



Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary

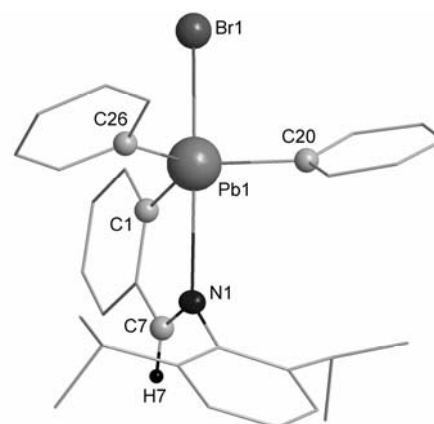
SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND SOLID STATE STRUCTURE OF [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br – A HYPERVALENT (10-Pb-5) SPECIES

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A new heteroleptic triorganolead(IV) halide containing an (imino)aryl ligand of the type 2-(RN=CH)C₆H₄, *i.e.* [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br (**1**), was prepared by reacting [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]MgBr (prepared *in situ* from (*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄Br and Mg filings) with Ph₂PbCl₂. The behaviour of compound **1** in solution was followed by multinuclear NMR studies and its crystal and molecular structure was established by single-crystal X-ray diffraction. The NMR data confirmed the identity of the compound and the presence of only one species in solution as well as they are consistent with one type of phenyl groups attached to the metal atom. The solid state structure indicated a strong intramolecular N→Pb interaction [2.657(8) Å] *trans* to the bromine atom [Br(1)–Pb(1)–N(1) 166.82(17)°], resulting in distorted trigonal bipyramidal geometry around the metal atom in a hypervalent 10-Pb-5 species. Supramolecular associations in solid state through intermolecular Br⋯H interactions and C–H⋯π contacts are discussed.



INTRODUCTION

The chemistry of hypercoordinated organotin compounds based on *ortho*-substituted phenyl ligands with a pendant arm containing a nitrogen atom able to coordinate intramolecularly to the metal centre raised considerable interest from theoretical aspects and potential applications. Largely used was the *sp*³ nitrogen-containing organic group 2-(Me₂NCH₂)C₆H₄,¹ but few publications on organotin compounds containing the related 2-(Et₂NCH₂)C₆H₄,² or (imino)aryl groups with *sp*²-nitrogen as donor atom, *e.g.* 2-

(RN=CH)C₆H₄ [R = PhCH₂, 2,4,6-Me₃C₆H₂, Me₂NCH₂CH₂, 2-PyCH₂, 2,6-ⁱPr₂C₆H₃],³ were also reported. By contrast, similar organometallic species were sparingly reported for the heaviest of the tetrel elements. So far, some organolead(IV) compounds containing the 2-(R₂NCH₂)C₆H₄ groups are known, *i.e.* tetraaryllead(IV) compounds - homoleptic [2-(Me₂NCH₂)C₆H₄]₄Pb,⁴ and heteroleptic [2-(R₂NCH₂)C₆H₄]₂R'₂Pb (R = Me, R' = Me, Ph; R = Et, R' = Ph)⁵ species; triorganolead(IV) halides - a chloride, [2-(Me₂NCH₂)C₆H₄]₂Ph₂PbCl,⁵ and several iodides, [2-(Me₂NCH₂)C₆H₄](4-MeC₆H₄)₂PbI,⁶ [2-

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(Me₂NCH₂)C₆H₄](4-MeC₆H₄)(4-MeOC₆H₄)PbI,^{6,7} [2-(R₂NCH₂)C₆H₄]Ph₂PbI (R = Me, Et);⁵ triorganolead(IV) dithiocarbamates - [2-(Me₂NCH₂)C₆H₄]Ph₂PbS(S)CNR₂ (R = Me, Et).⁸ Few diorganolead(II) derivatives with *sp*³ nitrogen-containing organic groups, *i.e.* [2-(Me₂NCH₂)C₆H₄]₂Pb,^{4,9} and the related derivatives, [CpFe{C₅H₃(CH₂NMe₂)-2}]₂Pb,¹⁰ and [CpFe{C₅H₃(CH₂NMe₂)-2}]₂PbM(CO)₅ (M = Cr, Mo, W),¹¹ were also described. So far, only one diorganolead(II) species containing (imino)aryl groups with *sp*²-nitrogen as donor atom, *i.e.* [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]₂Pb,^{3c} was reported.

