(κ^2-*P*,*S*)Pt(benzyl) complexes derived from 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene: facile synthesis of carbanion- and borate-containing zwitterions†

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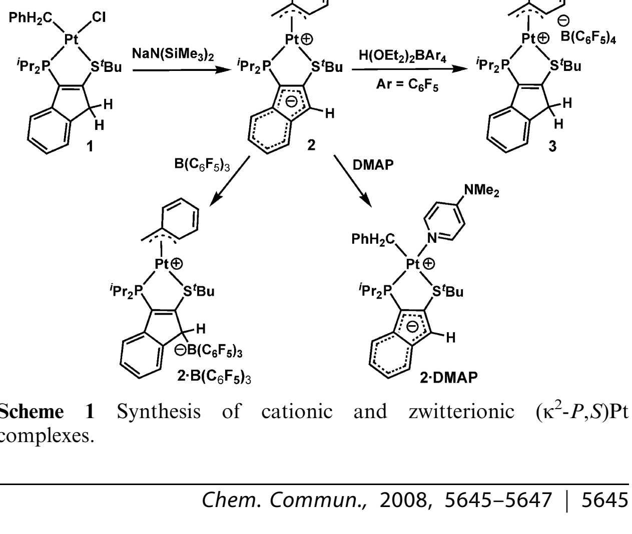
The versatile new ligand precursor 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene has been employed in the preparation of neutral and cationic (κ^2-*P*,*S*)Pt(benzyl) complexes, as well as structurally related zwitterions in which the formally cationic metal fragment is counterbalanced by an uncoordinated indenide or borate fragment that is contained within the ancillary ligand backbone.

Zwitterionic late transition metal complexes featuring enforced formal charge separation between a cationic metal fragment and an anionic moiety sequestered within a coordinated ancillary ligand have emerged as attractive alternatives to related cationic complexes in reactivity applications, owing to their heightened solubility in low-polarity media, increased tolerance to polar coordinating solvents, and avoidance of counteranion effects.[1] Indeed, such zwitterions can offer a useful intermediate range of electrophilicity relative to more traditional neutral and cationic species. Although significantly less well-explored than their group 9 relatives, zwitterionic Ni,[2] Pd,[3] and Pt[4] complexes have proven useful in a range of substrate transformations, including: Ni-catalyzed ethylene polymerization;[2a,d–f] Pd-catalyzed CO–ethylene co-polymerization[3c] and aldol condensation;[3d] and metal-mediated stoichiometric C–H bond activation of amines (Pd),[3b] as well as hydrocarbons (Pt).[4b–d] Notwithstanding these advances, further diversification in this field is limited by a dearth of ligation strategies for supporting group 10 zwitterionic complexes. Nearly all such zwitterionic species reported thus far feature borate-based ligation;[2–4] to the best of our knowledge, non-borate group 10 zwitterions are restricted to a limited class of Pd pincer complexes that contain tethered sulfate groups.[3a,d] In this regard, the identification of alternative ligation strategies that allow for the preparation of neutral, cationic, and zwitterionic group 10 complexes, ideally from a convenient single ligand precursor, represents an important goal in the quest for further control in tuning the reactivity of group 10 metal species.

We have reported on our investigations of cationic and formally zwitterionic complexes of Ru, Rh, and Ir, supported by 3-PR$_2$-2-NR$'_2$-indene and mono-deprotonated indenide ligands, respectively.[5,6] These zwitterions are unusual in that the 10π-electron indenide unit functions as an uncoordinated anionic charge reservoir to counterbalance the cationic κ^2-*P*,*N*-ML$_n$ fragment, rather than as a site for metal binding. Encouraged by the successful pairing of soft phosphine donors in (κ^2-Ph$_2$B(CH$_2$*P*R$_2$)$_2$)PtL$_n$ zwitterions,[4c,d] and in our quest to establish the first examples of zwitterionic group 10 complexes featuring heterobidentate indenide ligation, we turned our attention to the synthesis of complementary Pt complexes derived from new P,S-substituted indenes. We report herein that 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene functions as a convenient precursor for the construction of neutral, cationic, and zwitterionic (κ^2-*P*,*S*)Pt(benzyl) complexes. The versatility of this ligation strategy is further demonstrated through the direct transformation of the (κ^2-*P*,*S*-indenide)Pt(κ^3-benzyl) zwitterion into a structurally related borate-based zwitterion.

