

Electronic Supporting Information

for

Group 13 Complexes of Dipyridylmethane, a Forgotten Ligand in Coordination Chemistry

Petra Vasko,^a Virva Kinnunen,^a Jani Moilanen,^a Tracey L. Roemmele,^b René T. Boéré,^b Jari Konu,^a and Heikki M. Tuononen^{a,}*

^a University of Jyväskylä, Department of Chemistry, Nanoscience Centre, P.O. Box 35, FI-40014 University of Jyväskylä, Finland. Phone: +358-40-805-3713, Fax: +358-14-260-2501, E-mail:

heikki.m.tuononen@jyu.fi

^b Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, AB, Canada T1K 3M4.

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1. Crystallographic details and selected structural parameters for 1a·CH₂Cl₂, 1b·THF, 2c, 3·THF and 4

Table 1 Crystallographic data for compounds [(dpma)₂GaCl₂]⁺[GaCl₄]⁻·CH₂Cl₂ (**1a**·CH₂Cl₂), [(dpma)₂AlCl₂]⁺[AlCl₄]⁻·C₄H₈O (**1b**·THF), [(dpma)GaCl₂]⁺[GaCl₄]⁻ (**2c**), (dpma)InCl₃·C₄H₈O (**3**·THF) and (dpma)(BCl₃)₂ (**4**)

	1a ·CH ₂ Cl ₂ ^b	1b ·THF ^a	2c ^b	3 ·THF ^b	4 ^a
emp. formula	C ₂₃ H ₂₂ Cl ₈ Ga ₂ N ₄	C ₉₂ H ₈₈ Al ₈ Cl ₂₄ N ₁	C ₁₁ H ₁₀ Cl ₆ Ga ₂ N ₂	C ₁₅ H ₁₈ Cl ₃ InN ₂ O	C ₁₁ H ₁₀ B ₂ Cl ₆ N ₂
formula weight	777.49	2500.42	522.35	463.48	404.53
cryst. system	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> , Å	12.134(5)	13.0514(7)	9.87(5)	8.255(5)	7.5511(4)
<i>b</i> , Å	12.930(5)	13.7004(8)	14.980(5)	15.233(5)	10.7802(6)
<i>c</i> , Å	19.258(5)	16.9566(9)	24.874(5)	14.100(5)	11.2368(6)
α , deg.	90.000	68.062(5)	90.000	90.000	112.339(5)
β , deg.	104.453(5)	83.116(4)	90.000	98.980(5)	98.875(5)
γ , deg.	90.000	82.799(5)	90.000	90.000	101.174(5)
<i>V</i> , Å ³	2926(2)	2781.5(3)	3678(2)	1751(1)	803.40(8)
<i>Z</i>	4	1	8	4	2
<i>T</i> , °C	-150	-150	-150	-150	-150
ρ_{calcd} , g cm ⁻³	1.765	1.493	1.887	1.758	1.672
μ , mm ⁻¹	2.595	6.433	3.794	1.809	9.675
crystal size, mm ³	0.24×0.20×0.16	0.15×0.15×0.05	0.24×0.16×0.12	0.28×0.16×0.10	0.30×0.16×0.09
<i>F</i> (000)	1544.0	1272.0	2032.0	920.0	404.00
Θ range, deg	2.39–25.02	4.59–66.60	2.60–25.02	3.66–25.02	4.39–67.00
reflns collected	8768	18717	6007	5957	5268
unique reflns	5151	9793	3225	3086	2831
<i>R</i> _{int}	0.0307	0.0626	0.0215	0.0165	0.0248
reflns [<i>I</i> >2 σ (<i>I</i>)]	4424	7794	2754	2874	2667
<i>R</i> ₁ [<i>I</i> >2 σ (<i>I</i>)] ^c	0.0595	0.0811	0.0390	0.0232	0.0554
<i>wR</i> ₂ (all data) ^d	0.1145	0.2045	0.0684	0.0437	0.1591
GOF on <i>F</i> ²	1.103	1.012	1.146	1.084	1.085
completeness	0.997	0.998	0.993	0.997	0.990

^a λ (CuK α) = 1.54184 Å. ^b λ (MoK α) = 0.71073 Å. ^c $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. ^d $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) of compounds [(dpma)₂GaCl₂]⁺[GaCl₄]⁻·CH₂Cl₂ (**1a**·CH₂Cl₂), [(dpma)₂AlCl₂]⁺[AlCl₄]⁻·C₄H₈O (**1b**·THF), [(dpma)GaCl₂]⁺[GaCl₄]⁻ (**2c**), (dpma)InCl₃·C₄H₈O (**3**·THF) and (dpma)(BCl₃)₂ (**4**)

	1a ·CH ₂ Cl ₂ (M = Ga)	1b ·THF (M = Al)	2c (M = Ga)	3 ·THF (M = In)	4 (M = B)
M(1)-N(1)	2.113(4)	2.060(4)	1.964(3)	2.295(2)	1.621(4)
M(1)-N(2)	2.145(4)	2.081(3)	1.961(3)	2.323(2)	-
M(1)-N(3)	2.126(4)	2.063(3)	-	-	-
M(1)-N(4)	2.115(4)	2.057(4)	-	-	-
M(2)-N(2)	-	-	-	-	1.612(4)
M(1)-Cl(1)	2.316(1)	2.268(1)	2.133(2)	2.4422(8)	1.843(3)
M(1)-Cl(2)	2.296(1)	2.283(1)	2.119(1)	2.4226(8)	1.851(3)
M(1)-Cl(3)	-	-	-	2.452(1)	1.829(3)
M(2)-Cl(4)	-	-	-	-	1.849(3)
M(2)-Cl(5)	-	-	-	-	1.844(3)
M(2)-Cl(6)	-	-	-	-	1.853(3)
N(1)-C(5)	1.351(6)	1.354(5)	1.343(5)	1.349(3)	1.366(4)
N(2)-C(7)	1.351(6)	1.353(5)	1.347(5)	1.352(3)	1.371(4)
N(3)-C(16)	1.341(6)	1.360(6)	-	-	-
N(4)-C(18)	1.356(6)	1.363(6)	-	-	-
C(5)-C(6)	1.512(7)	1.517(6)	1.513(5)	1.512(3)	1.516(4)
C(6)-C(7)	1.518(7)	1.508(6)	1.502(5)	1.507(3)	1.507(4)
C(16)-C(17)	1.513(7)	1.505(7)	-	-	-
C(17)-C(18)	1.500(7)	1.514(6)	-	-	-
N(1)-M(1)-N(2)	85.5(2)	86.1(2)	93.2(1)	79.25(7)	-
N(3)-M(1)-N(4)	88.0(2)	87.0(2)	-	-	-
N(1)-M(1)-Cl(1)	92.8(1)	96.5(1)	109.51(9)	164.19(5)	106.8(2)
N(1)-M(1)-Cl(2)	88.1(1)	91.1(1)	110.1(1)	94.10(6)	109.3(2)
N(1)-M(1)-Cl(3)	-	-	-	93.23(5)	111.4(2)
N(2)-M(1)-Cl(1)	176.6(1)	176.3(1)	110.8(1)	87.67(6)	-
N(2)-M(1)-Cl(2)	87.4(1)	87.0(1)	114.3(1)	165.31(5)	-
N(2)-M(1)-Cl(3)	-	-	-	97.70(6)	-
N(2)-M(2)-Cl(4)	-	-	-	-	109.3(2)
N(2)-M(2)-Cl(5)	-	-	-	-	111.2(2)
N(2)-M(2)-Cl(6)	-	-	-	-	108.1(2)
N(3)-M(1)-Cl(1)	85.1(1)	87.2(1)	-	-	-
N(3)-M(1)-Cl(2)	179.3(1)	176.7(1)	-	-	-
N(4)-M(1)-Cl(1)	88.3(1)	90.0(1)	-	-	-
N(4)-M(1)-Cl(2)	92.0(1)	95.3(1)	-	-	-
Cl(1)-M(1)-Cl(2)	95.55(5)	90.38(5)	116.42(5)	96.50(3)	111.8(2)
Cl(1)-M(1)-Cl(3)	-	-	-	97.32(4)	109.9(2)
Cl(2)-M(1)-Cl(3)	-	-	-	95.73(3)	107.7(2)
Cl(4)-M(2)-Cl(5)	-	-	-	-	109.0(2)
Cl(4)-M(2)-Cl(6)	-	-	-	-	111.2(2)

2. ^1H NMR spectra and details of variable temperature NMR experiments

^1H NMR discussion related to the 1:1 reaction between dpma and GaCl_3

The room temperature ^1H NMR spectrum (in d_8 -THF) recorded for the product from 1:1 reaction between dpma and GaCl_3 in Et_2O shows a singlet at 4.14 ppm and four multiplets from 7.58 to 8.99 ppm (Fig. S1). Although all ^1H NMR signals are of equal intensity, the singlet corresponding to the methylene hydrogens is extremely broad, as is also the case for one of the multiplets in the aromatic region. This indicates the presence of a dynamic process with an exchange rate faster than the NMR timescale. Consequently, the product was characterized in d_8 -THF solution using variable temperature ^1H NMR spectroscopy.

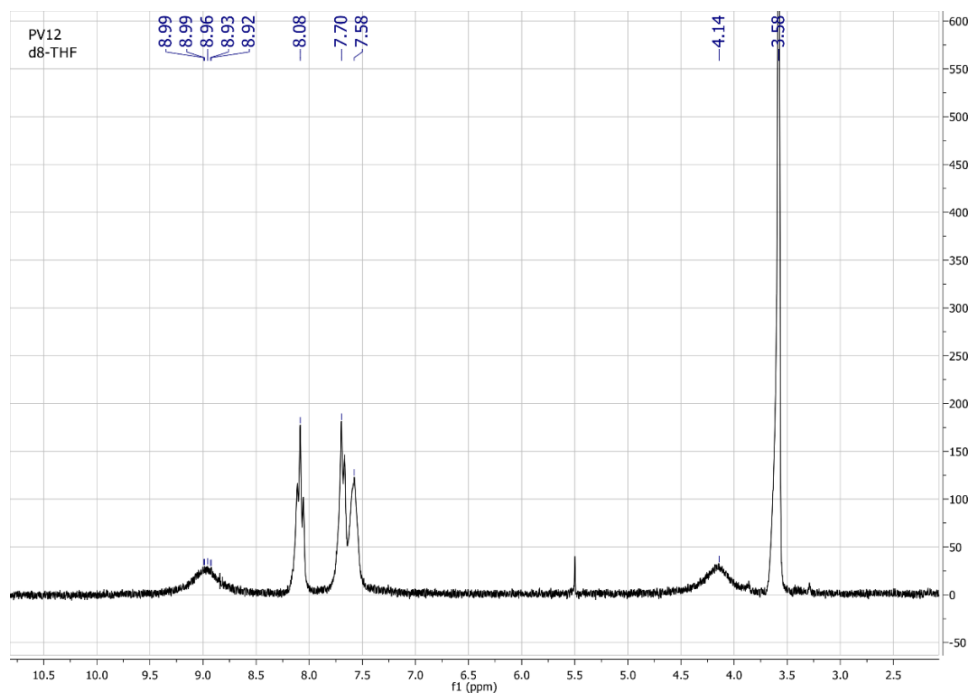


Fig. S1 ^1H NMR spectrum (in d_8 -THF) recorded for the product from 1:1 reaction between dpma and GaCl_3 in Et_2O .