We report here on the synthesis, the solution behaviour as well as the molecular structure of the first hypercoordinated (imino)aryl-containing triorganolead (IV) bromide, [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br.

RESULTS

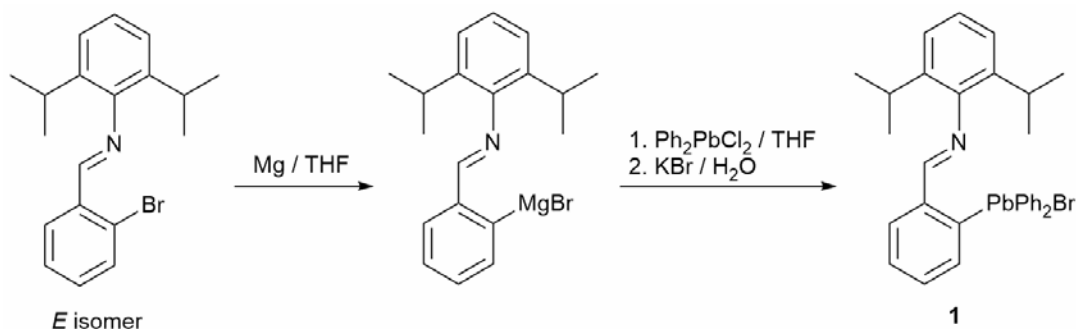
A Grignard reagent, [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]MgBr, prepared *in situ* from the organic bromide and magnesium filings, was added to a solution of Ph₂PbCl₂ in THF, at -78 °C. The resulted reaction mixture contained a mixture of organometallic chloride/bromide due to halide exchange. Its treatment with an aqueous solution of

KBr resulted in total conversion to the bromide **1** (Scheme 1), isolated in a fair yield as a very pale yellow solid.

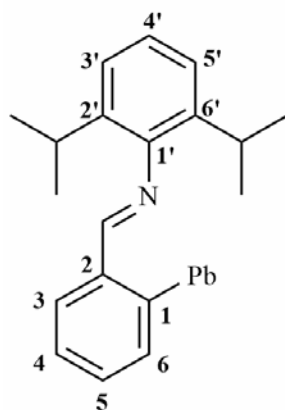
Details of the preparation is given in the Experimental section. The compound exhibits a good solubility in chloroform.

The ¹H and ¹³C NMR spectra were used to characterize the bromide **1** in CDCl₃ solution, at room temperature. The observed ¹H and ¹³C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC), according to the numbering scheme shown in Scheme 2 for the (imino)aryl substituent of the lead atom.

The NMR spectra are consistent with the nature of compound **1** and the presence of only one organolead(IV) species in solution. The expected resonances for the aromatic groups attached to the lead atom were observed both in the alkyl and aryl regions of the ¹H and ¹³C NMR spectra. Only one set of resonances was observed for the two phenyl groups attached to the metal centre. For some of the aromatic resonances the satellites corresponding to lead-proton and lead-carbon couplings, respectively, were also observed. In the ¹³C NMR spectrum the largest deshielding was observed for the resonance (δ 167.83 ppm) assigned to the carbon of the imino -CH=N- bond.



