transition metal catalysis,[15] DitopDAB and DmpDAB are the first α-dialdimines.

Both α-dialdimines exhibit *N*-arylimine symmetrical chemical environments in solution, as evidenced by ^{1}H NMR spectroscopy (C_6D_6). This suggests C_2-symmetric *E-anti* or *-syn* isomerism.[16] The *E-anti* structure of DitopDAB in the solid-state was determined by XRD methods (Fig. 2, POV-RAY illustration, 10% van der Waals radii), wherein DitopDAB crystallises in the monoclinic space group $P2_1/c$ with half a molecular unit in the asymmetric unit. The bonding parameters of DitopDAB (C═N 1.279(3) Å, C–C 1.453(5) Å) are comparable with those of the related α-diimines Ar′N═C(Me)–C(Me)═N′Ar, where Ar′ is 3- or 4-trimethylsilylphenyl, which also exist as *E-anti* isomers in the solid-state.[17] The imine functionalities of both DmpDAB and DitopDAB are evidenced by medium intensity C═N absorptions at *ca.* 1610 cm^{-1} in the IR spectra of both α-dialdimines.

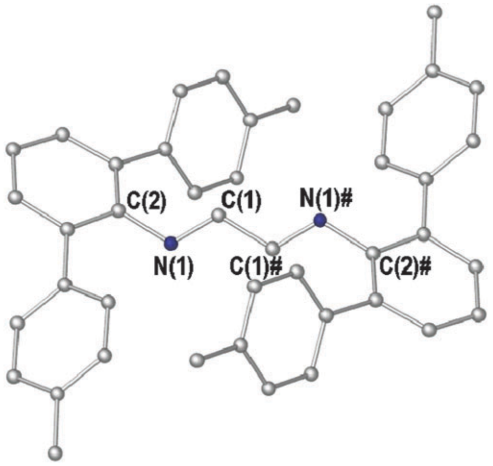


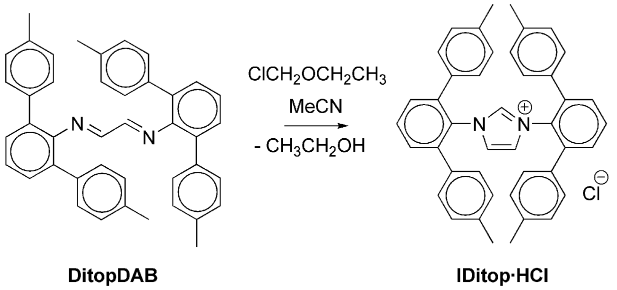
Fig. 2 Molecular structure of DitopDAB. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.279(3), C(1)–C(1)# 1.453(5), N(1)–C(2) 1.421(3), C(1)–N(2)–C(2) 118.9(2), N(1)–C(1)–C(1)# 119.2(3). Symmetry tranformation used to generate '#' atoms: $2 - x$, $-y$, $1 - z$.

The preparation of 1,3-bis(2,6-terphenyl)imidazolium salts from DitopDAB and DmpDAB was initially attempted using paraformaldehyde in the presence of hydrochloric acid, as per the method described by Nolan and co-workers for IDip·HCl.[14] This led to hydrolysis of the diazabutadiene to regenerate the parent anilines as their hydrochloride salts. Arduengo and co-workers have described an alternative preparation of IMes·HCl and IDip·HCl (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) involving treatment of a diazabutadiene with chloromethyl ethyl ether in acetonitrile at ambient temperature.[18] This method was successfully applied to DitopDAB to give IDitop·HCl (Scheme 3) but the analogous reaction of DmpDAB, even at elevated temperatures, afforded only Dmp anilinium chloride. As cyclisation of diazabutadienes to imidazolium salts necessitates an *E-syn* isomer for formylation,[16] it is likely that the steric buttressing of DmpDAB prevents imidazolium formation.

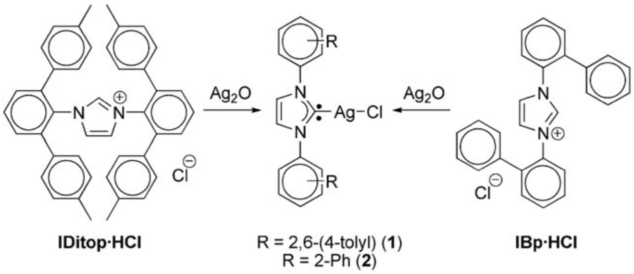
The imidazolium salt IDitop·HCl is a colourless deliquescent thermally robust solid (dec. 188 °C without melting). As per DitopDAB, its ^{1}H NMR spectrum (d_6-DMSO) exhibits a single well-defined methyl singlet at 2.35 ppm that is indicative of symmetrical Ditop chemical environments in solution.

