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Interaction of In(I) and Tl(I) Cations with 2,6-Diaryl Pyridine Ligands: Cation Encapsulation within a Very Weakly Interacting N/Arene Host Environment

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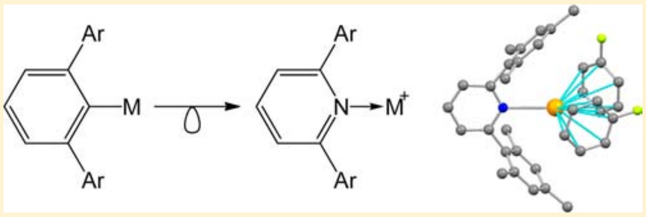
S *Supporting Information*



ABSTRACT: The interaction of 2,6-dimesitylpyridine with Tl(I) and In(I) cations has been investigated with a view to developing tractable molecular M(I) compounds which are soluble in organic media. In stark contrast to isosteric and isoelectronic terphenyl systems, complexes featuring the [(2,6-Mes$_2$py)M]$^+$ fragment feature very weak metal−ligand interactions in the solid state, as revealed by M-N distances of the order of 2.45 Å (M = In) and 2.64 Å (M = Tl). While additional weak π interactions are observed with arene solvate molecules in these systems, the related 2:1 complex [(2,6-Mes$_2$py)$_2$In][BAr$^f_4$] features an In(I) center wholly encapsulated by the bulky Mes$_2$py donors, and even longer In−N distances [2.586(6) and 2.662(5) Å]. These contacts are about 0.5 Å greater than the sum of the respective covalent radii (2.13 Å) and provide evidence for an effectively "naked" In(I) cation stabilized to a minor extent by orbital interactions.

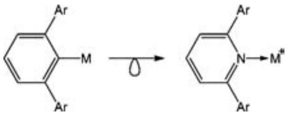
■ INTRODUCTION

There has been recent widespread interest in the isolation of well-defined molecular species featuring the Group 13 elements in the formal +I oxidation state,[1] both from a fundamental structure/bonding perspective and with a view to their potential uses, for example as ligands or as reagents in organic synthesis (notably in reductive coupling methodologies).[2−4] Thus, a range of organometallic and related derivatives of In(I) and Tl(I) have been synthesized,[2c,5−7] including the remarkable one-coordinate 2,6-diarylphenyl (terphenyl) complexes M(C$_6$H$_3$-2,6-Trip$_2$) (M = In, Tl; Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) reported by Power and co-workers in 1998.[8,9] Ligand steric bulk is a key factor in determining both redox stability and structure for such systems; thus, related Dipp-functionalized compounds [M(C$_6$H$_3$-2,6-Dipp$_2$)]$_2$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) are dimeric in the solid state, featuring planar, *trans*-bent geometries, while [Tl(C$_6$H$_3$-2,6-Xyl$_2$)]$_3$ (Xyl = 2,6-Me$_2$C$_6$H$_3$) is trimeric, and simple phenyl Tl(I) systems are unstable with respect to disproportionation.[1,10−12]

An alternative approach to the isolation of tractable organic-soluble univalent derivatives is the encapsulation of very weakly coordinated M$^+$ cations within a weakly interacting lipophilic host. Indeed, such a methodology can be applied not only to Group 13 monocations, but also to related valence isoelectronic Group 14 dications,[13] by employing, for example, macrocyclic crown ethers or tridentate nitrogen "donors". Within Group 13 systems Gorelsky and Richeson have reported that In$^+$ can be encapsulated within a series of diiminopyridine systems to give triflate salts that are soluble in aromatic hydrocarbons, and which feature minimal N−In donor−acceptor orbital interactions.[14] In a similar fashion, MacDonald has exploited the chemistry of crown ether donors for the isolation of In$^+$ and related valence isoelectronic cations.[15]

Given their isoelectronic relationship with the ground-breaking terphenyl family (Chart1), and the ability of multifunctional N-donor ligands to encapsulate M$^+$ cations,[14] we were interested in the potential mode(s) of interaction of 2,6-diarylpyridine systems with In$^+$ and Tl$^+$ cations. In doing so, we hoped to probe the influence of net charge on secondary interactions either with other metal centers (cf. the oligomeric structures adopted by isosteric terphenyl complexes), with the flanking aryl rings,[16] or with the solvent/counteranion. In particular, given that the 2,6-di*mesityl*pyridine ligand (2,6-Mes$_2$py) has been shown to be capable of stabilizing highly electrophilic lighter Group 13 cations via π interactions involving the flanking aryl rings,[17] we sought to investigate the use of this ligand in In(I) and Tl(I) chemistry.