Scheme 1



Scheme 2

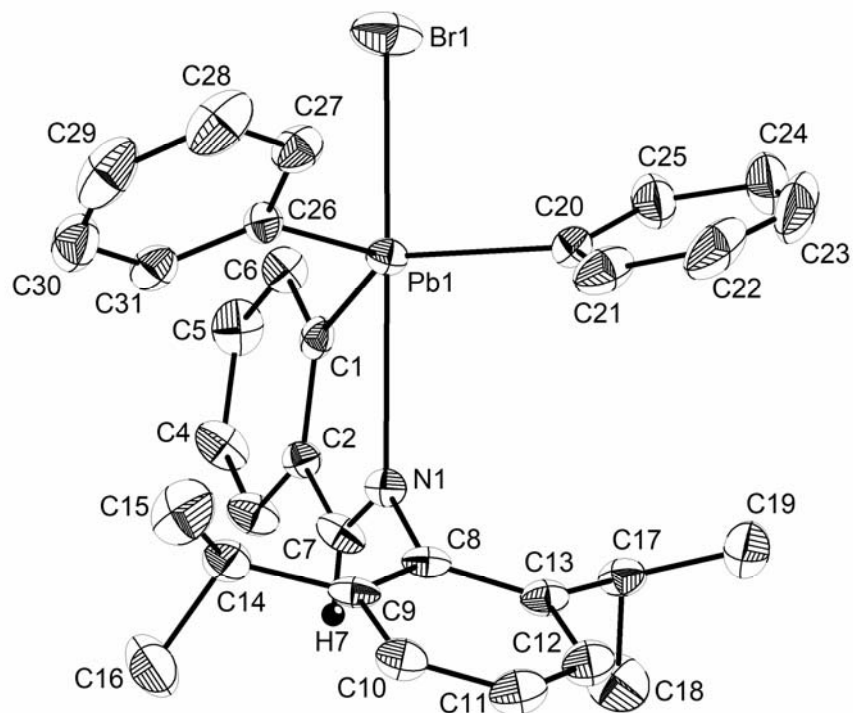


Fig. 1 – ORTEP representation at 25% probability and atom numbering scheme for [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br (**1**). Hydrogen atoms, less the imino hydrogen atom, are omitted for clarity.

Table 1

Selected interatomic distances (Å) and angles (deg) in [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br (**1**).

1			
Pb(1)–C(1)	2.194(10)	Br(1)–Pb(1)–N(1)	166.82(17)
Pb(1)–C(20)	2.183(10)	C(1)–Pb(1)–C(20)	125.8(4)
Pb(1)–C(26)	2.185(9)	C(1)–Pb(1)–C(26)	117.2(4)
Pb(1)–Br(1)	2.7041(15)	C(20)–Pb(1)–C(26)	115.0(4)
Pb(1)–N(1)	2.657(8)	Br(1)–Pb(1)–C(1)	95.5(3)
		Br(1)–Pb(1)–C(20)	92.6(3)
N(1)–C(7)	1.295(12)	Br(1)–Pb(1)–C(26)	95.8(3)
N(1)–C(8)	1.418(11)	N(1)–Pb(1)–C(1)	72.1(3)
		N(1)–Pb(1)–C(20)	91.2(3)
		N(1)–Pb(1)–C(26)	94.0(3)
		C(7)–N(1)–Pb(1)	106.5(6)
		C(8)–N(1)–Pb(1)	133.5(6)
		C(7)–N(1)–C(8)	119.9(8)

A single crystal of **1** was investigated by X-ray diffraction studies. It was shown to contain discrete monometallic units, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. The

ORTEP-like view of the molecular structure of [(*E*)-2-{(2',6'-ⁱPr₂C₆H₃)N=CH}C₆H₄]PbPh₂Br (**1**), with the atom numbering scheme, is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

DISCUSSION

Solution behaviour

Both ^1H and ^{13}C NMR spectra, recorded at room temperature, exhibit only one set of resonances for the substituents in *ortho* positions as well as for the *meta*-positions of the aromatic 2',6'- $^i\text{Pr}_2\text{C}_6\text{H}_3$ group attached to nitrogen. This is consistent with the lack of restriction for the free rotation of this group around the C–N(=C) single bond. The presence of two doublets for the methyl protons of the ^iPr groups in the ^1H NMR spectrum indicates their diastereotopic nature. Accordingly, in the ^{13}C NMR spectrum two resonances were observed for the corresponding methyl carbons. The ^1H singlet resonance for the imino proton, –CH=N–, is surrounded by lead satellites (δ 8.51 ppm, $^4J_{\text{PbH}} = 30.5$ Hz), as it is the corresponding ^{13}C resonance of the imino group (δ 167.83 ppm, $^3J_{\text{PbC}} = 13.2$ Hz).

In the aromatic region, the resonances for several protons are overlapped in the ^1H NMR spectrum. However, the large deshielding of the resonance for the H_6 proton of the (imino)aryl substituent (δ 8.89 ppm) allowed the observation of the satellites due to lead-proton coupling. The magnitude of this coupling constant ($^3J_{\text{PbH}} = 124.9$ Hz) is indicative for the presence of a triaryllead(IV) moiety in compound **1**.^{5,8} In contrast to the ^1H NMR spectrum, the aromatic region of the ^{13}C NMR spectrum of **1** is better resolved and contains, in addition to the expected resonances for the (imino)aryl substituent, only one set of four resonances for the phenyl groups attached to lead atom, thus indicating their equivalence in solution. Except the resonance for the *ipso* carbon, those for the other carbon atoms of the phenyl groups are surrounded by lead satellites due to lead-carbon coupling.