Attempts to obtain crystalline samples of IDitop·HCl suitable for single crystal X-ray structure determination have not been successful to date.

NHC silver(I) coordination compounds are commonly utilised precursors for transmetallation of NHCs onto catalytically active group 8–10 metals.[8,9] As a preliminary foray into the coordination chemistry of IDitop, a silver(I) chloride coordination complex, [AgCl(IDitop)] (**1**), was prepared by reaction of IDitop·HCl with excess silver(I) oxide in dichloromethane (Scheme 4).[10,19] In order to assess the contribution of both 2- and 6-aryl substituents on the principal *N*-aryls of IDitop and its overall steric bulk, a silver(I) chloride complex coordinated by *N*,*N*′-bis(2-phenylphenyl)imidazol-2-ylidene (IBp), [AgCl(IBp)] (**2**), was also prepared using analogous preparative procedures.



Scheme 3 Preparation of IDitop·HCl by treatment of DitopDAB with chloromethyl ethyl ether.



Scheme 4 Preparation of silver(I) chloride complexes from 1,3-bis-(2,6-tolylphenyl)- and -(2-phenylphenyl)imidazolium chloride salts.

Compounds **1** and **2** are thermally robust complexes (dec. > 315 °C) that, even on prolonged exposure to sunlight, do not reductively deposit silver. Both compounds are soluble in dichloromethane and may be isolated in analytically pure form simply by filtration of Ag$_2$O–NHC·HCl reaction mixtures and removal of volatiles under reduced pressure. Single crystals of **1** and **2** suitable for single crystal X-ray structure determination were grown from dichloromethane–hexane solutions (Fig. 3, POV-RAY illustration, 10% van der Waals radii). Compound **1** crystallises with half a molecule in the asymmetric unit that lies about a two-fold axis with Ag(1), Cl(1) and C(1) on the two-fold axis. Compound **2** crystallises with one whole molecule in the asymmetric unit.

The molecular structures of **1** and **2** provide considerable insight into the steric bulk of coordinated NHCs bearing *N*-2,6-terphenyl and *N*-2-phenylphenyl substituents. Calculation of 'Tolman' type cone angles[20] for the NHCs of **1** and **2** using the structural location of the Ag atoms calculated here indicate angles of 184.01(20)° and 131.07(5)°, respectively. The former angle exceeds the 155.1° angle calculated for the Ag(IDip) unit of [AgCl(IDip)],[19] which exhibits Ag–Cl–C bonding parameters consistent with those of **1** and **2** (Ag–Cl 2.316(17), Ag–C 2.056(6) Å).[19] The impressive cone angles of 1,3-bis-(Tmt)imidazol-2-ylidene (Tmt = 3,5-bis(2,4,6-trimethyl)phenyl)[13] and 1,3-bis(4-(2′,3′,4′,5-tetraphenylphenyl)phenyl)imidazol-2-ylidene,[10] which are both likely to exceed 180°, are calculated such that their steric bulk is beyond the metal coordination sphere. This effects minimal spatial influence at the metal. Thus, to our knowledge, IDitop possesses the largest cone angle of any NHC prepared to date.

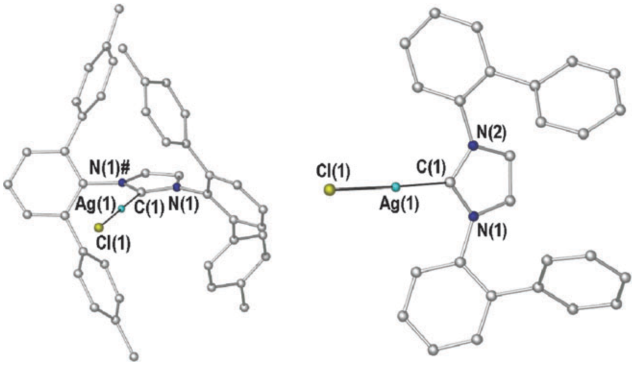


Fig. 3 Molecular structures of compounds **1** and **2**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) (those of **2** listed in square parentheses after those of **1**): Ag(1)–Cl(1) 2.345(2) [2.3440(11)], Ag(1)–C(1) 2.062(8) [2.079(2)], 4,5-C–C 1.326(11) [1.343(3)], N(1)–C(1)–N(1)# 103.1(7) [103.79(18)], Tolman cone angle[20] formed by NHC about Ag(1) 184.01(20) [131.07(5)]. Symmetry transformation used to generate '#' atoms of **1**: $-x$, y, $1/2 - z$.