Chart 1. Terphenyl and 2,6-Diarylpryidine Ligands



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■ EXPERIMENTAL SECTION

General Considerations. Manipulations of air-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. With the exception of fluorobenzene (which was distilled from CaH_2), nondeuteriated solvents were dried using a commercially available Braun Solvent Purification System. CD_2Cl_2 (Goss) was degassed and stored over molecular sieves prior to use. The known compounds $Na[BAr^f_4]$ and 2,6-Mes_2py were prepared by literature procedures.[18,19] All other reagents were used as received from commercial sources. NMR spectra were measured on a Varian Mercury VX-300 or Bruker AVII 500 FT-NMR spectrometer. Residual signals of solvent were used as reference for ^1H and ^{13}C NMR measurements; ^{11}B and ^{19}F NMR spectra were referenced with respect to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively. Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Elemental microanalyses were carried out at London Metropolitan University. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet. Resonances due to $[BAr^f_4]^-$ anion: ^1H NMR (300 MHz, CD_2Cl_2): δ_H 7.57 (s, 4H, *para*-CH), 7.73 (s, 8H, *ortho*-CH). ^{13}C NMR (126 MHz, CD_2Cl_2): δ_c 118.0 (*para*-CH), 124.1 (q, $^1J_{CF}$ = 275.0 Hz, CF_3), 129.8 (q, $^2J_{CF}$ = 33.1 Hz, *meta*-C), 135.5 (*ortho*-CH), 162.7 (q, $^1J_{CB}$ = 48.0 Hz, *ipso*-C). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7. ^{19}F NMR (283 MHz, CD_2Cl_2): δ −63 (CF_3).

Syntheses of Novel Compounds. ***[Tl(Mes₂py)(C₆H₅F)₂][BArᶠ₄] (1).*** To a suspension of TlCl (0.23 g, 0.95 mmol) in fluorobenzene (30 cm^3) was added a suspension of $Na[BAr^f_4]$ (0.67 g, 0.76 mmol) also in fluorobenzene (20 cm^3). After stirring for 1 h at 20 °C, a solution of Mes_2py (0.30 g, 0.95 mmol) in fluorobenzene (20 cm^3) was added, and the reaction mixture stirred at 20 °C for a further 24 h. The resulting colorless solution was filtered and volatiles removed in vacuo. The residual solid was washed with hexanes and recrystallized from fluorobenzene/pentane to yield **1** as colorless crystals suitable for X-ray crystallography. Isolated yield: 0.50 g, 42%. ^1H NMR (300 MHz, CD_2Cl_2): (resonances due to cation) δ_H 1.96 (s, 12H, *ortho*-CH_3 of Mes), 2.32 (s, 6H, *para*-CH_3 of Mes), 7.03 (s, 4H, *meta*-CH of Mes), 7.48 (d, 2H, $^3J_{HH}$ = 9.0 Hz, β-CH), 8.09 (t, 1H, $^3J_{HH}$ = 9.0 Hz, γ-CH). ^{13}C NMR (126 MHz, CD_2Cl_2): (resonances due to cation) δ_c 20.5 (*para*-CH_3 of Mes), 21.2 (*ortho*-CH_3 of Mes), 123.9 (β-CH), 126.1 (*meta*-CH of Mes), 130.5 (γ-CH), 136.9 (*para*-C of Mes), 141.9 (*ortho*-C of Mes), 148.2 (α-C), 159.9 (*ipso*-C of Mes). Microanalysis: calc. C 51.06, H 3.01, N 0.89; meas. C 51.36, H 3.18, N 0.74.

[Tl(Mes₂py)(C₇H₈)₂][BArᶠ₄] (2). A sample of **1** prepared as outlined above was extracted into minimum toluene, and the resulting solution layered with pentane and stored at 20 °C, yielding **2** as colorless crystals suitable for X-ray crystallography. Isolated yield: 0.57 g, 38%. ^1H NMR (300 MHz, CD_2Cl_2): (resonances due to cation) δ_H 2.03 (s, 12H, *ortho*-CH_3 of Mes), 2.34 (s, 6H, *para*-CH_3 of Mes), 7.09 (s, 4H, *meta*-CH of Mes), 7.57 (d, 2H, $^3J_{HH}$ = 8.0 Hz, β-CH), 8.15 (t, 1H, $^3J_{HH}$ = 8.0 Hz, γ-CH). ^{13}C NMR (126 MHz, CD_2Cl_2): (resonances due to cation) δ_c 20.6 (*para*-CH_3 of Mes), 21.3 (*ortho*-CH_3 of Mes), 123.9 (β-CH), 125.8 (*meta*-CH of Mes), 130.4 (γ-CH), 136.5 (*para*-C of Mes), 141.7 (*ortho*-C of Mes), 148.2 (α-C), 160.8 (*ipso*-C of Mes). Microanalysis: calc. C 52.85, H 3.41, N 0.89; meas. C 52.89, H 3.24, N 0.97.