When the temperature is lowered, the ^1H NMR signals start to separate below $0\text{ }^\circ\text{C}$ (Fig. S2). At $-40\text{ }^\circ\text{C}$, the ^1H NMR spectrum becomes well resolved and there is hardly any change in its appearance when further cooling the sample to $-80\text{ }^\circ\text{C}$. It is obvious from Fig. S2 that at temperatures below $-40\text{ }^\circ\text{C}$, the ^1H NMR spectrum is in the slow-exchange limit and consists of two AB doublets (3.34 and 4.40 ppm, $^2J(^1\text{H}, ^1\text{H}) = 16.5\text{ Hz}$) for the methylene hydrogens,¹ as well as of eight multiplets of equal intensity from 7.52 to 9.90 ppm of which two are partially overlapping at 7.70 ppm. The low temperature ^1H NMR spectrum is well-resolved and reveals the presence of a minor component with a singlet for the methylene hydrogens at 4.62 ppm (at $-80\text{ }^\circ\text{C}$) along with several partially resolved multiplets in the aromatic region. The solution behaviour of the reaction product can be explained by assuming that the reaction yields the expected salt $[(\text{dpma})_2\text{GaCl}_2]^+[\text{GaCl}_4]^-$ (**1a**) as the primary product, but that it also gives the salt $[(\text{dpma})\text{GaCl}_2]^+[\text{Cl}]^-$ (**2a**) in equilibrium with **1a**. Both products have 1:1 ligand to GaCl_3 ratio and they are able to interconvert in solution *i.e.* $[(\text{dpma})_2\text{GaCl}_2]^+[\text{GaCl}_4]^-$ (**1a**) \rightleftharpoons $2[(\text{dpma})\text{GaCl}_2]^+[\text{Cl}]^-$ (**2a**).

The above explanation is consistent with the observed NMR data. Specifically, the major component present at low temperatures can be identified as $[\textit{cis}-(\text{dpma})_2\text{GaCl}_2]^+$ cation: both the number and intensities of the observed signals agree with a rigid structure with two identical dpma ligands, each containing two inequivalent pyridyl moieties and methylene hydrogens (C_2 symmetry).² The minor component present in the low temperature ^1H NMR spectrum would then be the $[(\text{dpma})\text{GaCl}_2]^+$ cation with a tetrahedral metal centre and C_s point group, though most of the multiplets arising from pyridyl bound hydrogens are not resolved. We note that the low temperature spectrum shows no evidence of free dpma ligand that displays a characteristic methylene singlet at *ca.* 4.25 ppm.

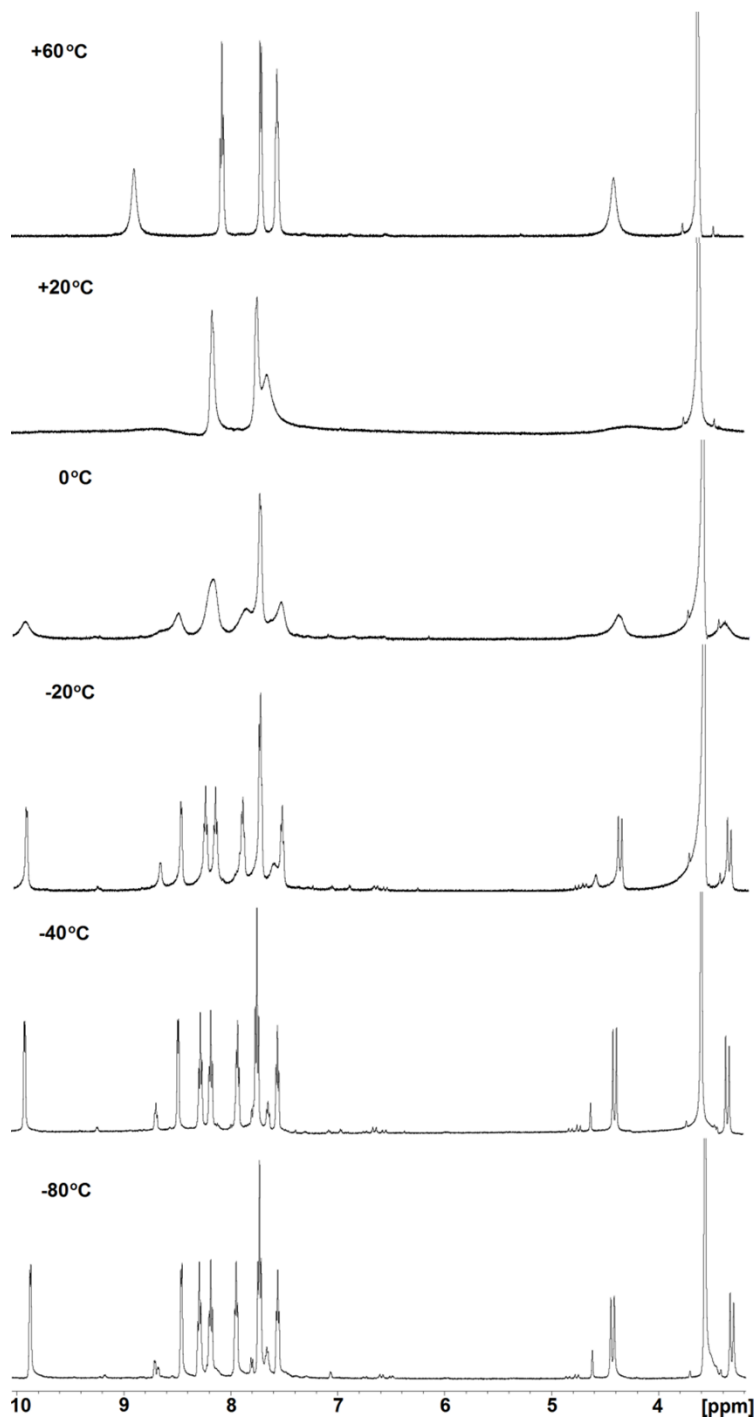


Fig. S2 Variable temperature ¹H NMR spectra (in *d*₈-THF) recorded for the product from 1:1 reaction between dpma and GaCl₃ in Et₂O.

Detailed NMR investigations revealed that the dynamic process $[(\text{dpma})_2\text{GaCl}_2]^+[\text{GaCl}_4]^-$ (**1a**) \rightleftharpoons $2[(\text{dpma})\text{GaCl}_2]^+[\text{Cl}]^-$ (**2a**) is not only temperature but also solvent dependent. While the room temperature ^1H NMR spectrum of the product in CD_2Cl_2 is similar to that in d_8 -THF (Fig. S3), a complete conversion to $[(\text{dpma})\text{GaCl}_2]^+[\text{Cl}]^-$ *i.e.* **2a** takes place rapidly in CD_3CN (Fig. S4). However, **2a** was found to be unstable in CD_3CN and it decomposes gradually into the free dpma ligand as well as to other uncharacterized products.

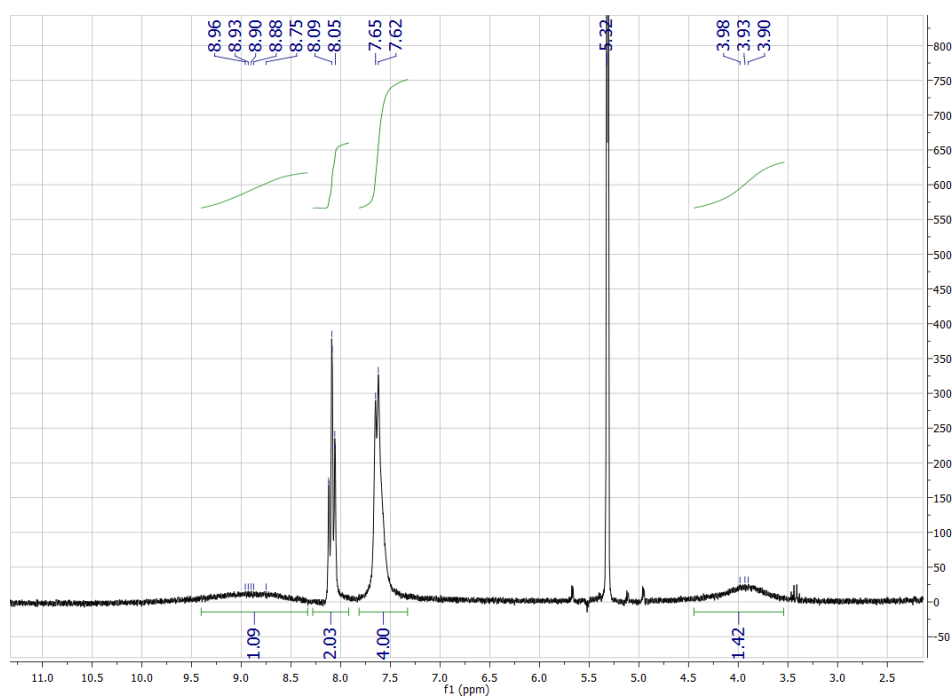


Fig. S3 ^1H NMR spectrum (in CD_2Cl_2) recorded for the product from 1:1 reaction between dpma and GaCl_3 in Et_2O . Quartet at 3.4 ppm is residual Et_2O .

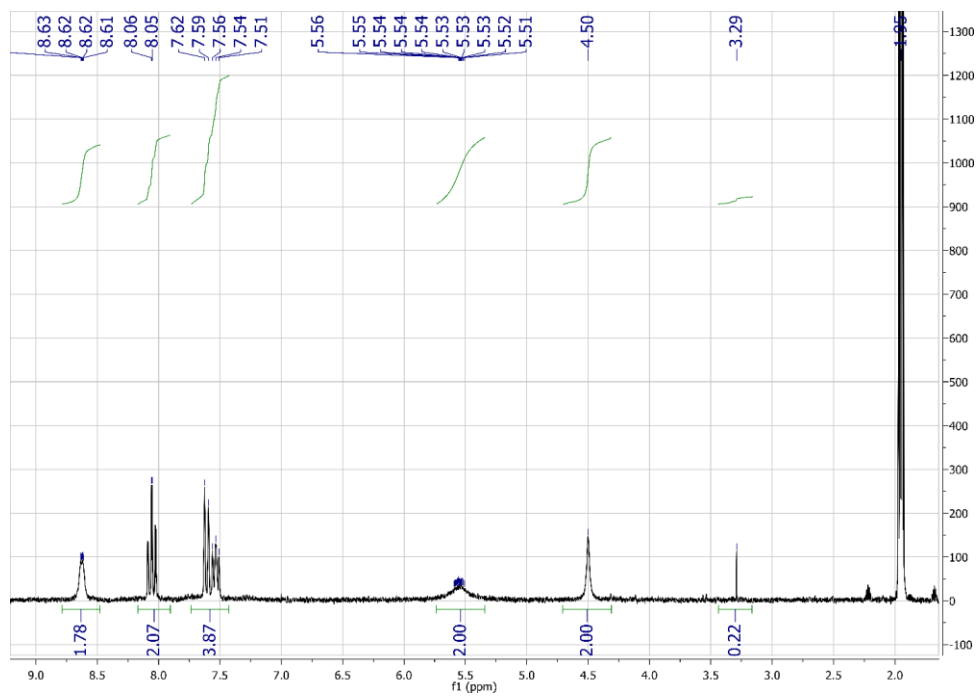


Fig. S4 ^1H NMR spectrum (in CD_3CN) recorded for the product from 1:1 reaction between dpma and GaCl_3 in Et_2O .