The solution NMR spectra of **1** suggest either (i) a trigonal bipyramidal (C,N) C_2PbBr core (due to the presence of an intramolecular N→Pb interaction in solution) as found in solid state (*vide*

infra), or (ii) a tetrahedral C_3PbBr core, due to the lack of the intramolecular coordination in solution.

Solid state structure

The crystal of **1** contains discrete molecules separated by normal van der Waals distances between heavy atoms. The imine nitrogen is coordinated intramolecularly to the lead atom in *trans* to the bromine atom [Br(1)–Pb(1)–N(1) 166.82(17)°]. Due to the presence of the imino –CH=N– double bond within the resulted NC_3Pb chelate ring, this system is basically planar (the N atom deviates from the best C_3Pb plane by 0.05 Å). In spite of an expected better donor properties of a $\text{N}(sp^2)$ atom *versus* a $\text{N}(sp^3)$ atom, the magnitude of the lead-nitrogen interatomic distance in **1** [Pb(1)–N(1) 2.657(8) Å; *c.f.* $\Sigma r_{\text{vdW}}(\text{Pb},\text{N})$ 3.54 Å¹²] is similar to those observed for the related chloride [2-(Me₂NCH₂)C₆H₄]Ph₂PbCl [Pb–N distance of average value of 2.641(8) Å for the independent molecules present in the unit cell]⁵ or iodide [2-(Me₂NCH₂)C₆H₄](4-MeC₆H₄)(4-MeOC₆H₄)PbI [Pb–N 2.686(8) Å].⁷ The coordination geometry at the lead atom is distorted trigonal bipyramidal [(C,N) C_2PbBr core], with the aromatic carbon atoms in the equatorial positions.

In the crystal of **1** the molecules are connected into a chain polymer through two intermolecular Br⋯H interactions of different strength [Br(1)⋯H(3) 2.76 Å and Br(1)⋯H(7) 3.09 Å; *c.f.* sum of the covalent and van der Waals radii, respectively, for bromine and hydrogen, $\Sigma r_{\text{vdW}}(\text{Br},\text{H})$ 3.15 Å],¹² in addition to an intramolecular Br(1)⋯H(6) interaction of 2.80 Å (Fig. 2). Parallel chains are associated into 2D architecture (Fig. 3) through C–H⋯ π contacts [C(18)–H(18A)_{methyl}⋯Ph_{centroid}{C(26')–C(31')} 2.98 Å, $\gamma = 12.1^\circ$; *c.f.* H⋯Ar_{centroid} contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and Ar_{centroid} smaller than 30°].¹³ There are no further contacts between such parallel layers in the crystal of **1**.

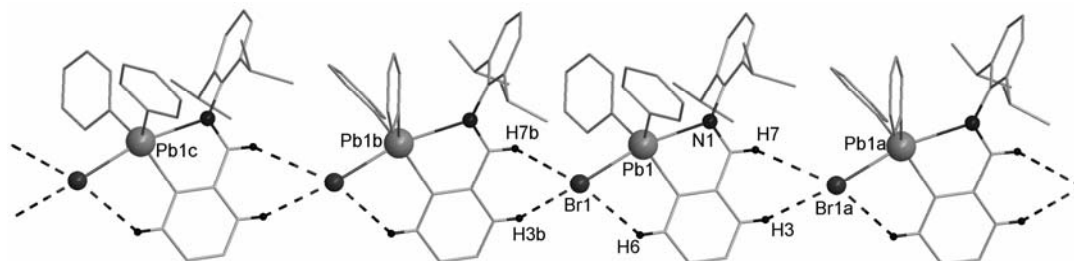


Fig. 2 – View of the chain polymer association in the crystal of **1** (only hydrogens involved in intra- and intermolecular C–H_{aryl}⋯Br interactions are shown) [symmetry equivalent atoms (–0.5+x, 0.5–y, –0.5+z), (0.5+x, 0.5–y, 0.5+z) and (1+x, y, 1+z) are given by “a”, “b” and “c”].