[In(Mes₂py)(C₆H₅F)][Na(Mes₂py)(C₆H₅F)][BArᶠ₄]₂ (3). To a suspension of InBr (0.15 g, 0.79 mmol) in fluorobenzene (30 cm^3) was added a suspension of $Na[BAr^f_4]$ (0.56 g, 0.63 mmol) also in fluorobenzene (20 cm^3). After stirring for 1 h at 20 °C, a solution of Mes_2py (0.25 g, 0.79 mmol) in fluorobenzene (20 cm^3) was added, and the reaction mixture stirred at 20 °C for a further 24 h. The resulting orange solution was filtered and volatiles removed in vacuo. The residual solid was washed with hexanes and recrystallized from fluorobenzene/pentane to yield **3** as colorless crystals suitable for X-ray crystallography. Isolated yield: 0.43 g, 51%. ^1H NMR (300 MHz, CD_2Cl_2): (resonances due to cation) δ_H 1.89 (s, 12H, *ortho*-CH_3 of Mes), 2.29 (s, 6H, *para*-CH_3 of Mes), 6.96 (s, 4H, *meta*-CH of Mes), 7.31 (d, 2H, $^3J_{HH}$ = 9.0 Hz, β-CH), 7.99 (t, 1H, $^3J_{HH}$ = 9.0 Hz, γ-CH). ^{13}C NMR (126 MHz, CD_2Cl_2): (resonances due to cation) δ_c 20.3 (*para*-CH_3 of Mes), 21.4 (*ortho*-CH_3 of Mes), 124.7 (β-CH), 126.3 (*meta*-CH of Mes), 136.0 (γ-CH), 140.1 (*para*-C of Mes), 142.9 (*ortho*-C of Mes), 149.2 (α-C), 160.0 (*ipso*-C of Mes).

[In(Mes₂py)₂][BArᶠ₄] (4). To a suspension of InBr (0.08 g, 0.40 mmol) in fluorobenzene (30 cm^3) was added a suspension of $Na[BAr^f_4]$ (0.28 g, 0.32 mmol) also in fluorobenzene (20 cm^3). After stirring for 1 h at 20 °C, a solution of Mes_2py (0.25 g, 0.79 mmol) in fluorobenzene (20 cm^3) was added, and the reaction mixture stirred at 20 °C for a further 24 h. The resulting orange solution was filtered and volatiles removed in vacuo. The residual solid was washed with hexanes, and recrystallized from fluorobenzene/pentane to yield **4** as colorless crystals suitable for X-ray crystallography. Isolated yield: 0.35 g, 68%. ^1H NMR (300 MHz, CD_2Cl_2): (resonances due to cation) δ_H 1.73 (s, 12H, *ortho*-CH_3 of Mes), 2.28 (s, 6H, *para*-CH_3 of Mes), 6.95 (s, 4H, *meta*-CH of Mes), 7.29 (d, 2H, $^3J_{HH}$ = 6.0 Hz, β-CH), 7.78 (t, 1H, $^3J_{HH}$ = 6.0 Hz, γ-CH). ^{13}C NMR (126 MHz, CD_2Cl_2): (resonances due to cation) δ_c 20.2 (*para*-CH_3 of Mes), 21.4 (*ortho*-CH_3 of Mes), 120.3 (β-CH), 122.7 (*meta*-CH of Mes), 129.6 (γ-CH), 140.1 (*para*-C of Mes), 142.2 (*ortho*-C of Mes), 148.4 (α-C), 161.7 (*ipso*-C of Mes). Microanalysis: calc. C 58.20, H 3.89, N 1.74; meas. C 58.36, H 3.88, N 1.64.