¹H NMR discussion related to the 1:1 reaction between dpma and AlCl₃

The room temperature ¹H NMR spectrum (in *d*₈-THF) for the product from 1:1 reaction between dpma and AlCl₃ in Et₂O shows that the reaction yields a mixture of two main species as judged by the number and intensity of signals in the aliphatic region (Fig. S5): a singlet at 4.43 ppm as well as two AB doublets at 3.09 and 4.33 ppm (²J(¹H,¹H) = 17.5 Hz). There is no indication of ligand redistribution with an exchange rate faster than the NMR timescale. The spectrum can be compared to the low temperature ¹H NMR data of the equilibrium between **1a** and **2a** (Fig. S2), which allows the identification of the main products from the AlCl₃ reaction as [*cis*-(dpma)₂AlCl₂]⁺[GaCl₄]⁻ (**1b**) and [(dpma)AlCl₂]⁺[Cl]⁻ (**2b**) in *ca.* 2:1 ratio at room temperature. Interestingly, the ¹H NMR spectrum shows also a second very low-intensity set of AB doublets at 4.70 and 6.69 ppm (²J(¹H,¹H) = 16.4 Hz). The identity of this minor product cannot be univocally established as the corresponding multiplets in the aromatic region are not resolved, but considering the similarity of its spectral data with [*cis*-(dpma)₂GaCl₂]⁺[GaCl₄]⁻, we tentatively assign the unknown species as [*trans*-(dpma)₂AlCl₂]⁺[AlCl₄]⁻. If the ¹H NMR spectrum of the product was measured in CD₃CN a conversion from a mixture of **1b** and **2b** to pure **2b** took place within a couple of hours. The salt **2b** could also be obtained pure by doing the synthesis in CH₃CN (Fig. S6).

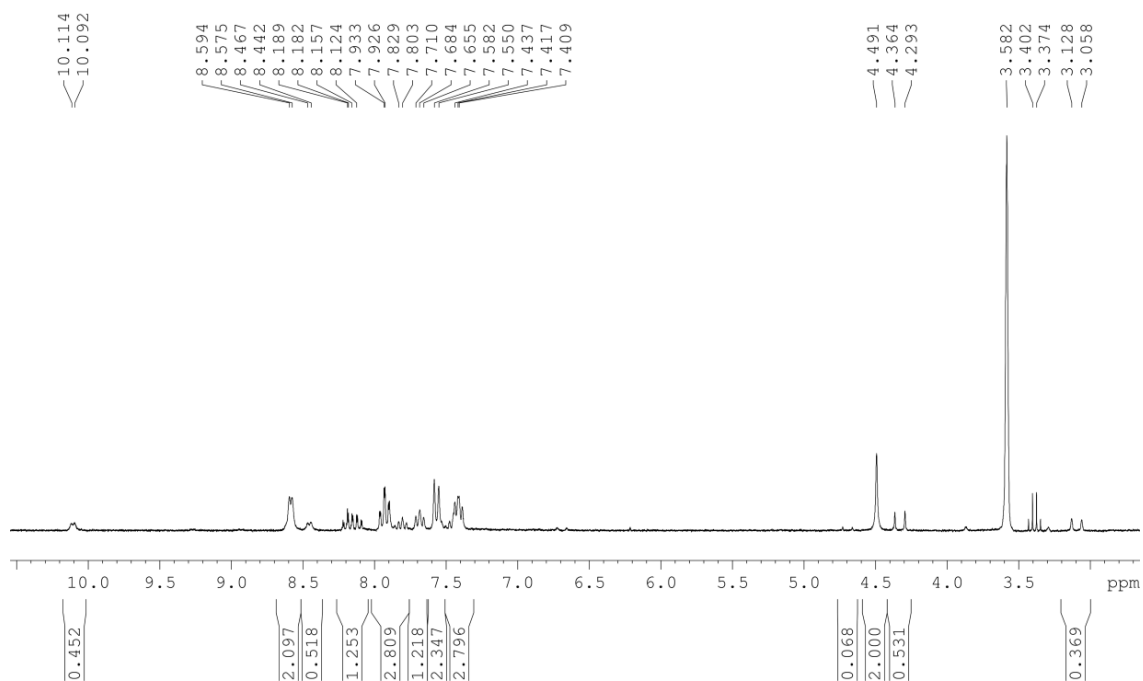


Fig. S5 ^1H NMR spectrum (in d_8 -THF) recorded for the product from 1:1 reaction between dpma and AlCl_3 in Et_2O . Quartet at 3.4 ppm is residual Et_2O .

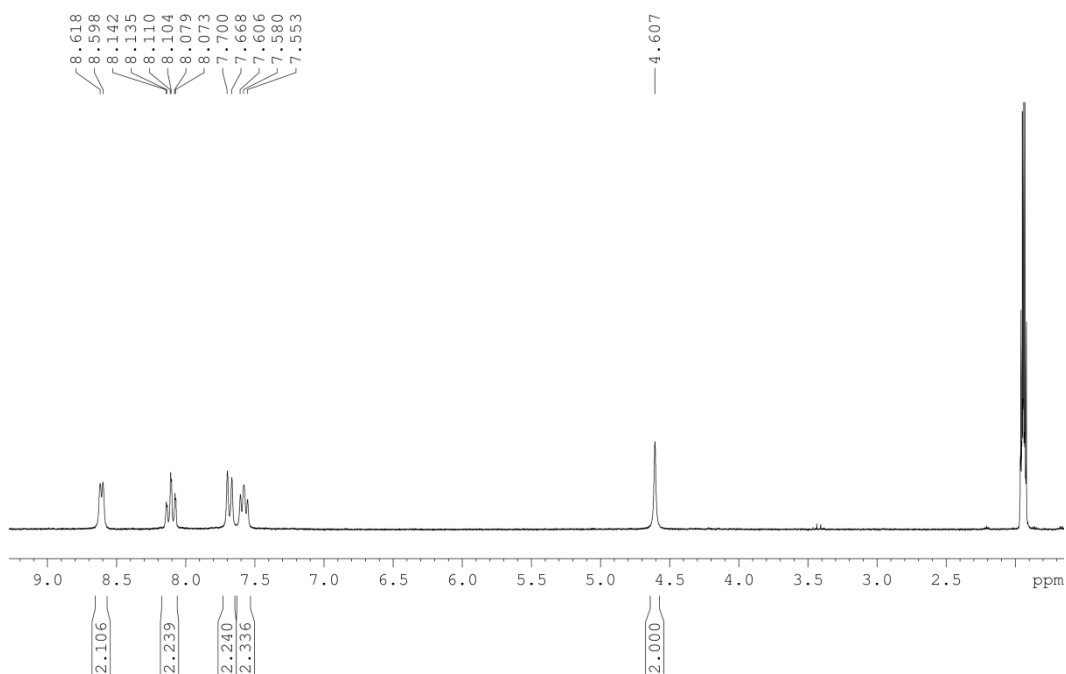


Fig. S6 ^1H NMR spectrum (in CD_3CN) recorded for the product (**2b**) from 1:1 reaction between dpma and AlCl_3 in CH_3CN . Quartet at 3.4 ppm is residual Et_2O .

¹H NMR discussion related to the 1:2 reaction between dpma and GaCl₃

The room temperature ¹H NMR spectrum (in *d*₈-THF) recorded for the product from 1:2 reaction between dpma and GaCl₃ in Et₂O is similar to that found for the 1:1 reaction (Fig. S7): a very broad singlet for the methylene hydrogens is observed at 4.75 ppm, while the pyridyl bound hydrogens show a set of multiplets from 7.81 to 8.97 ppm with a relative integration of 2:8. The broadness of the observed ¹H NMR signals is reminiscent of the solution behaviour observed earlier, which prompted us to conduct variable temperature NMR measurements also in this case.

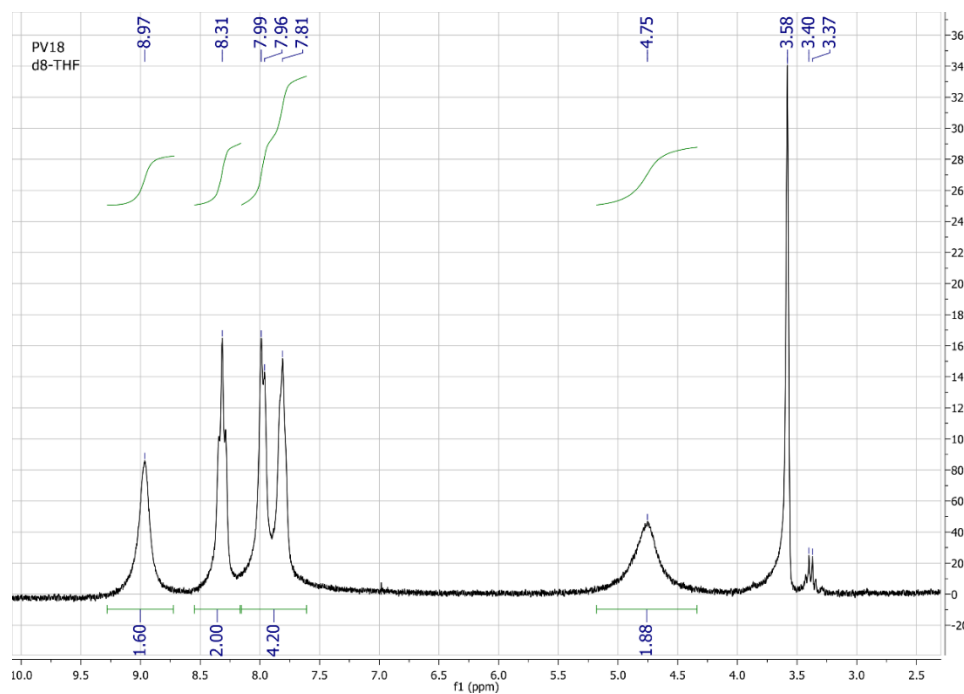


Fig. S7 ¹H NMR spectrum (in *d*₈-THF) recorded for the product from 1:2 reaction between dpma and GaCl₃ in Et₂O. Quartet at 3.4 ppm is residual Et₂O.