Lithiation of 2-S^{t}Bu-indene followed by quenching with ClP^{i}Pr$_2$ provided 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene in 87% isolated yield. In targeting Pt(benzyl) derivatives due to their ability to adopt η^1, η^3, and other coordination modes, 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene was added to (COD)Pt(η^1-benzyl)Cl, affording (κ^2-3-P^{i}Pr$_2$-2-S^{t}Bu-indene)-Pt(η^1-benzyl)Cl **1** in 68% isolated yield (Scheme 1; COD = η^4-1,5-cyclooctadiene). Monitoring of this reaction by use of ^{1}H and ^{31}P NMR methods confirmed that **1** is formed quantitatively as a single diastereomer, the identity of which was ascertained on the basis of X-ray crystallographic data (see Fig. 1 and Table 1).‡ While crystallographically characterized (κ^2-*P*,*S*)Pt(benzyl) species have not been reported previously, the *trans*-disposition of chloride and phosphorus ligands in **1** mirrors that observed in a related (κ^2-*P*,*N*)Pt(η^1-benzyl)Cl complex,[7] in keeping with the greater *trans*-directing ability of phosphorus relative to sulfur.[8]

Dehydrohalogenation of **1** employing NaN(SiMe$_3$)$_2$ produced the κ^2-*P*,*S*-indenide complex **2**, which was isolated as an



Scheme 1 Synthesis of cationic and zwitterionic (κ^2-*P*,*S*)Pt complexes.

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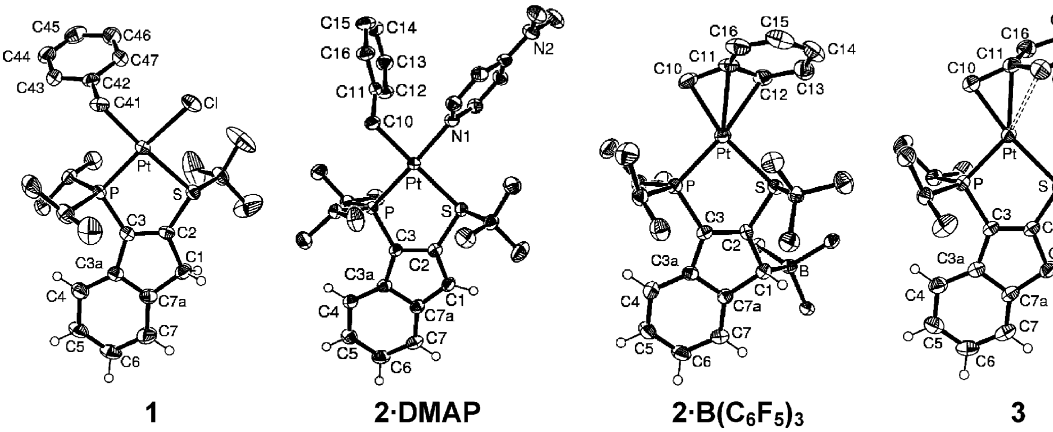

Fig. 1 ORTEP diagrams for **1**, **2·DMAP**, **2·B(C_6F_5)$_3$**(C_7H_8), and **3**, shown with 50% ellipsoids. Selected hydrogen atoms, the toluene solvate and portions of the C_6F_5 groups in **2·B(C_6F_5)$_3$**(C_7H_8), as well as the $B(C_6F_5)_4^-$ anion in **3**, have been omitted for clarity.