Crystallographic Details. Data for **1**−**4** were collected at 150 K using an Enraf-Nonius Kappa CCD diffractometer. Raw frame data were reduced using Denzo-SMN including unit cell refinement, integration, interframe scaling, and absorption corrections.[20a] The structures were solved with SIR92[20b] or SuperFlip,[20c] and refined using the CRYSTALS software suite,[20d,e] as per the information contained in the CIF. Graphics were generated using XP.[20f] Selected structural details are included below and full crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre, with reference codes 903731−903734, respectively.

Crystallographic data for **1**: $C_{67}H_{47}BF_{26}NTl$, M_r = 1575.24, monoclinic, $P\,2_1/n$, a = 12.8413(1), b = 13.8219(1), c = 35.7025(4) Å, β = 91.5709(3)°, V = 6334.5(1) $Å^3$, Z = 4, ρ_c = 1.652 Mg m^{-3}, T = 150 K, λ = 0.71073 Å. 53209 reflections collected, 14330 independent [R(int) = 0.046], of which 14327 were used in all calculations ($I > -3\sigma(I)$). R_1 = 0.0753, wR_2 = 0.1825 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.1062, wR_2 = 0.2159 for data used in refinement. Max/min residual electron densities 2.79 and −1.54 e $Å^{-3}$.

Crystallographic data for **2**: $C_{69}H_{53}BF_{24}NTl$, M_r = 1567.32, monoclinic, $P2_1/n$, a = 12.8041(1), b = 13.8915(2), c = 35.7688(4) Å, β = 91.6851(5)°, V = 6359.38(13) $Å^3$, Z = 4, ρ_c = 1.637 Mg m^{-3}, T = 150 K, λ = 0.71073 Å. 94242 reflections collected, 14328 independent [R(int) = 0.053], of which 12642 were used in all calculations ($I > -3\sigma(I)$; weak high angle data removed as appropriate). R_1 = 0.0836, wR_2 = 0.1901 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.1303, wR_2 = 0.2429 for data used in refinement. Max/min residual electron densities 3.49 and −2.52 e $Å^{-3}$.

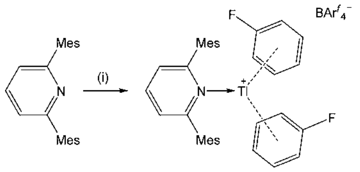
Crystallographic data for **3**: $C_{122}H_{84.24}B_2F_{50}N_2InNa_{0.76}$, M_r = 2682.15, monoclinic, $P\,2_1/c$, a = 26.1194(2), b = 12.9528(1), c = 35.1578(3) Å, β = 96.8964(3)°, V = 11808.50(16) $Å^3$, Z = 4, ρ_c = 1.509 Mg m^{-3}, T = 150 K, λ = 0.71073 Å. 79560 reflections collected, 21098 independent [R(int) = 0.047], of which 18127 were used in all calculations ($I > -3\sigma(I)$; weak high angle data removed as appropriate). R_1 = 0.1224, wR_2 = 0.3095 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.1653, wR_2 = 0.3591 for data used in refinement. Max/min residual electron densities 3.32 and −2.09 e $Å^{-3}$.

Crystallographic data for **4**: $C_{78}H_{62}BF_{24}InN_2$, M_r = 1608.95, monoclinic, $P\,2_1/n$, a = 15.811(1), b = 26.2876(2), c = 17.9324(1) Å, β = 98.3967(3)°, V = 7373.41(8) $Å^3$, Z = 4, ρ_c = 1.449 Mg m^{-3}, T = 150 K, λ = 0.71073 Å. 94242 reflections collected, 16778 independent [R(int) = 0.045], which were all used in all calculations. R_1 = 0.0996, wR_2 = 0.2531 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.1248, wR_2 = 0.2820 for all unique reflections. Max./min residual electron densities 3.54 and −2.85 e $Å^{-3}$.

■ RESULTS AND DISCUSSION

Halide abstraction reactions of M(I) halides (M = In, Tl) in the presence of Mes_2py, and in a suitable weakly coordinating solvent, were targeted as routes to complexes featuring the $[(Mes_2py)M]^+$ fragment, isoelectronic with known neutral terphenyl systems $[(Ar_2C_6H_3)M]_n$.[8−11] The possibility of forming related bis(pyridine) systems $[(Mes_2py)_2M]^+$ utilizing these highly sterically demanding ligand systems was also of interest with a view to forming wholly "encapsulated" sources of M^+ soluble in organic media. Accordingly, the reaction of a suspension of TlCl in fluorobenzene with slightly less than 1 equiv of $Na[BAr^f_4]$, followed by 1 equiv of Mes_2py results in the formation of the salt $[Tl(Mes_2py)(C_6H_5F)_2][BAr^f_4]$ (**1**) in moderate isolated yield (42%; Scheme 1).