The ^1H NMR spectra (in d_8 -THF) recorded for the product within temperature range from -60 to $+40$ $^\circ\text{C}$ show separation of merged signals at -40 $^\circ\text{C}$ (Fig. S8), which allows identification of the cations $[(\text{dpma})\text{GaCl}_2]^+$ (singlet at 4.97 ppm) and $[(\text{dpma})_2\text{GaCl}_2]^+$ (AB doublets at 3.34 and 4.40 ppm) as the two species, present in ca. 3:1 ratio. Hence, the primary product from the reaction is the salt $[(\text{dpma})\text{GaCl}_2]^+[\text{GaCl}_4]^-$ (**2c**), as expected from reaction stoichiometry. However, a significant amount of the cation $[(\text{dpma})_2\text{GaCl}_2]^+$ is also present in solution at lower temperatures.

Detailed NMR investigations revealed that the dynamic process is not only temperature but also solvent dependent. In CD_2Cl_2 , the NMR data are consistent with **2c** being the only species present in solution (Fig. S9), whereas a very small amount of **1a** is visible in the CD_3CN spectrum with no indication of a dynamic process that is faster than the NMR timescale (Fig. S10).

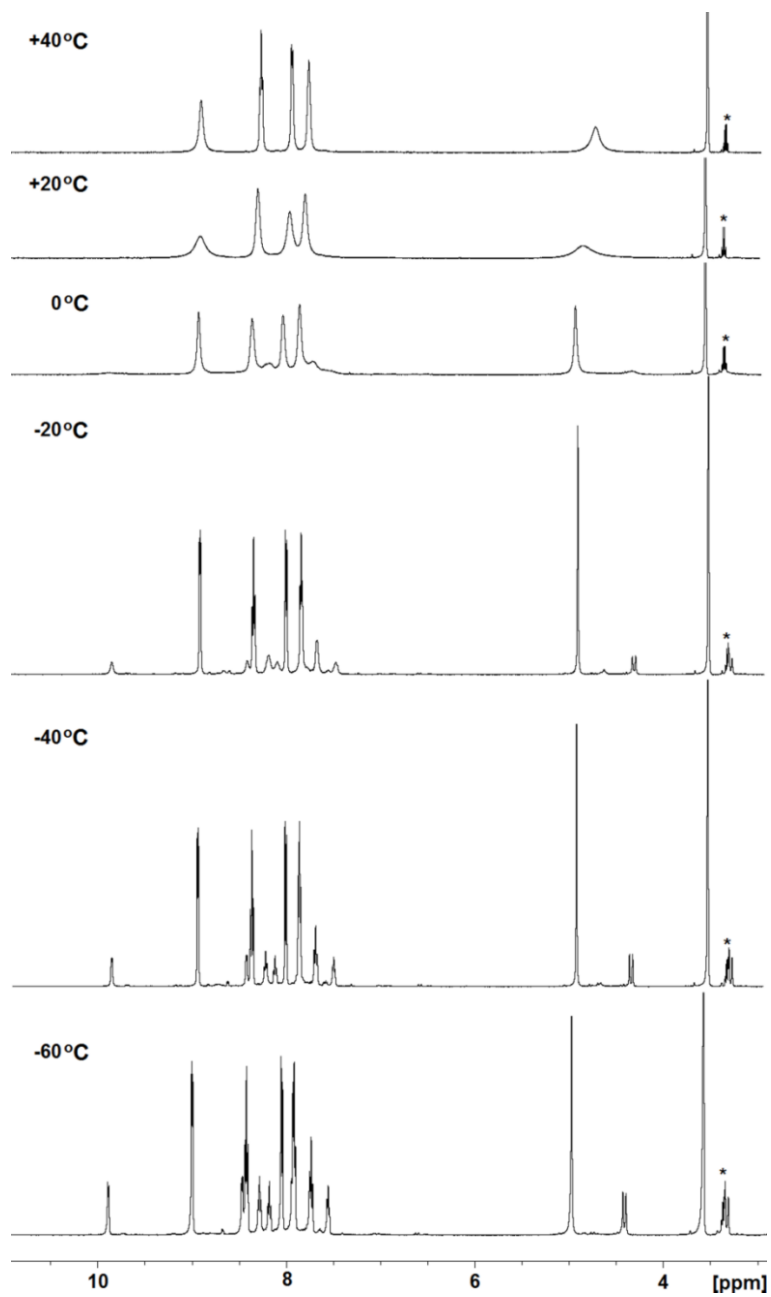


Fig. S8 Variable temperature ^1H NMR spectra (in d_8 -THF) recorded for the product from 1:2 reaction between dpma and GaCl_3 in Et_2O . Quartet at 3.4 ppm is residual Et_2O .

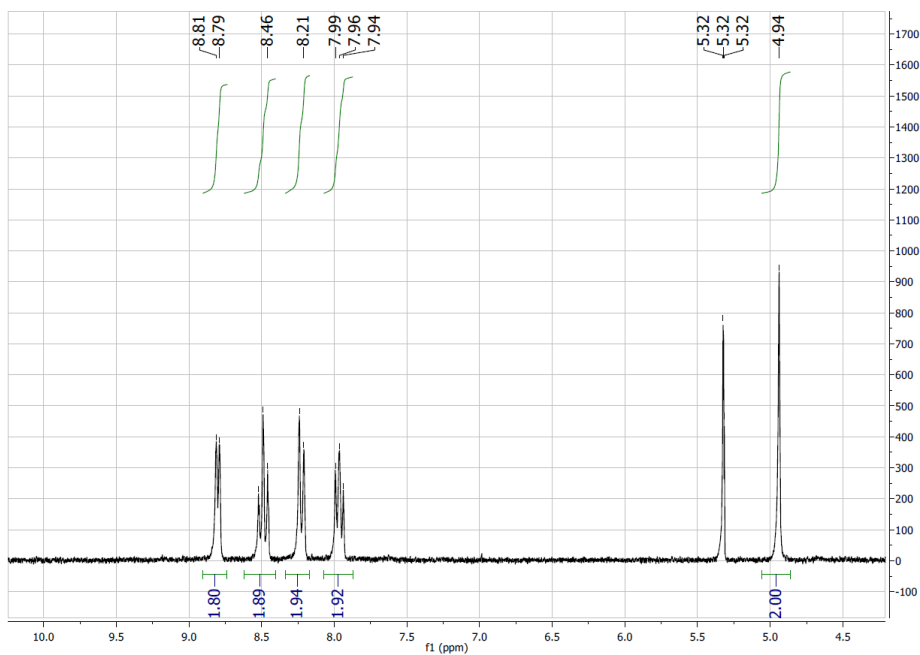


Fig. S9 ^1H NMR spectrum (in CD_2Cl_2) recorded for the product from 1:2 reaction between dpma and GaCl_3 in Et_2O .

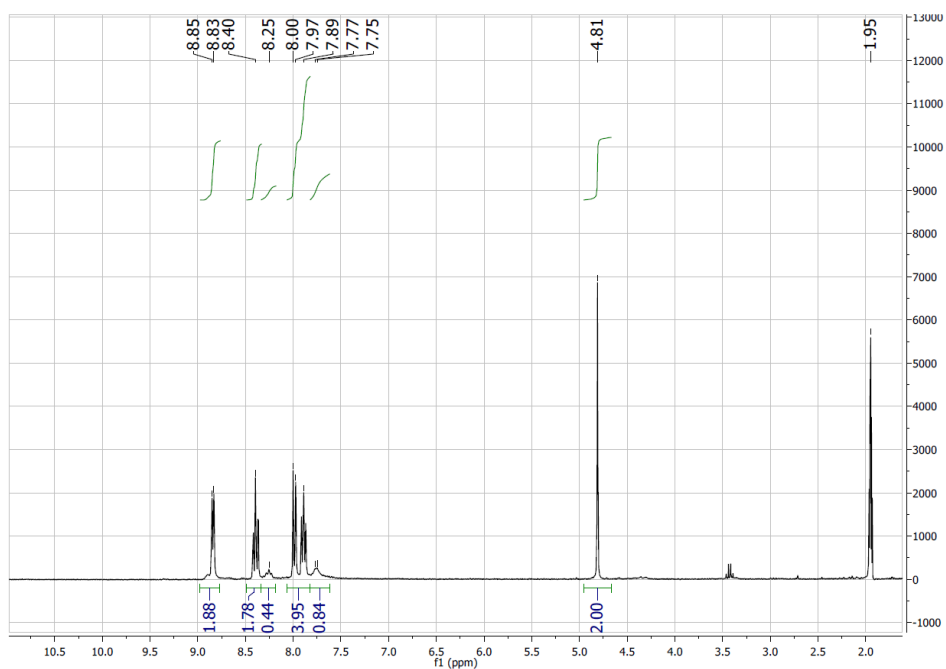


Fig. S10 ^1H NMR spectrum (in CD_3CN) recorded for the product from 1:2 reaction between dpma and GaCl_3 in Et_2O . Quartet at 3.4 ppm is residual Et_2O .

¹H NMR discussion related to the 1:2 reaction between dpma and AlCl₃

The room temperature ¹H NMR spectrum (in *d*₈-THF) for the product from 1:2 reaction between dpma and AlCl₃ in Et₂O shows the formation of three distinct products in an analogous fashion to what was observed when using a 1:1 reagent ratio (Fig. S11). However, if the reaction was carried out in CH₃CN, a single product **2d** was formed (Fig. S12). The salt **2d**, [(dpma)AlCl₂]⁺[AlCl₄]⁻, could also be obtained by treating [(dpma)AlCl₂]⁺[Cl]⁻ (**2b**) with an equimolar amount of AlCl₃ (Fig. S13).

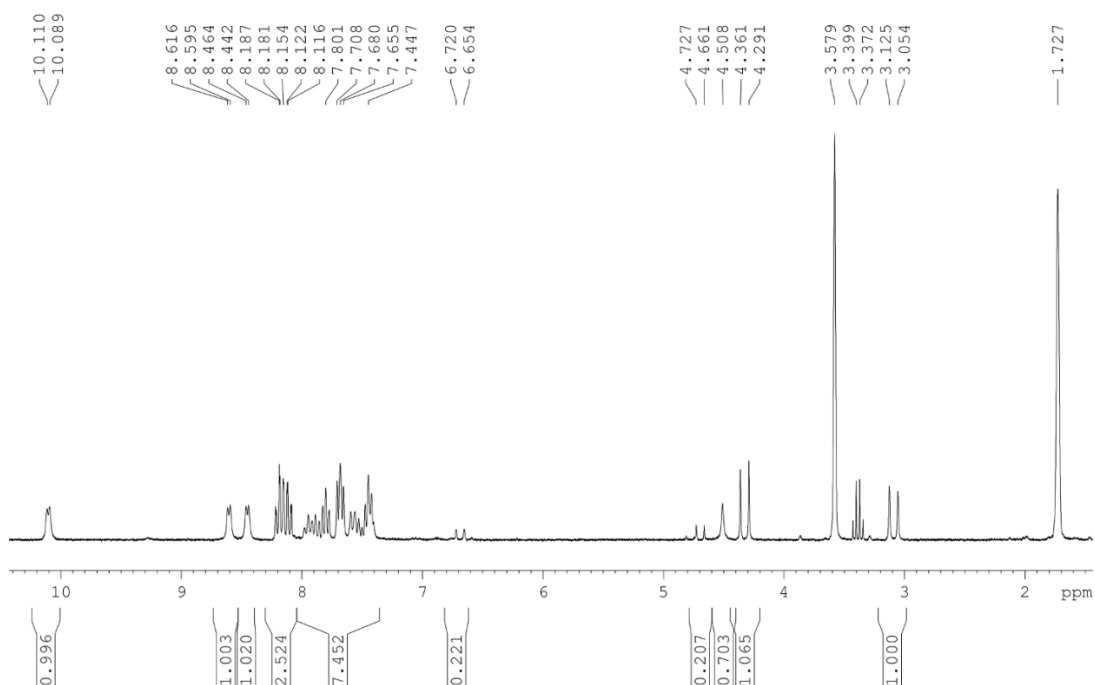


Fig. S11 ¹H NMR spectrum (in *d*₈-THF) recorded for the product from 1:2 reaction between dpma and AlCl₃ in Et₂O. Quartet at 3.4 ppm is residual Et₂O.