The 2-phenyl placement of **2** (Fig. 3) has precedent in the 1,3-bis(2-phenylphenyl)imidazolin-2-ylidene NHC of Bellemin-Laponnaz *et al.*,[21] which differs to **2** in its saturation of the 4,5-heterocyclic C–C bond, and the recent chiral imidazolin-2-ylidenes of Shi and Xu[22] that utilise the asymmetric principles of Grubbs, *cf.* asymmetric olefin metathesis catalysts (chirality at 4- and 5-position of heterocycle, *e.g.* 4*R*,5*R*-NC(H)PhC(H)PhN),[23] to guide the 2-phenyl groups in order to effect C_2–NHC symmetry at a coordinated metal.

In summary, we have successfully prepared the first *N*,*N′*-bis(2,6-terphenyl) substituted imidazol-2-ylidene, IDitop, as its silver(I) transmetallation complex in readiness for catalytic application as a support ligand. Attempts to undertake similar chemistry using the bulkier terphenyl Dmp were unsuccessful. Molecular structure comparison of AgCl coordinated IDitop with IBp indicates a significantly greater 'cone angle' for the former which surpasses that of the presently favoured 'bulky' NHC·IDip.

The synthesis and application of IDitop, IBp and related NHCs to homogeneous and organocatalysis are ongoing in our laboratory.

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Experimental

Diethyl ether and hexane were dried over sodium and freshly distilled from sodium diphenylketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. Dichloromethane was dried over calcium hydride and freshly distilled prior to use. DmpNH$_2$ and DitopNH$_2$ were prepared using the procedure of Tilley and Gavenonis for the preparation of DmpNH$_2$.[24] BpDAB was made using the same procedure as that used for DitopDAB with ethanol as solvent. All other chemicals were purchased from Sigma-Aldrich and used as received. The preparations of compounds **1** and **2** were performed using conventional Schlenk techniques under an atmosphere of ultra high purity argon.

Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 MHz and 75.46 MHz, respectively, using a Varian Gemini 2000 spectrometer with chemical shifts referenced to the residual ^{1}H resonances of the *deuterated* solvents used. Melting points were determined in glass capillaries. Mass spectrometric analyses were conducted on a Finnegan LCQMS under electronic ionisation conditions. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand.

Syntheses

DitopDAB. DitopNH$_2$ (3.30 g, 12.07 mmol), 40% aqueous glyoxal (0.86 g, 6.03 mmol), and acetonitrile (20 mL) were stirred at 50 °C for three days, resulting in a colour change to brown and the formation of DmpDAB as a yellow precipitate. Filtration and washing with cold methanol afforded analytically pure DmpDAB (1.81 g, 53%), mp 208 °C. Elemental analysis calculated (%) for $C_{42}H_{36}N_2$: C 88.69, H 6.38, N 4.93; found: C 88.94, H 6.31, N 4.91; ^{1}H NMR (C_6D_6): δ 2.20 (s, 12H, *p*-C*H*$_3$), 6.98 (d, 8H, $^3J_{HH}$ 7.8 Hz, 2/3-Ar′C*H*), 7.00 (t, 2H, $^3J_{HH}$ 7.5 Hz, 4-ArC*H*), 7.14 (d, 8H, $^3J_{HH}$ 7.8 Hz, 2/3-Ar′C*H*), 7.23 (d, 4H, $^3J_{HH}$ 7.5 Hz, 3/5-ArC*H*), 7.62 (s, 2H, N=C*H*); ^{13}C{^{1}H} NMR (C_6D_6): δ 21.6 (*p*-*C*H$_3$), 125.9, 129.3, 130.6, 133.8 (Ar*C*H), 129.5, 136.4, 137.7, 148.0 (Ar*C*), 165.5 (N=*C*); IR (Nujol), cm^{-1}: 1613 m, 1571 w, 1303 w, 1289 w, 1188 w, 1111 w, 1076 w, 1035 w, 1017 w, 948 w, 941 w, 846 w, 830 w, 812 m, 787 m, 764 m, 745 m, 660 w; EIMS (*m*/*z*) 568.3 (100% [M$^+$]).