Scheme 1. Synthesis of $[Tl(Mes_2py)(C_6H_5F)_2][BAr^f_4]$ (1)^a



1

^{a}Key reagents and conditions: (i) TlCl (1.0 equiv)/$Na[BAr^f_4]$ (0.8 equiv), fluorobenzene, 20 °C, 24 h, 42% isolated yield.

Extremely air- and moisture-sensitive colorless crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with pentane, and **1** has been further characterized by multinuclear NMR spectroscopy and elemental microanalysis. The structure determined by single crystal X-ray diffraction (Figure 1), reveals monometallic $[Tl(Mes_2py)(C_6H_5F)_2]^+$ cations featuring a single Mes_2py ligand coordinated to the thallium(I) center, and additional (weak) π-interactions involving two fluorobenzene solvent molecules. No close contacts of the thallium center with the $[BAr^f_4]^-$ counterion are evident.

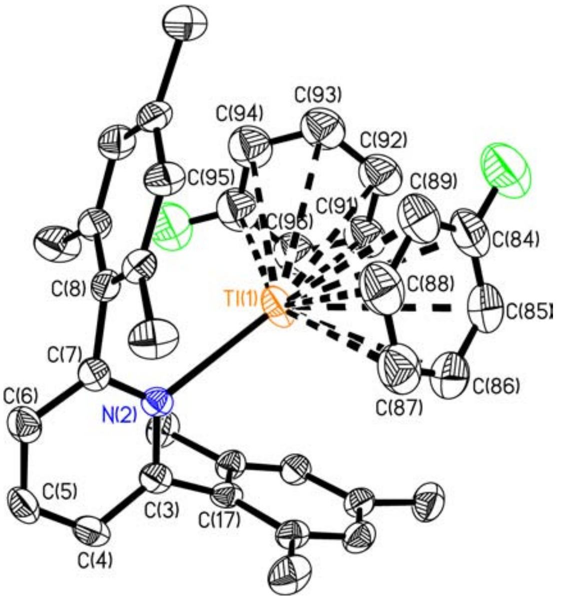


Figure 1. Molecular structure of the cationic component of $[Tl(Mes_2py)(C_6H_5F)_2][BAr^f_4]$ (**1**) determined by single crystal X-ray diffraction. Hydrogen atoms, minor disorder components, and counterion omitted for clarity, and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (deg): Tl(1)−N(2) 2.639(6), Tl(1)−C(84−89) 3.19(1)−3.51(1), Tl(1)−C(91−96) 3.35(1)−3.58(1), Tl(1)−centroid(C84−89) 3.12, Tl(1)−centroid(C91−96) 3.19, N(2)−Tl(1)−centroid(C84−89) 117.7, N(2)−Tl(1)−centroid(C91−96) 136.0, centroid(C84−89)−Tl(1)−centroid(C91−96) 106.3.

Of primary interest is the Tl−N distance measured for **1** [2.639(6) Å]. By means of comparison this separation is >0.25 Å longer than the Tl−N distances measured for one-coordinate thallium amides [e.g., 2.364(3) Å for $TlN(Me)(C_6H_3\text{-}2,6\text{-}Mes_2)$ and 2.148(12) Å for the vapor-phase $TlN(SiMe_3)_2$ monomer],[21,22] and 0.06 Å longer even than the *bridging* Tl−N linkages in dimeric $Tl_2\{\mu\text{-}N(SiMe_3)_2\}$.[23] It is more in line with contacts determined for thallium(I) bipyridyl coordination polymers [2.661(10)−2.839(8) Å],[24] and for thallium(I) pyridyl tris(pyrazolyl)-borates [2.759(3)−2.942(3) Å].[25] By comparison with isoelectronic terphenyl systems, the Tl−N separation in **1** is considerably longer than the Tl−C distances in either $Tl(C_6H_3\text{-}2,6\text{-}Trip_2)$ [2.340(1) Å],[9] $[Tl(C_6H_3\text{-}2,6\text{-}Dipp_2)]_2$ [2.313(5) Å],[10] or $[Tl(C_6H_3\text{-}2,6\text{-}Xyl_2)]_3$ [2.331(8) Å].[10] While a number of these observations, of course, reflect the greater strength of simple covalent bonds over related donor/acceptor interactions,[26] it is noteworthy that the Tl−N separation in **1** is of the order of 0.5 Å greater than the sum of the covalent radii of thallium (1.45 Å) and nitrogen (0.71 Å).[27]