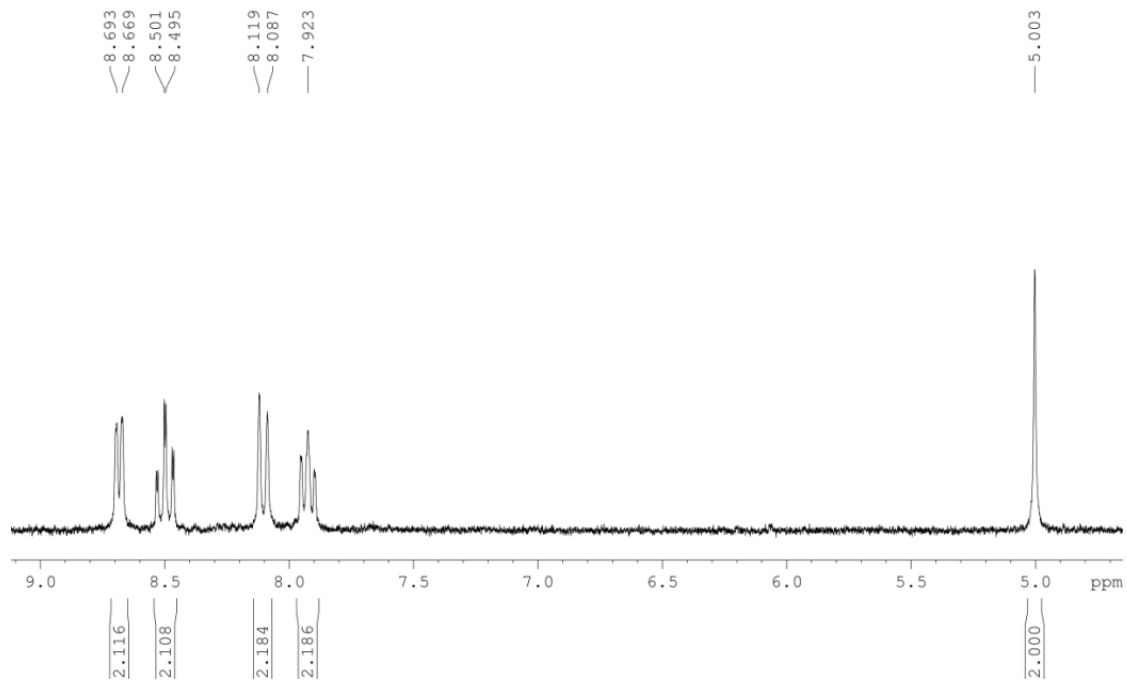


Fig. S12 ^1H NMR spectrum (in CD_3CN) recorded for the product (**2d**) from 1:2 reaction between dpma and AlCl_3 in CH_3CN .

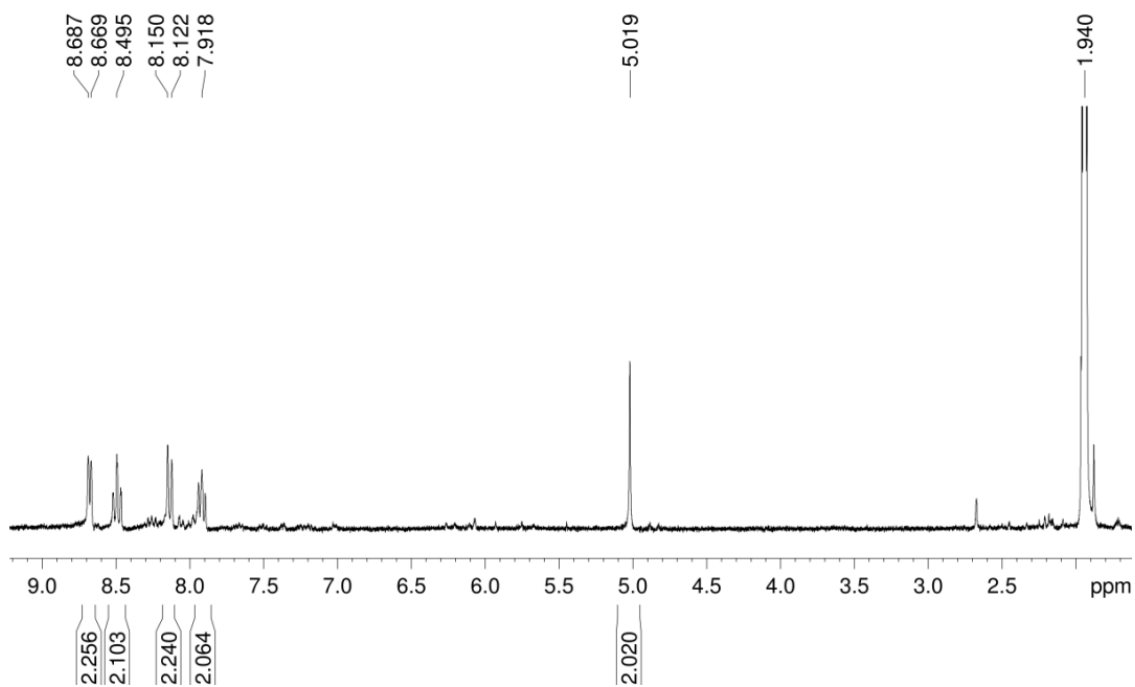


Fig. S13 ^1H NMR spectrum (in CD_3CN) recorded for the product (**2d**) from 1:1 reaction between **2b** and AlCl_3 . Singlet at 2.6 ppm and multiplet at 7.2 ppm is residual toluene.

^1H NMR discussion related to the 1:1 and 1:2 reactions between dpma and InCl_3

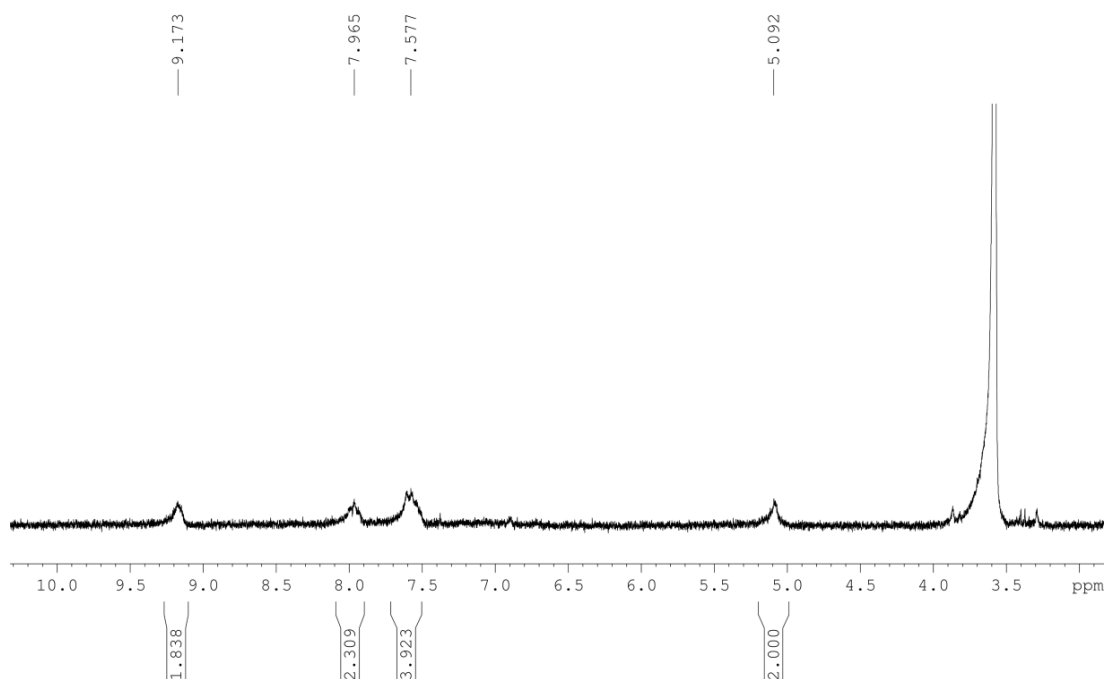


Fig. S14 ^1H NMR spectrum (in d_8 -THF) recorded for the product (**3**) from 1:1 reaction between dpma and InCl_3 . Quartet at 3.3 ppm is residual Et_2O .

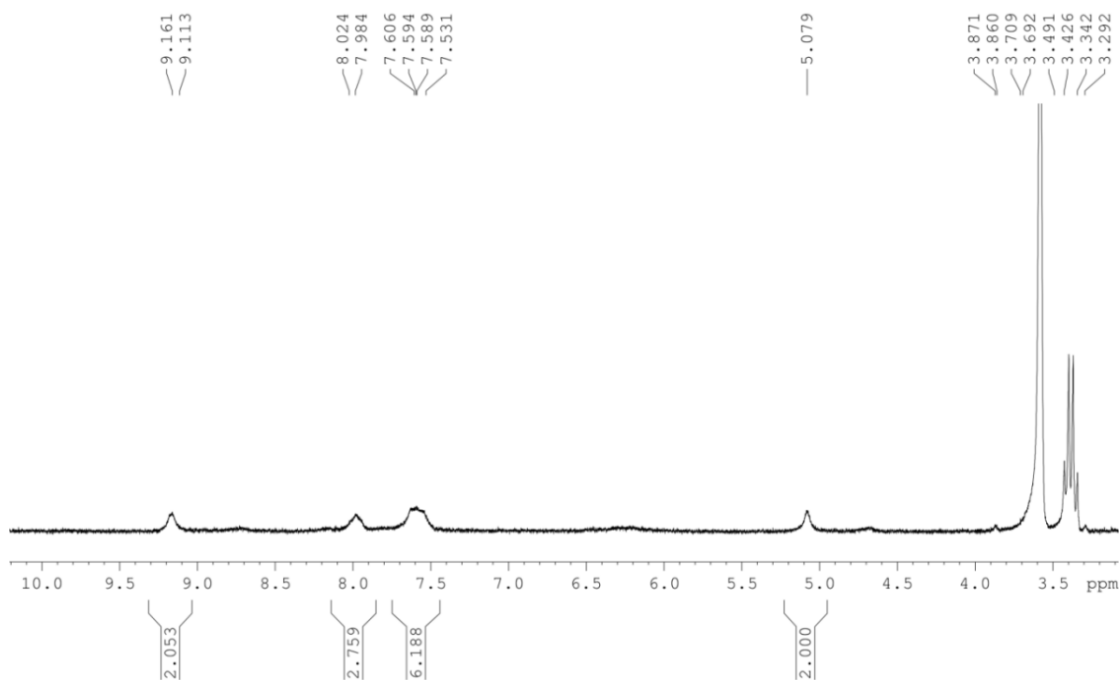


Fig. S15 ^1H NMR spectrum (in d_8 -THF) recorded for the product (**3**) from 1:2 reaction between dpma and InCl_3 . Quartet at 3.3 ppm is residual Et_2O .