DmpDAB. DmpNH$_2$ (1.10 g, 3.90 mmol), 40% aqueous glyoxal (0.4 mL, 1.95 mmol), and acetonitrile (10 mL) were stirred for two days at 60 °C resulting in the precipitation of DmpDAB as a yellow solid. The product was filtered, washed with acetonitrile (10 mL) and recrystallised from ethyl acetate to afford a microcrystalline powder (0.819 g, 72%), mp 252–253 °C. Elemental analysis calculated (%) for $C_{50}H_{52}N_2$: C 88.19, H 7.70, N 4.11; found: C 87.59, H 7.97, N 4.16; ^{1}H NMR (C_6D_6,): δ 1.86 (s, 24H, *o*-C*H*$_3$), 2.29 (s, 12H, *p*-C*H*$_3$), 6.81 (s, 8H, 3/5-Ar′C*H*), 6.89 (d, 4H, $^3J_{HH}$ 6.0 Hz, 3/5-ArC*H*), 6.90 (t, 2H, $^3J_{HH}$ 6.0 Hz, 4-ArC*H*) 7.13 (s, 2H, N=C*H*); ^{13}C{^{1}H} NMR (C_6D_6): δ 20.8 (*o*-*C*H$_3$), 21.7 (*p*-*C*H$_3$), 126.0, 130.0, 132.5, 136.2, 136.5, 136.6, 148.0, (Ar*C*), 161.4 (N=*C*); IR (Nujol), cm^{-1}: 1612 m; 1574 w, 1414 m, 1290 m, 1261 m, 1192 w, 1156 w, 1096 m, 1072 m, 1029 m, 932 w, 848 s, 825 m, 803 s, 799 w, 765 s, 741 m, 659 w, 604 s; EIMS (*m*/*z*) 681.5 (25% [MH$^+$]), 703.6 (100% [MNa$^+$]).

IDitop·HCl. DitopDAB (0.57 g, 1.0 mmol) and chloromethyl ethyl ether (2.0 mL, 22 mmol) were stirred for 5 minutes before adding acetonitrile (3 mL). The resultant brown solution was stirred for 1 hour after which all volatiles were removed *in vacuo* to afford a brown solid. The crude product was extracted with water (10 mL), washed with diethyl ether (10 mL) and recrystallised from acetone to afford fine white needles (0.44 g, 70%), mp 288 °C (dec). Microanalyses for IDitop·HCl were repeatedly low in carbon, perhaps suggesting cocrystallisation with acetone or residual moisture. Representative example: elemental analysis calculated (%) for $C_{43}H_{37}N_2Cl$: C 83.68, H 6.04, N 4.54; found: C 83.15, H 6.09, N 4.36; ^{1}H NMR (*d*$_6$-DMSO): δ 2.35 (s, 12H, *p*-C*H*$_3$), 6.85 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar′C*H*), 7.12 (d, 8H, $^3J_{HH}$ 8.2 Hz 2/3-Ar′C*H*), 7.41 (d, 4H, $^3J_{HH}$ 7.6 Hz, 4-ArC*H*), 7.49 (s, 2H, 4,5-C$_2$*H*$_2$), 7.68 (s, 2H, $^3J_{HH}$ 7.6 Hz, 3/5-ArC*H*), 9.41 (s, 1H, 2-C*H*); ^{13}C{^{1}H} NMR (*d*$_6$-DMSO): 20.8 (*C*H$_3$), 124.8 (4,5-*C*$_2$), 128.5, 129.2, 130.6, 131.5 (Ar*C*H), 129.3, 133.6, 137.5, 138.8 (Ar*C*), 139.1 (2-*C*); IR (Nujol), cm^{-1}: 1512 m, 1402 m, 1309 m, 1243 s, 1202 s, 1107 m, 1088 m, 1036 m, 1019 m, 954 w, 937 w, 924 w, 851 m, 841 m, 814 s, 790 s, 768 m, 749 m, 670 w, 616 w.