The long Tl−N distance in **1** signals very weak σ-coordination between the thallium(I) center and the N-donor atom, presumably reflecting (at least in part) the sterically crowded nature of the 2,6-Mes_2py ligand. The coordination sphere at Tl(I), such as it is, is augmented by additional weak Tl···arene interactions with two fluorobenzene solvent molecules. The associated Tl···C distances fall within the range 3.19(1)−3.58(1) Å [mean 3.50(1) Å], the majority of which are within the sum of the van der Waals radii for thallium and carbon (3.50 Å).[28] *Chemical* evidence also supports the idea that the coordinated fluorobenzene molecules are weakly bound and readily exchanged. Thus, exposure to toluene leads to the formation of the bis(toluene) adduct $[Tl(Mes_2py)(C_7H_8)_2][BAr^f_4]$ (**2**) in moderate yield (38%), which possesses a structural motif closely related to that of **1**. Characterization of **2** was achieved by NMR spectroscopy, elemental microanalysis, and single crystal X-ray diffraction (Figure 2). **2** features a very similar thallium(I) environment to **1**, with the thallium(I) cation interacting weakly with the pyridine N-donor and with the aromatic rings of two toluene molecules. A similar Tl−N separation [2.655(8) Å] and shorter Tl···C contacts [mean 3.39(1) Å] are observed compared to **1**, with the differences in the latter presumably reflecting the different donor capabilities of toluene and fluorobenzene. That said, the structural data clearly imply that *both* arenes are weakly bound in the solid state, a finding given further credence by the observation that on dissolution in dichloromethane the free arene is generated in either case.[29]

Superficially, similar chemistry can also be carried out for In(I); the reaction of $InBr/Na[BAr^f_4]$ with 1 equiv of Mes_2py in fluorobenzene, however, leads to the isolation of the mixed salt $[In(Mes_2py)(C_6H_5F)][Na(Mes_2py)(C_6H_5F)][BAr^f_4]_2$ (**3**). Together with structural evidence outlined below, the formation of this mixed In^+/Na^+ system is further (albeit circumstantial) indication of the weak coordination of the Mes_2py ligand at the Group 13 metal center. The structure of the indium-containing cation, $[In(Mes_2py)(C_6H_5F)]^+$, determined by single crystal X-ray diffraction (Figure 3) has a number of features in common with compound **1**, namely, a very long M-N contact [d(In−N) = 2.447(6) Å] and a weak η^6 π-interaction with a fluorobenzene

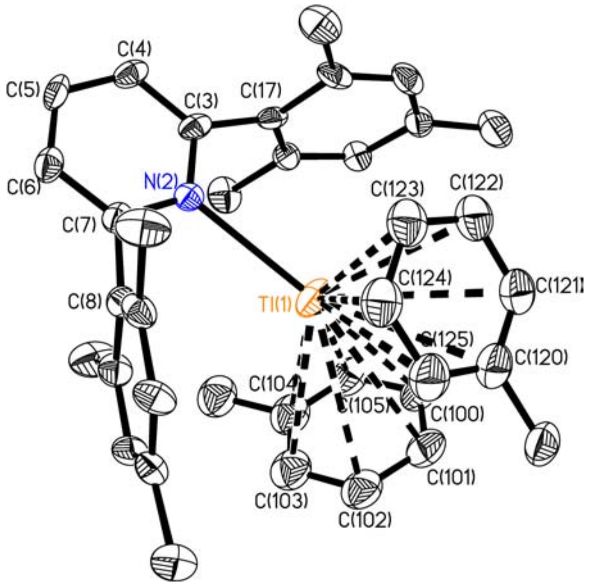


Figure 2. Molecular structure of the cationic component of $[Tl(Mes_2py)(C_7H_8)_2][BAr^f_4]$ (**2**) determined by single crystal X-ray diffraction. Hydrogen atoms, minor disorder component and counterion omitted for clarity and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (deg): Tl(1)−N(2) 2.655(8), Tl(1)−C(100−105) 3.36(1)−3.54(1), Tl(1)−C(120−125) 3.18(1)−3.57(1), Tl(1)−centroid(C100−105) 3.10, Tl(1)−centroid(C120−125) 3.18, N(2)−Tl(1)−centroid(C100−105) 135.4, N(2)−Tl(1)−centroid(C120−125) 116.3, centroid(C100−105)−Tl(1)−centroid(C120−125) 107.9.