Table 1 Selected interatomic distances (Å)

	1[a]	**2·DMAP**[b]	**2·B(C_6F_5)$_3$**[c,d]	**3**[d]
Pt–S	2.3637(14)	2.4005(7)	2.3658(12)	2.3608(10)
Pt–P	2.2135(14)	2.2342(7)	2.2254(13)	2.2116(10)
Pt–CH_2	2.096(5)	2.075(3)	2.085(5)	2.061(4)
Pt-C*ipso*	—	—	2.255(5)	2.269(4)
Pt-C*ortho*	—	—	2.354(5)	2.566(4)
P–C3	1.814(6)	1.767(3)	1.817(5)	1.800(4)
S–C2	1.757(5)	1.775(3)	1.785(5)	1.775(4)
C1–C2	1.502(7)	1.399(4)	1.513(6)	1.505(5)
C1–C7a	1.498(8)	1.411(4)	1.517(6)	1.515(6)
C2–C3	1.368(7)	1.420(4)	1.354(6)	1.347(5)
C3–C3a	1.479(8)	1.433(4)	1.458(6)	1.480(5)
C3a–C4	1.394(8)	1.412(4)	1.392(7)	1.382(6)
C4–C5	1.399(9)	1.374(4)	1.370(7)	1.387(6)
C5–C6	1.368(9)	1.405(4)	1.383(7)	1.384(6)
C6–C7	1.405(9)	1.373(4)	1.381(7)	1.381(7)
C7–C7a	1.393(8)	1.405(4)	1.390(7)	1.373(6)
C7a–C3a	1.388(8)	1.441(4)	1.402(7)	1.411(5)

[a] Pt–Cl = 2.3695(14). [b] Pt–N = 2.102(2). [c] B–Cl = 1.701(7). [d] Benzyl distances in **2·B(C_6F_5)$_3$** (in **3**): C10–C11 1.451(8) (1.456(6)); C11–C12 1.416(7) (1.407(6)); C12–C13 1.408(7) (1.400(6)); C13–C14 1.361(8) (1.371(6)); C14–C15 1.397(9) (1.388(6)); C15–C16 1.355(8) (1.375(6)); C11–C16 1.424(8) (1.411(6)).

analytically pure solid in 67% yield (Scheme 1). Notably, **2** represents the first isolable Pt zwitterion to feature non-borate ancillary ligation. In contrast to the relatively sharp NMR signals observed for **1** at 300 K, the ^{1}H NMR spectrum of **2** at this temperature exhibited very broad features, possibly attributable to slow inversion at sulfur, and/or η^1–η^3 dynamics of the coordinated benzyl ligand.[9,10] While upon cooling to 273 K some diagnostic ^{1}H NMR signals associated with **2** could be assigned qualitatively, further cooling to 185 K provided no gains in spectral resolution. Conversely, the ^{31}P{^{1}H} NMR resonance for **2** remained sharp between 273–300 K, apparently precluding an observable temperature-dependent equilibrium involving **2** and other phosphorus-containing species. Exposure of **2** to 4-dimethylaminopyridine (DMAP) afforded the adduct **2·DMAP** as an analytically pure solid in 82% isolated yield (Scheme 1). As with **2**, this adduct exhibited broad ^{1}H NMR features (and a single sharp ^{31}P{^{1}H} NMR resonance) in the range 185–300 K. While we have yet to obtain X-ray quality crystals of **2**, the identification of **2·DMAP** (and indirectly **2**) as a κ^2-*P*,*S*-indenide complex was confirmed by use of diffraction methods (Fig. 1).‡ Our assignment of **2·DMAP** as a formally zwitterionic[6] species is supported by the observation of C–C distances within the carbocyclic backbone that are consistent with a delocalized 10π-electron indenide framework (Table 1). However, as noted for κ^2-*P*,*N*-indenide complexes of groups 8 and 9,[5b–d] the relatively short P–C3 distance in **2·DMAP** suggests that a non-zwitterionic $R_2P{=}C3$ resonance contributor featuring a formal negative charge on phosphorus[11] should be considered in describing the electronic structure of this adduct.