^1H NMR discussion related to the 1:2 reaction between dpma and BCl_3

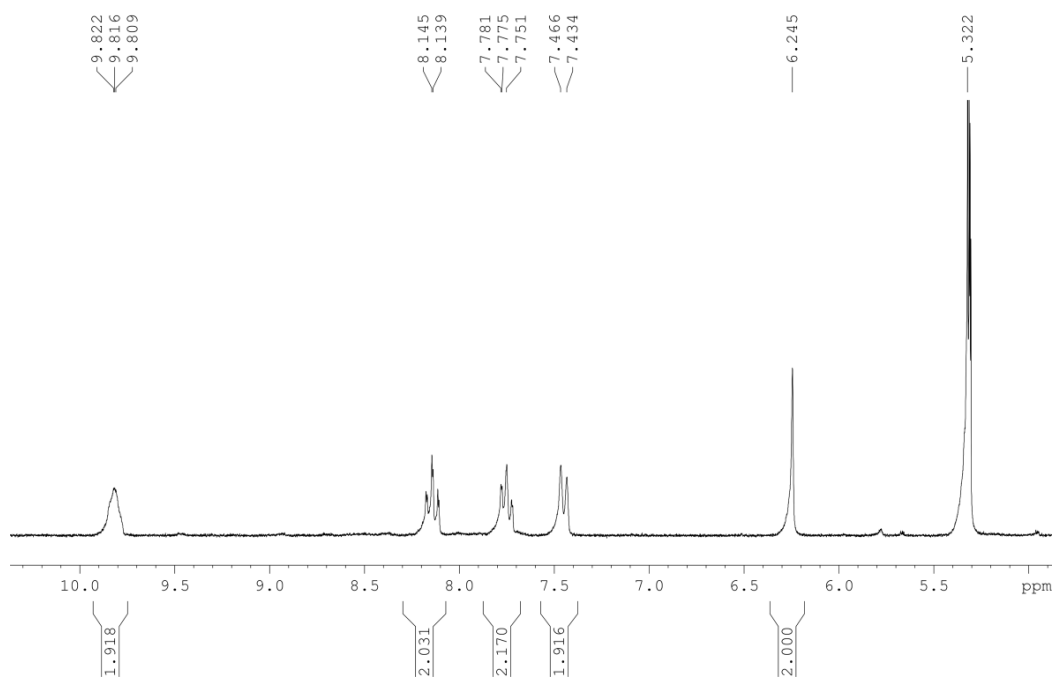


Fig. S16 ^1H NMR spectrum (in CD_2Cl_2) recorded for the product (**4**) from 1:2 reaction between dpma and BCl_3 .

¹H NMR discussion related to the 1:1 reaction between dpma and BCl₃

The room temperature ¹H NMR spectrum (in CD₂Cl₂) for the product from 1:1 reaction between dpma and BCl₃ in toluene is very complex (Fig. S17) and shows that the solution phase contains three major products based on the three singlets at 4.53, 5.23 and 5.49 ppm; a similar mixture was observed if the reaction was performed in Et₂O. There are also two singlets at 5.71 and 6.25 ppm, indicative of two minor products, of which the former is not discussed further.

Of all the singlets observed, the one at 6.25 ppm belongs to the diadduct **4**, though only one of the associated four multiplets in the aromatic region (broad doublet at 9.81 ppm) is resolved. The singlet at 4.53 ppm is assigned to the salt [(dpma)BCl₂][Cl]⁻ based on the spectral information for **2a** and **2b**. This signal should be accompanied with four equal intensity multiplets at the aromatic region of which the doublet and triplet at 7.52 and 8.09 ppm, respectively, are the only ones that are adequately resolved. The singlet at 5.49 ppm is assigned to the neutral complex (dpme)BCl₂. This compound should also display four equal intensity multiplets, each with a relative integration of 2:1 to the methene bridge signal. In good agreement with this assignment, the spectrum in Fig. S17 shows a triplet at 6.60 ppm as well as two doublets at 6.84 and 8.22 ppm; the second triplet expected for this species is not resolved. The last unknown singlet at 5.23 ppm is tentatively assigned to the monoadduct (dpma)BCl₃. This species has an asymmetric structure and should therefore display eight equal intensity multiplets in the aromatic region. However, due to the flexibility of the dpma backbone, a singlet is expected for the methylene hydrogens. The experimental spectrum displays a number of high-intensity signals from 7.2 to 8.5 ppm of which none can be assigned to the monoadduct with certainty. However, we note that the broad doublet at 9.71 ppm has the expected relative integration with the singlet at 5.23 ppm,

and it is also very close, but not identical, to one of the doublets observed for the related diadduct **4** at 9.81 ppm.

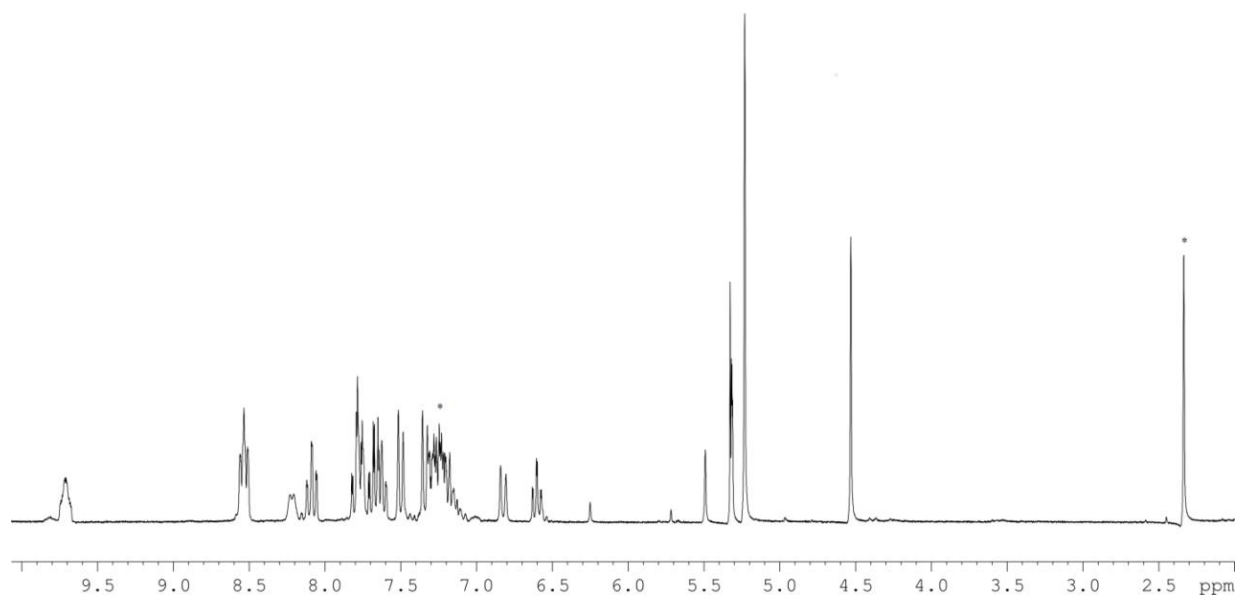


Fig. S17 ^1H NMR spectrum of the product mixture from the 1:1 reaction between dpma and BCl_3 in CD_2Cl_2 . Singlet at 2.6 ppm and multiplet at 7.2 ppm is residual toluene.

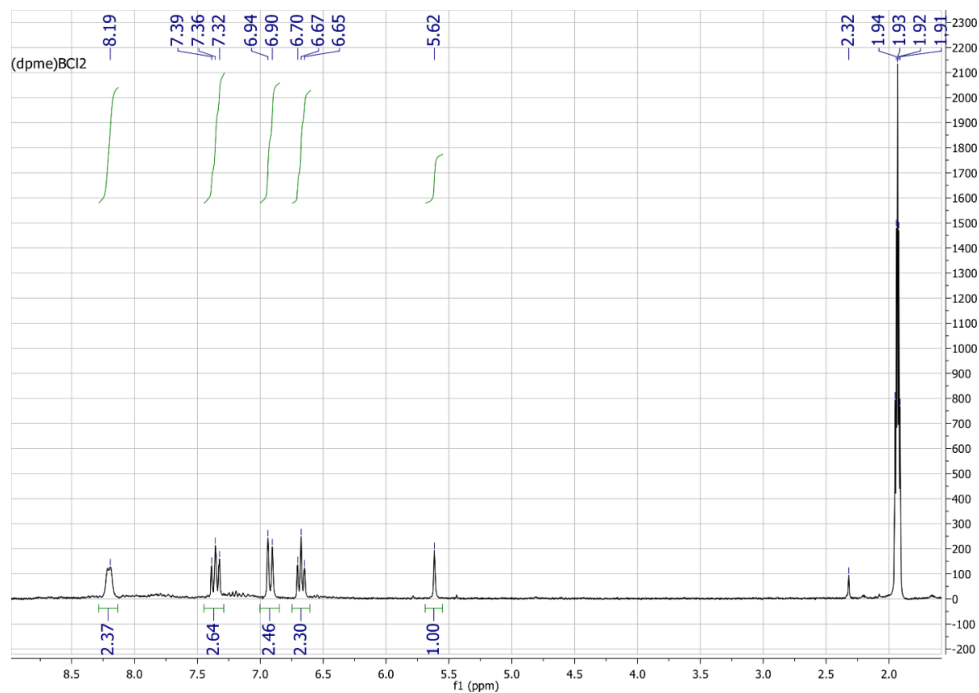


Fig. S18 ^1H NMR (CD_3CN) spectrum of $(\text{dpme})\text{BCl}_2$. Singlet at 2.6 ppm and multiplet at 7.2 ppm is residual toluene.