IBp·HCl. BpDAB (1.08 g, 3.0 mmol) and chloromethyl ethyl ether (4.0 mL, 44 mmol) were stirred for 2 minutes before adding acetonitrile (10 mL). The resultant brown solution was stirred for 1 hour, after which the volatiles were removed *in vacuo* to afford a brown solid. After washing with diethyl ether (30 mL), the crude product was extracted into water (30 mL) and dried under reduced pressure to give the title compound as a brown solid that was washed with toluene (5 mL) (0.78 g, 64%), mp 140–143 °C. As per IDitop·HCl, microanalyses for IBp·HCl were repeatedly low in carbon. Representative example: elemental analysis calculated (%) for $C_{27}H_{21}N_2Cl$: C 79.30, H 5.18, N 6.85; found: C 79.37, H 5.53, N 6.37; ^{1}H NMR (*d*$_6$-DMSO): δ 7.20 (d, 4H, $^3J_{HH}$ 6.0 Hz, 2/6-Ar′C*H*), 7.42 (coincident dd and t, 6H, 3,4,5-Ar′C*H*), 7.62 (coincident d and s, 4H, 3-ArC*H* and 4,5-C$_2$H$_2$), 7.69 (dd, 2H, $^3J_{HH}$ 7.8 Hz, 7.8 Hz, 4-ArC*H*), 7.74 (dd, 2H, $^3J_{HH}$ 7.8 Hz, 7.8 Hz, 5-ArC*H*), 7.75 (d, 2H, $^3J_{HH}$ 7.8 Hz, 6-ArC*H*), 9.91 (s, 1H, 2-C*H*); ^{13}C{^{1}H} NMR (*d*$_6$-DMSO): δ 124.1 (4,5-*C*$_2$), 127.2, 128.4, 128.6, 128.8, 129.1, 131.2, 131.5, 131.3, 136.1, 137.3 (Ar*C*), 138.2 (2-*C*); IR (Nujol), cm^{-1}: 1662 w, 1596 w, 1538 m, 1338 m, 1266 m, 1224 m, 1159 m, 1118 m, 1069 m, 1009 w, 918 w, 763 s, 734 s, 702 s, 682 m, 654 m, 610 m.

[AgCl(IDitop)] (1). IDitop·HCl (0.46 g, 0.74 mmol) and Ag_2O (0.18 g, 0.74 mmol) were stirred under vacuum for 30 minutes before addition of dichloromethane (50 mL). The resulting slurry was stirred for 20 hours to afford a pale brown solution. Filtration, followed by removal of volatiles under reduced pressure, afforded the title compound as a pale brown solid that was subsequently recrystallised from dichloromethane–hexane as colourless plates (0.40 g, 73%), mp > 315 °C. Elemental analysis calculated (%) for $C_{44}H_{38}AgCl_3N_2$ (NB: $+CH_2Cl_2$): C 65.32, H 4.73, N 3.46; found: C 65.97, H 4.64, N 3.79; ^{1}H NMR (CD_2Cl_2): δ 2.35 (s, 12H, *p*-C*H*$_3$), 6.33 (s, 2H, 4,5-C$_2$*H*$_2$), 6.92 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar′C*H*), 7.19 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar′C*H*), 7.33 (d, 4H, $^3J_{HH}$ 7.2 Hz, 3/5-ArC*H*), 7.48 (t, 2H, $^3J_{HH}$ 7.2 Hz, 4-ArC*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.0 (*p*-*C*H$_3$), 122.9 (4,5-*C*$_2$), 128.8, 129.3, 131.7, 137.5 (Ar*C*H), 128.6, 130.0, 136.0, 139.2 (Ar*C*); IR (Nujol), cm^{-1}: 1944 w, 1890 m, 1831 w, 1781 w, 1736 w, 1642 w, 1609 w, 1566 w, 1512 s, 1470 s, 1449 s, 1402 s, 1309 m, 1243 s, 1206 s, 1203 s, 1197 m, 1107 m, 1088 m, 1036 m, 1019 w, 954 w, 937 w, 924 w, 851 m, 841 m, 815 s, 791 s, 768 m, 749 m, 670 w, 616 w; EIMS (*m*/*z*) 581.4 (100% IDitopH$^+$).

[AgCl(IBp)]·CH_2Cl_2 (2). IBp·HCl (0.82 g, 2.0 mmol) and Ag_2O (0.46 g, 2.0 mmol) were reacted and worked up in an identical fashion to **1**. Recrystallisation from dichloromethane–hexane afforded **2** as small colourless plates (0.64 g, 62%), mp 135–137 °C, dec. > 315 °C. Elemental analysis calculated (%) for $C_{28}H_{22}AgCl_3N_2$: C 55.98, H 3.69, N 4.66; found: C 55.41, H 3.70, N 4.69; ^{1}H NMR (CD_2Cl_2): δ 6.79 (s, 2H, 4,5-C$_2$*H*$_2$), 7.19 (br d, 4H, 2/6- or 3/5-Ar′C*H*), 7.36 (m, 6H, coincident 2/6- or 3/5-Ar′C*H* and ArC*H*), 7.46 (br d, 2H, 3- or 6-ArC*H*), 7.54 (m, 4H, coincident 3- or 6-ArC*H* and 4- or 5-ArC*H*), 7.59 (br t, 2H, 4- or 5-ArC*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 123.7