Notably, the indenide-based zwitterion **2** serves as a convenient synthon in the preparation of alternative cationic and zwitterionic (κ^2-*P*,*S*)Pt(η^3-benzyl) complexes. Treatment of **2** with $B(C_6F_5)_3$ afforded the borate-based zwitterion **2·B(C_6F_5)$_3$** in 68% isolated yield, while addition of $H(OEt_2)_2B(C_6F_5)_4$ to **2** produced the cationic complex **3** in 88% isolated yield (Scheme 1). The ability of **2** to serve as a precursor to **3** is of particular significance, since efforts to prepare **3** from **1** by use of $Li(Et_2O)_{2.5}B(C_6F_5)_4$ were unsuccessful. In contrast to the broad NMR spectral features that were noted for **2** and **2·DMAP** at 300 K (*vide supra*), under similar conditions the ^{1}H and ^{13}C{^{1}H} NMR spectra for each of **2·B(C_6F_5)$_3$** and **3** are consistent with a C_1-symmetric structure, with only modest line-broadening observed in the case of **2·B(C_6F_5)$_3$**. Data obtained from X-ray diffraction studies involving **2·B(C_6F_5)$_3$** and **3** also revealed C_1-symmetric connectivity for these complexes (Fig. 1),‡ and enabled further structural comparisons.[12] In contrast to the C–C bond delocalization and somewhat short P–C3 distance that are found in the κ^2-*P*,*S*-indenide complex **2·DMAP** (*vide supra*), more localized single (*e.g.* C1–C2) and double (*e.g.* C2–C3) bonds, along with typical P–C3 distances, are observed in both **2·B(C_6F_5)$_3$** and **3** (Table 1). In this regard, **2·B(C_6F_5)$_3$** and **3** can be viewed as (κ^2-*P*,*S*-indene)Pt(η^3-benzyl) complexes, in keeping with the line drawing representations in Scheme 1; whereas in **3** the formally cationic Pt fragment is counterbalanced by an outer-sphere $B(C_6F_5)_4^-$ counteranion, the indenylborate ligation featured in **2·B(C_6F_5)$_3$** gives rise to a structurally analogous zwitterionic (charge-neutral) complex.[13] Despite these apparent similarities, some structural variations within the coordinated η^3-benzyl ligands of **2·B(C_6F_5)$_3$** and **3** were observed. Progressive lengthening of the Pt–C linkage is noted for both complexes on going from Pt–CH$_2$ to Pt–C*ipso* to Pt–C*ortho* (Table 1), in keeping with structural trends commonly observed in L$_n$M(η^3-benzyl) complexes.[12,14] However, while the first two of these distances are statistically equivalent in $\mathbf{2\cdot B(C_6F_5)_3}$ and **3**, the elongation of the Pt–C*ortho* distance in **3** (2.566(4) Å) is significantly more pronounced than in $\mathbf{2\cdot B(C_6F_5)_3}$ (2.354(5) Å). While the potential influence of crystal packing as a source of such structural differences cannot be discounted, it is worthy of mention that the observed structural trend also matches the ^1J(PPt) values measured for **2** (5012 Hz), $\mathbf{2\cdot B(C_6F_5)_3}$ (5264 Hz), and **3** (5317 Hz), with the increasing ^1J(PPt) value signaling a progressively weaker interaction between Pt and the η^2-(C11=C12) moiety that occupies a position *trans* to phosphorus in $\mathbf{2\cdot B(C_6F_5)_3}$ and **3** (and presumably **2**).[10] When considered collectively, the solid state structural variations noted within the η^3-benzyl fragments of $\mathbf{2\cdot B(C_6F_5)_3}$ and **3**, as well as the differing solution dynamic behavior observed for **2**, $\mathbf{2\cdot B(C_6F_5)_3}$, and **3**, may presage divergent reactivity for these complexes, attributable in part to the unique electronic characteristics of the ancillary ligand backbone.