3. Additional cyclic voltammetry data for 2a–d

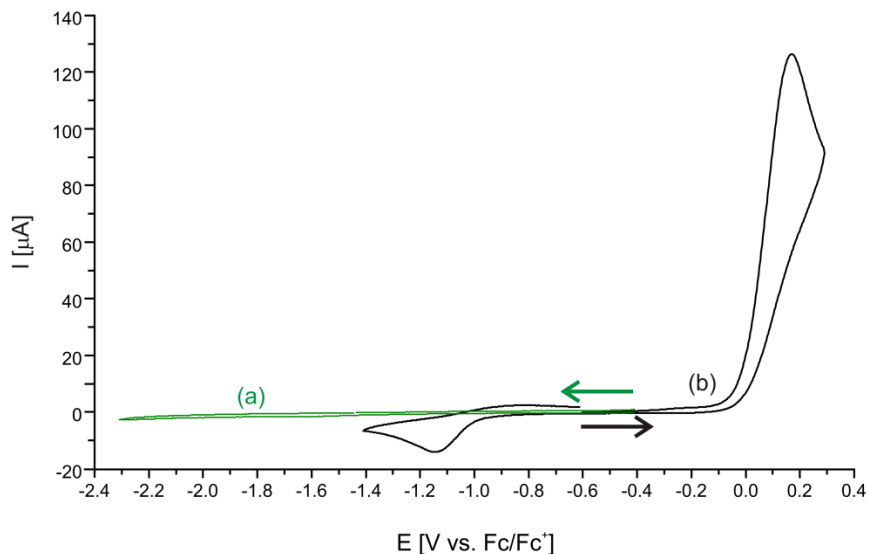


Fig. S19 Cyclic voltammogram of the dpma ligand in CH₃CN solution of 0.4 M [(*n*-Bu)₄N]⁺[PF₆]⁻ at a Pt electrode at room temperature, $\nu = 0.2 \text{ Vs}^{-1}$. (a) Initial scan in the negative direction (green) reversing at -2.3 V shows no reduction processes up to the solvent limit. (b) Subsequent scan in the positive direction (black) with an irreversible anodic wave at $+0.17 \text{ V}$ and a follow-up strongly offset cathodic process at -1.15 V .

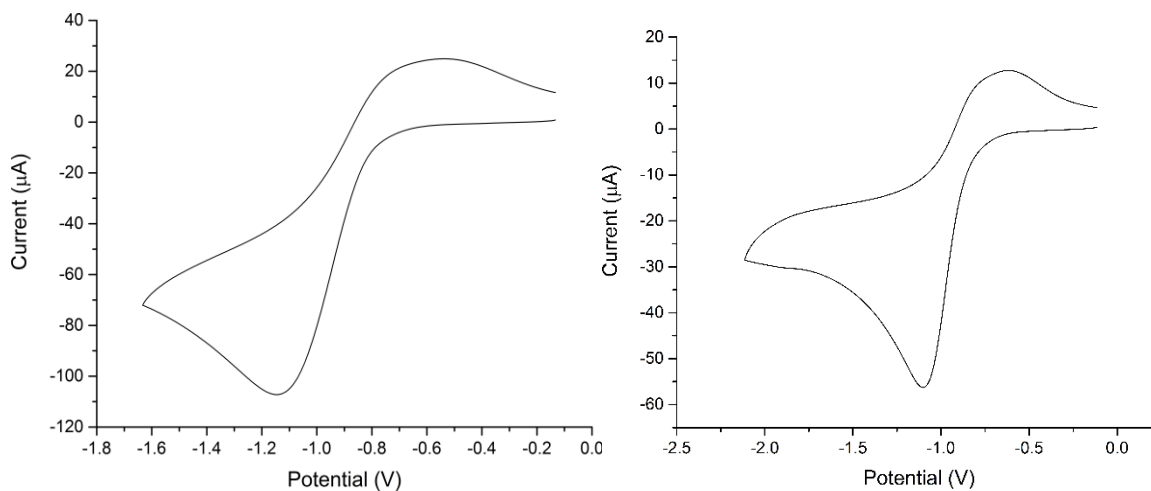


Fig. S20 Cyclic voltammograms of **2b** (left, 12.3 mM) and **2d** (right, 4.4 mM) in CH₃CN solutions containing 0.4 M [(*n*-Bu)₄N]⁺[PF₆]⁻ at a Pt electrode at room temperature, $\nu = 0.2 \text{ Vs}^{-1}$.

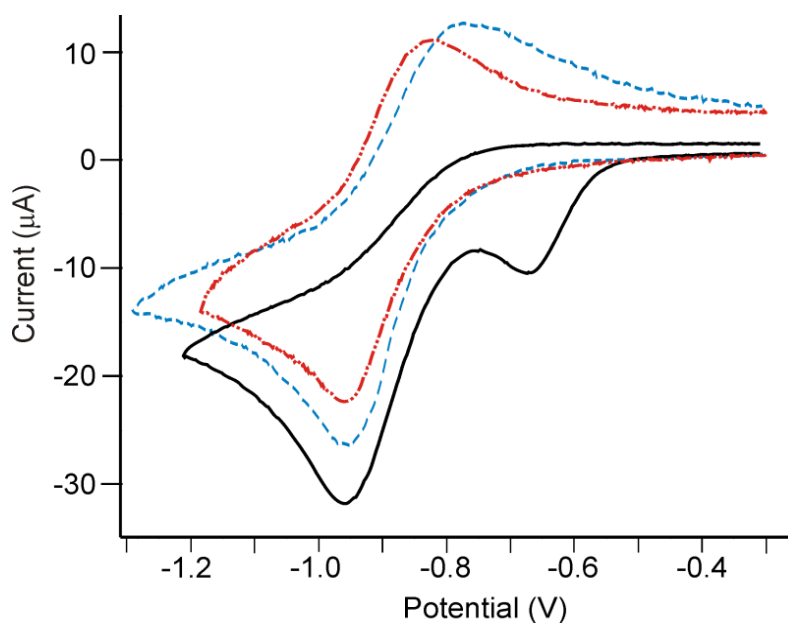


Fig. S21 Cyclic voltammograms of **2c** in CH₃CN solutions containing 0.4 M [(n-Bu)₄N][PF₆] and a) solid line, 6.3 mM **2c** only; b) dashed line, 1.4 equivalent [(n-Bu)₄N][Cl] (1.0 mL) added; and c) dashed and dotted line, 4.0 equivalents [(n-Bu)₄N][Cl] (2.5 mL) added, at a Pt electrode at room temperature, $\nu = 0.2 \text{ Vs}^{-1}$.

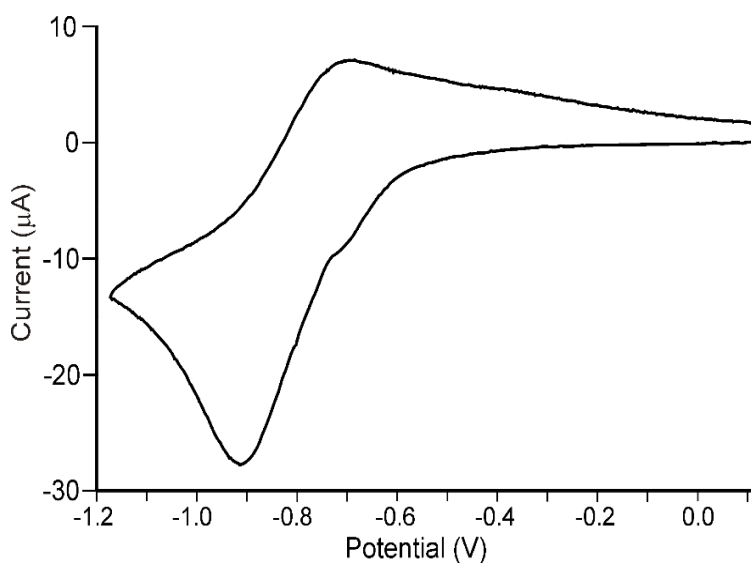


Fig. S22 Cyclic voltammogram of **2c** (6.3 mM) in CH₂Cl₂ containing 0.4 M [(n-Bu)₄N][PF₆] at a Pt electrode at room temperature, $\nu = 0.2 \text{ Vs}^{-1}$.

4. X-ray crystallographic data of $[\text{H}_2(\text{dpma})]^{2+}[\text{BCl}_4]^{-}[\text{Cl}]^{-}$ and $(\text{dpme})\text{BCl}_2$

Table S1 Crystal data and structure refinement for $[\text{H}_2(\text{dpma})]^{2+}[\text{BCl}_4]^{-}[\text{Cl}]^{-}$

empirical formula	$\text{C}_{11}\text{H}_{12}\text{BN}_2\text{Cl}_5$
formula weight	360.29
T , K	123.0
crystal system	monoclinic
space group	$P2_1/n$
a , Å	9.0046(3)
b , Å	18.1700(5)
c , Å	9.9074(3)
α , °	90.00
β , °	104.919(4)
γ , °	90.00
volume, Å ³	1566.34(8)
Z	4
ρ_{calc} , mg mm ⁻³	1.528
μ , mm ⁻¹	8.321
$F(000)$	728.0
crystal size, mm ³	$0.1 \times 0.1 \times 0.1$
2Θ range for data collection	9.74 to 133.88°
index ranges	$-10 \leq h \leq 10, -21 \leq k \leq 15, -10 \leq l \leq 11$
reflections collected	4969
independent reflections	2764 [$R(\text{int}) = 0.0335$]
data/restraints/parameters	2764/42/191
GOF on F^2	1.069
final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0528, wR_2 = 0.1238$
final R indexes [all data]	$R_1 = 0.0619, wR_2 = 0.1322$
largest diff. peak/hole / e Å ⁻³	0.51/−0.32

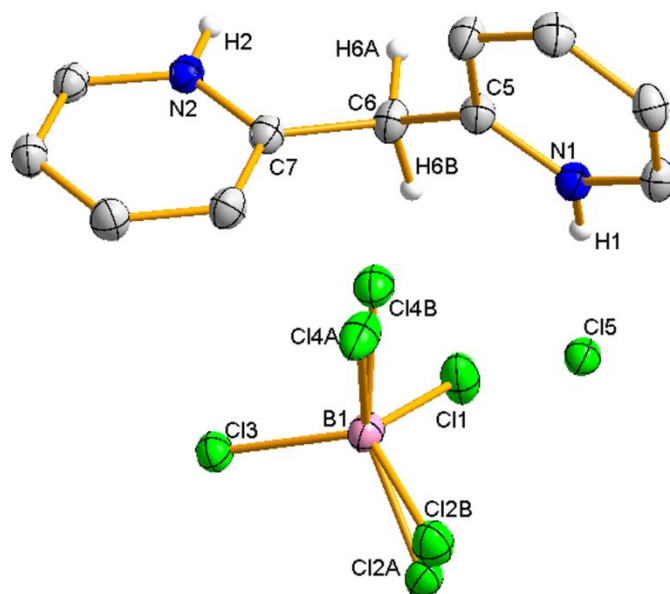


Fig. S18 X-ray crystal structure of $[\text{H}_2(\text{dpma})]^{2+}[\text{BCl}_4]^{-}[\text{Cl}]^{-}$. Thermal ellipsoids are drawn at the 20 % probability level and pyridyl hydrogens are omitted for clarity.