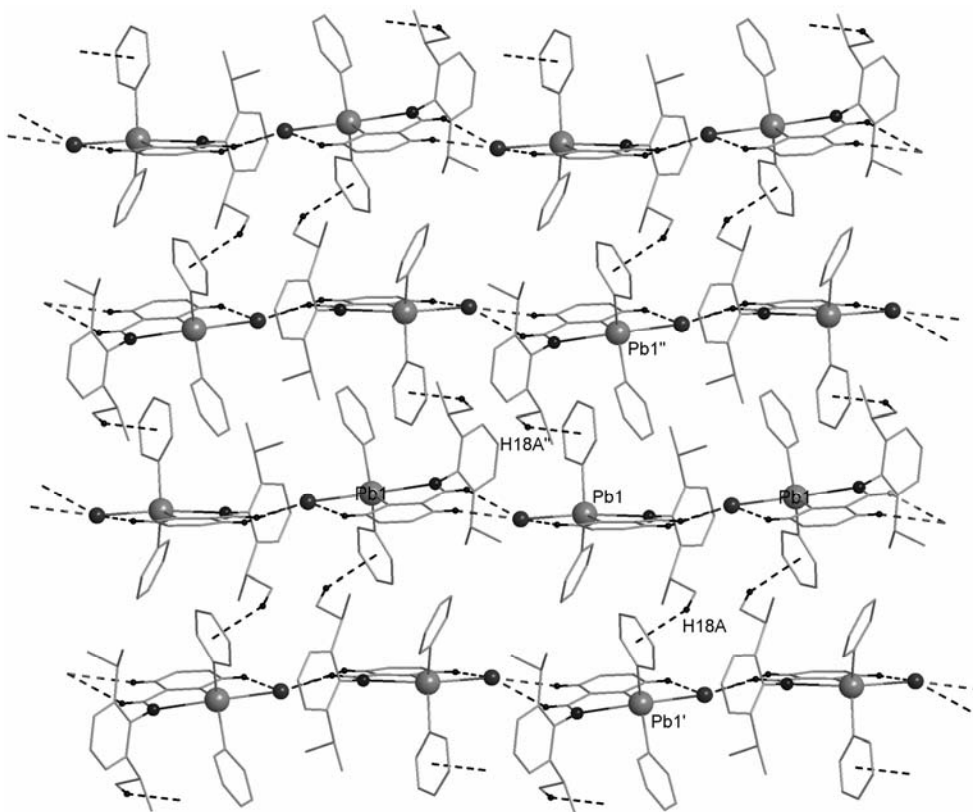


Fig. 3 – View of 2D association based on interchain C–H_{methyl}... π (Ph_{centroid}) interactions in the crystal of **1** (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms $(-0.5+x, 0.5-y, -0.5+z)$, $(0.5-x, -0.5+y, 1.5-z)$ and $(0.5-x, 0.5+y, 1.5-z)$ are given by “a”, “prime” and “double prime”].

EXPERIMENTAL

The synthesis was carried out under an inert atmosphere of argon using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. The (E) -2- $\{(2',6'$ - $^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{C}_6\text{H}_4\text{Br}$ was prepared according to a published method,¹⁴ while the Ph_2PbCl_2 was commercial product and was used as received. ^1H , ^{13}C and 2D NMR (COSY, HSQC, HMBC) spectra were recorded at room temperature on Bruker Avance 300 instrument, using solutions in CDCl_3 . The ^1H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl_3 , 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent (CDCl_3 , 77.16 ppm).¹⁵ The NMR spectra were processed using the *MestReC* and *MestReNova* software.¹⁶

Synthesis of $[(E)$ -2- $\{(2',6'$ - $^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{C}_6\text{H}_4]\text{PbPh}_2\text{Br}$ (**1**)

A solution of (E) -2- $\{(2',6'$ - $^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{C}_6\text{H}_4\text{Br}$ (1.10 g, 3.20 mmol) in 20 mL anhydrous THF was added dropwise, under stirring, to magnesium filings (0.077 g, 3.20 mmol, 6.7% excess) activated with 1,2-dibromoethane (0.028 g, 0.16 mmol). The reaction mixture was stirred for 4 h under reflux, which resulted in complete consumption of magnesium. The solution of the organomagnesium derivative thus obtained was cooled at -78°C and then added dropwise to a solution of Ph_2PbCl_2 (1.32 g, 3.05 mmol) in 50 mL THF, cooled at same temperature. The reaction mixture was stirred at -78°C for 1 h, then was left to reach the room temperature and stirred at this temperature for 6 h. An aqueous solution of KBr (0.6 g, 5 mmol) was added and the reaction mixture was stirred for 12 h, then the solvent was