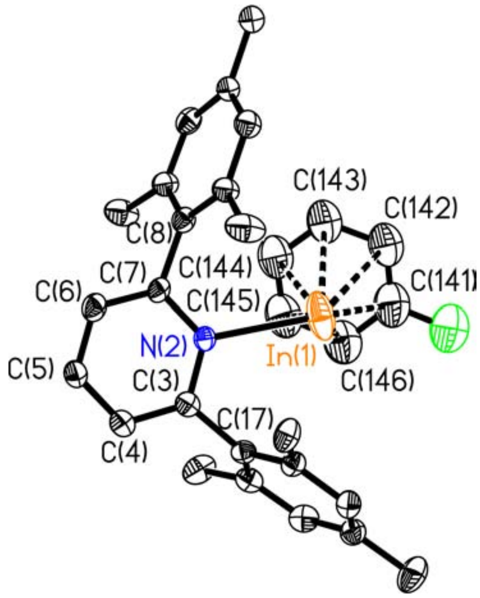


Figure 3. Molecular structure of the indium-containing cationic component of $[In(Mes_2py)(C_6H_5F)][Na(Mes_2py)(C_6H_5F)][BAr^f_4]_2$ (**3**) determined by single crystal X-ray diffraction; hydrogen atoms and counterion are omitted for clarity, and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (deg): In(1)−N(2) 2.447(6), In(1)−C(141−146) 3.146(6)−3.443(6), In(1)−C(17) 3.171(6), In(1)−C(24) 3.268(6), In(1)−centroid(C141−146) 3.01.

solvent molecule [with In−C π-contacts ranging from 3.15(1)−3.44(1) Å]. In the case of $[In(Mes_2py)(C_6H_5F)]^+$ only one fluorobenzene molecule is involved, with the indium center also engaging in further (weak) In···C contacts with the *ipso* and one *ortho* carbon of one of the flanking mesityl groups {*d*[In(1)−C(17)] = 3.171(6), *d*[In(1)−C(24)] = 3.268(6) Å}. This additional π stabilization of the indium(I) center contrasts with the terphenyl system $In(C_6H_3\text{-}2,6\text{-}Trip_2)$, which features a shorter In−C bond length [2.260(7) Å] and no close interactions between the indium center and the flanking π systems.[8] Contacts with the $[BAr^f_4]^-$ counterions in **3** lie outside of standard van der Waals limits.[28]

Even weaker interactions of the 2,6-dimesityl pyridine ligand with an In^+ cation can be identified in the 2:1 In(I) complex, $[In(Mes_2py)_2][BAr^f_4]$ (**4**) which is generated from the InBr/Na$[BAr^f_4]$ system in the presence of 2 equiv of Mes_2py. **4** can be isolated in 68% yield as air sensitive single crystals from fluorobenzene/pentane, and characterized by standard spectroscopic and microanalytical techniques, and by X-ray crystallography. The solid state structure of the cationic component is shown in Figure 4 and features an In(I) center encapsulated by two Mes_2py ligands in a manner reminiscent of the silver(I) compound $[Ag(Mes_2py)_2][CF_3SO_3]$ reported by Bosch and Barnes.[19] In(1) apparently interacts with the N-donor atoms of the two Mes_2py ligands, although the In−N distances {*d*[In(1)−N(2)] = 2.662(5), *d*[In(1)−N(26)] 2.586(6) Å} are very long indeed, being significantly greater than the sum of the covalent radii for indium and nitrogen (In = 1.42 Å and N = 0.71 Å).[27,30] This observation is clearly influenced by the high steric loading at indium, with the corresponding distance in $[In(Mes_2py)(C_6H_5F)]^+$, which features a single Mes_2py ligand, being 2.447(6) Å. Additionally, the In−N bond lengths in **4** are significantly longer than the Ag−N distances reported for $[Ag(Mes_2py)_2]^+$ [2.128(5) and 2.132(5) Å],[19] despite Ag^+ having a very similar covalent radius (1.45 Å) and identical formal charge to In^+.[27] Richeson and co-workers have reported the synthesis of indium(I) complexes bearing bis(imino)-pyridine scaffolds of the type $2,6\text{-}(ArN{=}CPh)_2C_5H_3N$, with $In{-}N_{py}$ distances of about 2.50 Å, in which the In(I) ion is