(4,5-C_2), 128.1, 128.4, 129.3, 129.4, 129.6, 130.4, 132.1 (Ar*C*H), 137.9, 138.4, 138.8 (s, Ar*C*); IR (Nujol), cm^{-1}: 1978 w, 1958 w, 1938 w, 1922 w, 1893 w, 1815 w, 1769 w, 1746 w, 1731 w, 1704 w, 1698 w, 1681 w, 1660 w, 1651 w, 1633 w, 1606 w, 1583 w, 1564 w, 1557 w, 1538 w, 1503 m, 1407 m, 1352 m, 1339 m, 1279 m, 1264 s, 1224 w, 1185 w, 1166 w, 1152 w, 1115 w, 1090 w, 1073 w, 1049 w, 1031 w, 996 w, 979 w, 968 w, 945 m, 925 w, 892 w, 871 w, 831 w, 761 s, 749 m, 725 s, 702 s, 686 m, 661 w, 611 m; EIMS (*m*/*z*) 373.4 (100% IBpH$^+$), 852.3 (24% Ag(IBp)$_2$$^+$).

Single crystal X-ray structure determination

All single crystal X-ray structure determinations were undertaken using samples mounted on glass fibres in silicone oil. Data were collected using graphite monochromated Mo$_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) at 123(2) K on a Bruker X8 Apex diffractometer. Structural solution and refinement were carried out using the SHELX suite of programs.[25]

Crystal data for DitopDAB: $C_{42}H_{36}N_2$, M = 568.764, monoclinic, $P2(1)/c$ (No. 14), a = 14.4140(8), b = 16.8693(10), c = 6.3926(3) Å, β = 90.377(3)°, V = 1554.35(15) Å^3, Z = 2, D_c = 1.215 g cm^{-3}, F_{000} = 604, μ = 0.070 mm^{-1}, $2\theta_{max}$ = 56.34°, 13 663 reflections collected, 3727 unique (R_{int} = 0.1345). Final *GooF* = 0.996, R_1 = 0.0796, wR_2 = 0.1660, *R* indices based on 1626 reflections with $I > 2\sigma(I)$ (refinement on F^2), 201 parameters, 0 restraints.

Crystal data for **1**: $C_{43}H_{36}AgClN_2$, M = 724.06, orthorhombic, *Pbcn* (no. 60), a = 15.701(2), b = 13.1938(16), c = 16.310(2) Å, V = 3378.8(8) Å^3, Z = 4, D_c = 1.423 g cm^{-3}, F_{000} = 1488, μ = 0.710 mm^{-1}, $2\theta_{max}$ = 55.88°, 20 798 reflections collected, 3748 unique (R_{int} = 0.0636). Final *GooF* = 1.227, R_1 = 0.0989, wR_2 = 0.1580, *R* indices based on 3244 reflections with $I > 2\sigma(I)$ (refinement on F^2), 206 parameters, 0 restraints.

Crystal data for **2**: $C_{27}H_{20}AgClN_2\cdot CH_2Cl_2$, M = 600.70, triclinic, $P\bar{1}$ (no. 2), a = 9.4785(19), b = 10.348(2), c = 14.088(3) Å, α = 69.73(3), β = 76.14(3), γ = 82.22(3)°, V = 1256.4(4) Å^3, Z = 2, D_c = 1.588 g cm^{-3}, F_{000} = 604, μ = 1.141 mm^{-1}, $2\theta_{max}$ = 55.98°, 21 644 reflections collected, 5938 unique (R_{int} = 0.0362). Final *GooF* = 1.038, R_1 = 0.0310, wR_2 = 0.0791, *R* indices based on 5476 reflections with $I > 2\sigma(I)$ (refinement on F^2), 307 parameters, 0 restraints.

Variata: The XRD data for compound **1** are of poor quality but the gross connectivity of the structure has been established. Two atoms could not be refined with satisfactory anisotropic thermal parameters. Attempts to refine these atoms (C(5) (*meta* carbon of primary Ditop aryl) and C(15) (methyl of one tolyl group) using ISOR refinements were also unsatisfactory. Both atoms have been refined with isotropic thermal parameters.

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