removed *in vacuo* to dryness. The remaining solid was extracted with CH_2Cl_2 (3×20 mL), the unified organic phases were dried over MgSO_4 and then the drying agent was filtered off. Evaporation of the clear solution afforded the isolation of **1** as a very pale yellow solid, which was dried under reduced pressure. Yield: 1.4 g (65%). M.p. = 272°C . ^1H NMR (300.11 MHz, 23°C): δ 0.43 [6H_A, d, $-\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.0$ Hz], 0.84 [6H_B, d, $-\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 6.8$ Hz], 2.21 [2H, hept, $-\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 6.8$ Hz], 6.97-7.18 (3H, AB₂ spin system, H-3'-5'), 7.28-7.45 (6H, m, C₆H₅-*meta*+*para*), 7.48-7.60 (4H, m, C₆H₅-*ortho*), 7.66-7.81 (2H, m, H-3,4), 7.89 (1H, ddd, H-5, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.6$ Hz), 8.51 (1H, $-\text{CH}=\text{N}-$, $^4J_{\text{PbH}} = 30.5$ Hz), 8.89 (1H, d, H-6, $^3J_{\text{HH}} = 7.5$, $^3J_{\text{PbH}} = 124.9$ Hz). ^{13}C NMR (75.46 MHz, 25°C): δ 21.65 [s, C_A, $-\text{CH}(\text{CH}_3)_2$], 25.69 [s, C_B, $-\text{CH}(\text{CH}_3)_2$], 28.39 [s, $-\text{CH}(\text{CH}_3)_2$], 123.54 (s, C-3',5'), 126.13 (s, C-4'), 129.47 (s, C₆H₅-*para*, $^4J_{\text{PbC}} = 25.8$ Hz), 130.15 (s, C₆H₅-*meta*, $^3J_{\text{PbC}} = 117.0$ Hz), 134.36 (s, C-3), 135.12 (s, C-5), 136.13 (s, C₆H₅-*ortho*, $^2J_{\text{PbC}} = 90.2$ Hz), 136.53 (s, C-4), 139.12 (s, C-2), 139.54 (s, C-6), 140.05 (s, C-2',6'), 146.43 (s, C-1'), 152.61 (s, C-1), 157.91 (s, C₆H₅-*ipso*), 167.83 (s, $-\text{CH}=\text{N}-$, $^3J_{\text{PbC}} = 13.2$ Hz).

Crystal structure determination

Single crystals of compound **1** were grown by slow diffusion from a mixture of CH_2Cl_2 /n-hexane (1/4, v/v). A colorless block crystal was attached on cryoloops using epoxy glue. The details of the crystal structure determination and refinement are given in Table 2. Data collection and processing was carried on a Bruker SMART APEX system using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), at room temperature.

Table 2

Crystallographic data for [(*E*)-2-(2',6'-¹Pr₂C₆H₃)N=CH]C₆H₄]PbPh₂Br (**1**)

Compound	1
Molecular formula	C ₃₁ H ₃₂ BrNPb
<i>M</i>	705.68
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	297(2)
<i>a</i> /Å	11.756(3)
<i>b</i> /Å	15.660(5)
<i>c</i> /Å	15.173(4)
α ^o	90
β ^o	95.044(6)
γ ^o	90
<i>V</i> /Å ³	2782.5(14)
<i>Z</i>	4
<i>D</i> _{calc} /gcm ⁻³	1.684
<i>F</i> (000)	1368
μ (Mo-K α)/mm ⁻¹	7.518
Crystal size mm ³	0.26 x 0.28 x 0.34
θ range for data collection °	1.87 to 25.00
Reflections collected	15950
Independent reflections	4844 [<i>R</i> _{int} = 0.0598]
Absorption correction	Multi-Scan ¹⁷
Maximum and minimum transmissions	0.2453 and 0.1843
Data / restraints / parameters	4844 / 0 / 311
Goodness-of-fit on <i>F</i> ²	1.124
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0565
	<i>wR</i> ₂ = 0.1201
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0759
	<i>wR</i> ₂ = 0.1277
Largest difference peak and hole (e Å ⁻³)	1.065 and -1.897

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.¹⁸ The drawings were created with the Diamond program.¹⁹

Supplementary material

Crystallographic data for the structural analysis of **1** (CCDC no. 871123) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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