In summary, we have demonstrated that 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene functions as a versatile new ligand precursor in the synthesis of cationic [(κ^2-*P*,*S*)Pt(η^3-benzyl)]$^+$X$^-$ species (**3**), as well as analogous zwitterionic (charge-neutral) complexes in which the formally cationic metal fragment is counterbalanced by an uncoordinated indenide (**2**) or borate ($\mathbf{2\cdot B(C_6F_5)_3}$) fragment within the ancillary ligand backbone. In addition to offering a new and complementary approach for the assembly of structurally related cationic and zwitterionic group 10 complexes, the convenience of employing a single ligand precursor in these syntheses may offer advantages over alternative strategies that require the preparation of distinct ligands for supporting cations and zwitterions. Having established the synthetic feasibility of heterobidentate indenide ligation in group 10 chemistry, we have initiated a comparative reactivity survey involving **2**, $\mathbf{2\cdot B(C_6F_5)_3}$, and **3**, in an effort to document the influence of the indenide, indenylborate, and indene ligand backbone (respectively) in tuning the reactivity of structurally related group 10 metal complexes. The results of these and related investigations will be reported in due course.

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Notes and references

‡ Crystallographic data have been deposited for **1** (CCDC 687093), **2·DMAP** (CCDC 687090), $\mathbf{2\cdot B(C_6F_5)_3}$(C$_7H_8$) (CCDC 687091), and **3** (CCDC 687092).† Selected crystal data for **1** (C$_{26}$H$_{36}$ClPPtS, 642.12 g mol^{-1}): a = 13.1479(3), b = 12.5326(4), c = 15.8100(5) Å, β = 98.1364(17)°, V = 2578.91(13) Å^3, space group = $P2_1/c$ (monoclinic), Z = 4, independent reflections = 5271 (R_{int} = 0.0389), GOF = 1.081, R_1 = 0.0335 ($F_o{}^2 > 2\sigma(F_o{}^2)$), w$R_2$ = 0.0810 (all data). Selected crystal data for **2·DMAP** (C$_{33}$H$_{45}$N$_2$PPtS, 727.83 g mol^{-1}): a = 10.6807(9), b = 14.1937(11), c = 20.6273(17) Å, β = 97.7681(9)°, V = 3098.4(4) Å^3, space group = $P2_1/c$ (monoclinic), Z = 4, independent reflections = 7060 (R_{int} = 0.0264), GOF = 1.059, R_1 = 0.0235 ($F_o{}^2 > 2\sigma(F_o{}^2)$), w$R_2$ = 0.0573 (all data). Selected crystal data for $\mathbf{2\cdot B(C_6F_5)_3}$(C$_7H_8$) (C$_{51}H_{43}BF_{15}$PPtS, 1209.78 g mol^{-1}): a = 21.679(2), b = 18.6294(17), c = 23.275(2) Å, V = 9400.0(15) Å^3, space group = *Pbca* (orthorhombic), Z = 8, independent reflections = 10 253 (R_{int} = 0.1001), GOF = 1.060, R_1 = 0.0379 ($F_o{}^2 > 2\sigma(F_o{}^2)$), w$R_2$ = 0.0892 (all data). Selected crystal data for **3** (C$_{50}$H$_{36}$BF$_{20}$PPtS, 1285.72 g mol^{-1}): a = 17.6907(18), b = 17.3368(18), c = 17.7636(18) Å, β = 117.9280(10)°, V = 4813.6(9) Å^3, space group = $P2_1/c$ (monoclinic), Z = 4, independent reflections = 11 034 (R_{int} = 0.0431), GOF = 1.058, R_1 = 0.0367 ($F_o{}^2 > 2\sigma(F_o{}^2)$), w$R_2$ = 0.0934 (all data).

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