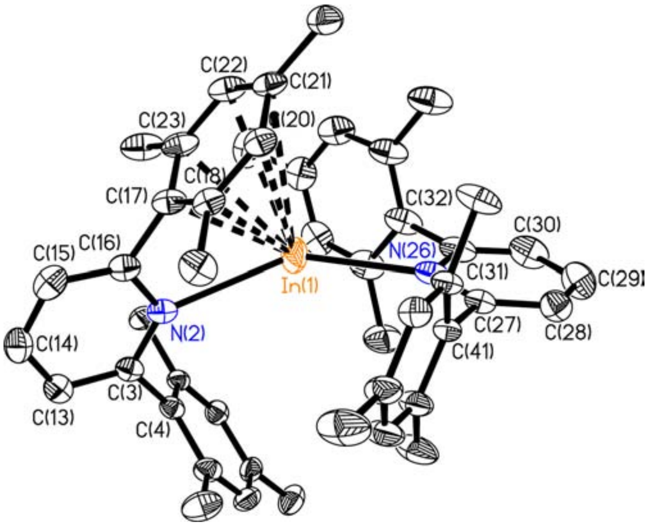


Figure 4. Molecular structure of the cationic component of $[In(Mes_2py)_2][BAr^f_4]_2$ (**4**) determined by single crystal X-ray diffraction; hydrogen atoms and counterion omitted for clarity and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (deg): In(1)−N(2) 2.662(5), In(1)−N(2) 2.586(6), In(1)−C(17) 2.863(6), In(1)−C(23) 2.981(6), In(1)−C(18) 3.218(6), N(2)−In(1)−N(26) 146.8(2).

described as being very weakly coordinated.[14] Relatively long In−N contacts have also been reported for (tmeda)·InBr [2.500(5), 2.531(4) Å],[31] In{(NDippCMe)$_2$CH} [2.268(3), 2.276(3) Å],[32] InTp^{tBu2} [2.458(4), 2.471(4), 2.474(3) Å; Tp^{tBu2} = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato],[33] and In{(NDipp)$_2$C^{t}Bu} [2.329(5) Å].[34] The fact that the mean In−N bond length in **4** (2.624 Å) is notably longer than those measured for all of these systems presumably implies even weaker interactions between the Mes_2py ligands and the encapsulated In^+ cation.

The putative two-coordinate indium(I) center in **4** is further stabilized by π-interactions with one of the flanking mesityl groups of each Mes_2py ligand; the In···C contacts range from 2.863(6)−3.402(6) Å, all of which are comfortably within the sum of the van der Waals radii of indium and carbon (3.47 Å).[28] That said, the In···C distances associated with the *ipso* and *ortho* carbons of each mesityl ring {d[In(1)−C(17)] = 2.863(6), d[In(1)−C(23)] = 2.981(6); d[In(1)−C(32)] = 2.872(8), d[In(1)−C(39)] = 3.031(8) Å] are notably shorter than the others, and a description in terms of a weak bis(η^2) binding motif is probably most appropriate. The interactions with the flanking arene π system in **4** result in the indium(I) center having a bent geometry with N−In−N bond angle of 146.8(2)°.

CONCLUSIONS

The 2,6-dimesityl pyridine ligand, although isoelectronic with anionic terphenyl donors of the type $[2,6\text{-}Ar_2C_6H_3]^-$, offers vastly different electronic capabilities for the stabilization of M(I) centers. Thus, extremely weak orbital interactions between the nitrogen donor and In^+ or Tl^+ are implied by M-N distances which are up to 0.5 Å greater than the sum of the respective covalent radii, and about 0.3 Å greater than the corresponding M-C distances in related terphenyl compounds. Presumably such weak contacts reflect an energy mismatch between (low lying) pyridine ligand donor and (high energy) metal acceptor orbitals similar to that described by Richeson for related imino-functionalized systems.[14] The effect of net charge is evident in the nature of secondary interactions persisting in the solid state. Thus, in $[M(Mes_2py)]^+$ complexes weak M(I)-arene interactions are observed with either solvate molecules or the flanking mesityl rings; no hint of metal−metal or metal-anion contacts is evident in any of these systems. Complete encapsulation of the M(I) center is observed for the bis(pyridine) system $[In(Mes_2py)_2]^+$, albeit with the effects of greater steric hindrance being reflected in even longer M···N contacts (>2.6 Å). These weakly interacting host frameworks for M^+ do appear to offer a viable means for the transfer of M(I) into organic media, and their further synthetic applications are currently under investigation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIFs for the four X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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