5. Results from density functional theory calculations

Optimized coordinates (xyz-format) of dpma, [(dpma)AlCl₂]⁺, [(dpma)GaCl₂]⁺, [(dpma)₂AlCl₂]⁺, [(dpma)₂GaCl₂]⁺, [(dpma)AlCl₂][•] and [(dpma)GaCl₂][•]

dpma				C	1.033729	2.768567	7.190698
				C	0.102084	4.275333	8.802948
				C	1.316143	4.935753	8.861408
23				C	-0.043048	3.184577	7.958712
				C	1.522592	6.147778	9.729998
C	0.475502	0.588874	0.012556	C	3.672407	6.221192	12.851237
C	0.358071	0.614903	1.391006	H	1.576715	6.495895	12.444110
C	1.241824	-0.143068	2.157774	H	5.925180	5.479971	10.448143
N	2.202564	-0.888525	1.612253	H	5.805603	5.879859	12.901351
C	2.305865	-0.903862	0.285807	H	3.101833	3.172434	6.730363
C	1.471461	-0.189551	-0.559337	H	0.961263	1.920590	6.522311
C	1.170983	-0.122803	3.663234	H	-0.723504	4.615958	9.415170
C	1.882378	1.078845	4.230586	H	-0.991338	2.662279	7.903252
N	1.128299	2.135687	4.531772	H	0.616019	6.332066	10.304082
C	1.733011	3.220475	5.009240	H	3.575506	6.394721	13.916894
C	3.101002	3.312896	5.211126	Cl	3.814132	7.346346	7.245805
C	3.883082	2.212202	4.892055	Cl	5.640978	4.224412	7.796234
C	3.266967	1.078169	4.393130	H	1.666933	7.021222	9.078261
H	-0.398811	1.216393	1.881177	[(dpma)GaCl₂]⁺			
H	3.099127	-1.525671	-0.120849	26			
H	1.600808	-0.244206	-1.633712	Ga	4.063797	5.539571	8.177666
H	1.084116	4.059712	5.245654	N	3.912270	5.814358	10.150976
H	3.537441	4.222066	5.607275	C	2.538768	6.259690	12.025609
H	3.839339	0.198750	4.121211	C	4.987184	5.727440	10.948352
H	4.958505	2.237630	5.031338	C	4.892230	5.913779	12.310764
H	0.131471	-0.082670	3.992178	C	2.693627	6.071861	10.663258
H	-0.200856	1.166828	-0.607997	N	2.341692	4.530720	8.082828
H	1.628409	-1.041953	4.032503	C	2.209145	3.456946	7.290210
[(dpma)AlCl₂]⁺				C	1.025772	2.753727	7.219381
26				C	0.110446	4.275032	8.827971
Al	4.034511	5.501592	8.223476	C	1.319174	4.948522	8.853367
N	3.903697	5.787876	10.146593	C	-0.039764	3.170758	8.002310
C	2.554557	6.279718	12.032375	C	1.537216	6.171451	9.704195
C	4.987812	5.718789	10.937680	C	3.646637	6.183643	12.856597
C	4.910595	5.937117	12.295763	H	1.555546	6.464933	12.430226
C	2.692295	6.060477	10.673525	H	5.929867	5.501081	10.463020
N	2.354272	4.521523	8.106316	H	5.779712	5.844422	12.926187
C	2.221815	3.458136	7.295415	H	3.082112	3.173601	6.713077

H	0.948404	1.895799	6.564283
H	-0.706595	4.616099	9.451415
H	-0.983772	2.638759	7.972497
H	0.627680	6.381840	10.264326
H	3.536305	6.333000	13.924577
Cl	3.825765	7.420734	7.190847
Cl	5.691503	4.225529	7.757149
H	1.708060	7.030885	9.041033

[(dpma)₂AlCl₂]⁺

49

Al	-4.142763	3.249278	15.446756
N	-2.088752	3.651053	15.269612
N	-3.924712	2.332678	13.527726
C	-4.423706	0.249812	16.208646
C	-4.902611	2.071072	11.358798
H	-5.752456	2.243951	10.711238
C	-5.548994	0.257979	15.217133
H	-5.149415	0.373029	14.206428
H	-6.049695	-0.708868	15.246868
C	-6.561131	1.334005	15.486958
C	-1.650538	1.587856	14.030485
H	-1.917067	0.903246	14.839625
H	-0.817602	1.131662	13.497104
C	-3.760112	1.430503	10.906389
H	-3.689142	1.075193	9.884747
C	-7.892980	1.002257	15.684295
H	-8.197232	-0.035937	15.634459
C	-0.405162	5.310258	15.625194
H	-0.145173	6.275196	16.040583
C	0.117057	3.312963	14.437684
H	0.811025	2.681473	13.896824
C	-8.815528	1.999881	15.951028
H	-9.859308	1.754302	16.110166
N	-3.709286	1.374287	16.378474
N	-6.141258	2.609320	15.540056
C	-8.375608	3.310184	16.019972
H	-9.051572	4.127478	16.235261
C	-2.701328	1.269115	11.781301
H	-1.783054	0.794418	11.458481
C	-2.807550	1.731499	13.087046
C	-1.195516	2.898404	14.605349
C	-2.414837	0.278390	18.067396
H	-1.621348	0.346530	18.800327

C	-4.936650	2.514052	12.663955
H	-5.791728	3.054583	13.045850
C	-4.154491	-0.896960	16.945171
H	-4.754886	-1.784091	16.786094
C	0.522348	4.531680	14.955336
H	1.544705	4.869250	14.829085
C	-7.036503	3.572242	15.812924
H	-6.642878	4.579240	15.857041
C	-2.741764	1.382733	17.309504
H	-2.232906	2.326012	17.452531
C	-3.135028	-0.890523	17.879624
H	-2.915948	-1.778468	18.461513
C	-1.695401	4.838577	15.757656
H	-2.457401	5.409664	16.271617
Cl	-4.648493	5.142089	14.355676
Cl	-4.280149	4.111069	17.512712

[(dpma)_{Ga}Cl₂]⁺

49

Ga	-4.147258	3.269204	15.453681
N	-2.037015	3.660442	15.261222
N	-3.904633	2.321305	13.480299
C	-4.458435	0.224162	16.251448
C	-4.858331	2.092396	11.301896
H	-5.705129	2.261412	10.649272
C	-5.572803	0.244605	15.245942
H	-5.159224	0.383035	14.243913
H	-6.068759	-0.725185	15.251421
C	-6.594673	1.311840	15.519469
C	-1.627807	1.603732	14.003845
H	-1.917910	0.935888	14.818760
H	-0.794773	1.128321	13.487579
C	-3.698205	1.486072	10.847309
H	-3.610603	1.156548	9.818338
C	-7.921224	0.974763	15.743086
H	-8.220348	-0.065841	15.715456
C	-0.360917	5.324050	15.597194
H	-0.094673	6.285474	16.016853
C	0.145583	3.338838	14.377837
H	0.832596	2.716443	13.817717
C	-8.846172	1.972068	16.005832
H	-9.885604	1.721979	16.185123
N	-3.716664	1.330745	16.406966
N	-6.190670	2.591381	15.544874

C	-8.417197	3.287482	16.042682
H	-9.097859	4.102765	16.250889
C	-2.643976	1.322125	11.728239
H	-1.714855	0.870522	11.402886
C	-2.771860	1.751394	13.043310
C	-1.160623	2.914600	14.570760
C	-2.455876	0.242976	18.120021
H	-1.662817	0.304378	18.854078
C	-4.913310	2.503996	12.617682
H	-5.782289	3.017411	13.007833
C	-4.220888	-0.913381	17.012764
H	-4.840204	-1.790162	16.868651
C	0.553942	4.556264	14.897741
H	1.571310	4.900886	14.751771
C	-7.082514	3.555269	15.810488
H	-6.692024	4.565203	15.827181
C	-2.752711	1.339814	17.337352
H	-2.221550	2.274686	17.459092
C	-3.205602	-0.910316	17.952716
H	-3.010949	-1.791026	18.553965
C	-1.645884	4.843224	15.754233
H	-2.402150	5.401533	16.291898
Cl	-4.670638	5.177543	14.333573
Cl	-4.270355	4.132755	17.553563

[(dpma)AlCl₂][•]

26

Al	3.997454	5.644596	8.162855
N	3.885578	5.910435	10.045899
C	2.467455	6.186284	11.955403
C	4.934434	5.686822	10.891537
C	4.801886	5.733929	12.249919
C	2.647557	6.154663	10.589044
N	2.365856	4.668390	8.044735
C	2.250875	3.493590	7.357836
C	1.122024	2.726434	7.404291
C	0.170668	4.309155	8.931003
C	1.317850	5.067914	8.838091
C	0.040330	3.133767	8.200384
C	1.531155	6.335915	9.606734
C	3.544111	5.997353	12.814150
H	1.473602	6.375252	12.344573
H	5.882873	5.466260	10.417103
H	5.671861	5.564308	12.871555

H	3.114982	3.204105	6.772354
H	1.080796	1.812101	6.826057
H	-0.630967	4.655220	9.573285
H	-0.871062	2.551315	8.243501
H	0.616667	6.608001	10.132340
H	3.415012	6.054258	13.887388
Cl	3.974637	7.464334	7.050742
Cl	5.650657	4.384759	7.689313
H	1.776420	7.155186	8.911985

[(dpma)GaCl₂][•]

26

Ga	4.025840	5.663677	8.129463
N	3.895076	5.943819	10.055179
C	2.452898	6.168483	11.946727
C	4.935454	5.700546	10.901973
C	4.786736	5.718156	12.259389
C	2.647618	6.166240	10.580933
N	2.346560	4.678221	8.016078
C	2.236651	3.494821	7.348161
C	1.116063	2.718124	7.425810
C	0.179948	4.310807	8.953685
C	1.318597	5.080034	8.830865
C	0.045699	3.127392	8.237801
C	1.539631	6.352344	9.590086
C	3.520386	5.967245	12.813304
H	1.453766	6.344000	12.328747
H	5.888345	5.491281	10.431196
H	5.649531	5.538039	12.888016
H	3.094341	3.207748	6.752023
H	1.071519	1.796440	6.859643
H	-0.611871	4.655760	9.608695
H	-0.859774	2.538089	8.304989
H	0.624808	6.633003	10.110618
H	3.378374	6.001918	13.885826
Cl	4.002221	7.517089	6.997052
Cl	5.700448	4.365402	7.663541
H	1.793906	7.165539	8.892266

6. Notes and references

1. This geminal coupling is in the typical range observed for methylene groups. See for example, R. C. Cookson, T. A. Crabb, J. J. Frankel, J. Hudec, *Tetrahedron* 1966, **22**, 355–390.
2. The [*trans*-(dpma)₂MCl₂]⁺ cation (M = Al, Ga) has C_{2v} point group with all four pyridyl rings equivalent. This means that its ¹H NMR spectrum should display not eight but four equal intensity multiplets in the aromatic region. The *trans*-isomer is also expected to show significant separation between the two AB doublets because of short contacts between the two chlorine atoms and one of hydrogens at the methylene bridge.