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A Lead(II) Substituted Triplet Carbene

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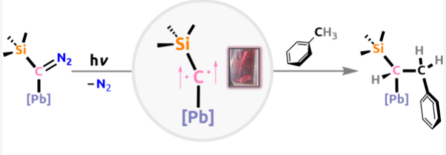
ABSTRACT: Reaction of the pincer-type ligand L_3 supported complex $[L_3PbBr][BArF_{24}]$ (**1**) with $Li[(C({=}N_2)TMS)]$ furnishes $[L_3Pb(C({=}N_2)TMS)][BArF_{24}]$ (**2**). Diazo-compound **2** eliminates dinitrogen upon irradiation affording formal plumba-alkyne **3**, which persists in cold fluoroarene solutions. Variable temperature UV/Vis and NMR spectroscopies in combination with quantum-chemical calculations identify **3** as a metal-substituted triplet carbene. In-crystallo irradiation of $[L_3Pb(C({=}N_2)TMS)(tol)][BArF_{24}]$ (**2**·tol) provides a snapshot of intermolecular C−H bond insertion with toluene (**4**).



Triplet Carbene, not Plumbaalkyne!

■ INTRODUCTION

Previously believed to be only transient, persistent carbenes are now commonly applied in drug design, catalysis, photochemistry, and materials science.[1−8] The reactivity of singlet carbenes is controlled by steric bulk, σ-, and mostly π-interactions following a push−push or push−pull pattern.[9,10] As exemplified by *N*-heterocyclic carbenes (NHCs) and cyclic (Alkyl)(Amino) carbenes (CAACs), stable carbene chemistry is dominated by *N*-donor substituents.[11−13] Imidazolin-based NHCs are more stable than CAACs as their formally vacant p_z-orbital profits from π-donation from two amino substituents, whereas it is only one for the latter. In stark contrast, carbenes without adjacent π-donors usually occur only as highly reactive and fleeting intermediates because of their small HOMO−LUMO energy gaps or even triplet ground states. In situ generated, short-lived triplet carbenes are employed in preparatively useful C−H (N−H, O−H, etc.) insertion and olefin addition reactions.[14] The field of persistent triplet carbenes was pioneered by Tomioka et al.,[15] who reported a fairly stable triplet carbene. Opposed to diphenylcarbenes, which were characterized by photocrystallography,[16,17] these carbenes are persistent thanks to extensive steric and mesomeric stabilization by two bulky aryl substituents, leading to anticipated few spin density on the carbenic carbon atom.[18−20] Likewise profiting from spin delocalization, a transient triplet vinylidene was characterized under matrix conditions.[21]

A complementary approach to triplet carbenes may be the synthesis of heavy *p*-block metalla-alkynes. The orbital interaction of the carbon atom with the metal decreases on descending the group of the periodic table,[22] thereby decreasing the bond order and distorting the molecule.[23−28] Formal multiple bonding with heavier *p*-block elements is an emerging research area as it promises to replace noble metal catalysts by compounds based on more abundant elements.[29−33] Elevating on photo- and transition metal catalysis[34,35] as well as ylid-chemistry,[36,37] plumba-alkynes could provide access to controlled C1/CR transfer.[38] Few heavier group 14 metalla-alkynes have been isolated and a handful chemically trapped (Figure 1).

Kato, Baceiredo, and colleagues reported on mesomerically stabilized **I**, which proved competent for C−C coupling with an isocyanide.[39,40] The same team investigated the transient germa-alkyne analogue, which rearranges to a heterocyclic germylene.[41] In 2024, the Liu group described a transient ambiphilic stannyne[42] and isolated the closed-shell stanna-alkyne **II**,[43] which is best described as a zwitterionic Sn=C=P allene and exhibits a large HOMO−LUMO energy gap according to its yellow color. Couret et al. reported diazo compound **III** as precursor for a germa-alkyne devoid of mesomeric stabilization.[44] Indeed, irradiation generated an exceedingly reactive intermediate, which was trapped through the reaction with alcohols. Similarly, in situ generated stanna-alkynes derived from **IV** undergo intramolecular C−H insertion and a cascade of ligand redistributions.[45,46] Computations predicted that bulky substituents and *Lewis* acids render the Pb≡CR triple bond stable.[47−49] Yet, and despite of reports on formal transition metal TM≡Pb[50,51] as well as Pb≡Pb triple bonds,[52] neither high-spin congeners nor a plumba-alkyne have been hitherto reported. Intermolecular C−H insertion reactivity of such compounds is likewise unknown. However, late transition metal-substituted carbenes, that is, formal metalla-carbynes, attract significant attention. The Schneider group studied pallada- and platina-triplet carbenes **Va** and **Vb** by photocrystallography.[53] Further studies

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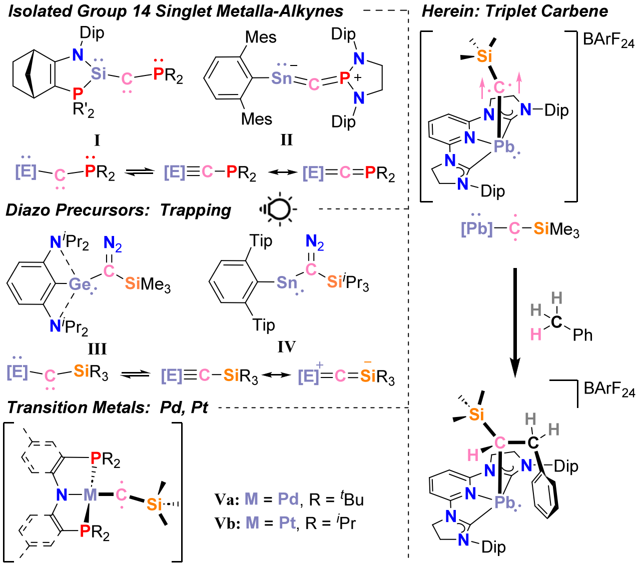


Figure 1. Mesomerically stabilized closed-shell metalla-alkynes of group 14 elements (left, top), precursors used in trapping studies (left, middle), in-crystallo characterized transition metal substituted triplet carbenes (left bottom), and triplet carbene studied herein (right). Mes, mesityl; Dip, 2,6-diisopropylphenyl; Tip, 2,4,6-triisopropylphenyl; $BArF_{24}$, Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

include Liu's gold[54] and the related Rh-supported $\sigma^0\pi^2$ singlet carbene[55] as well as copper-supported carbyne anion,[56] an isolable metallacyclic triplet iron carbyne[57] and in-crystallo generation of a copper alkenylidene,[58] and trapping studies with Rh,[59−61] Ir,[62] Ni,[63] Pd,[64] Pt,[65] Au,[66] and Zn[67] carbynes.

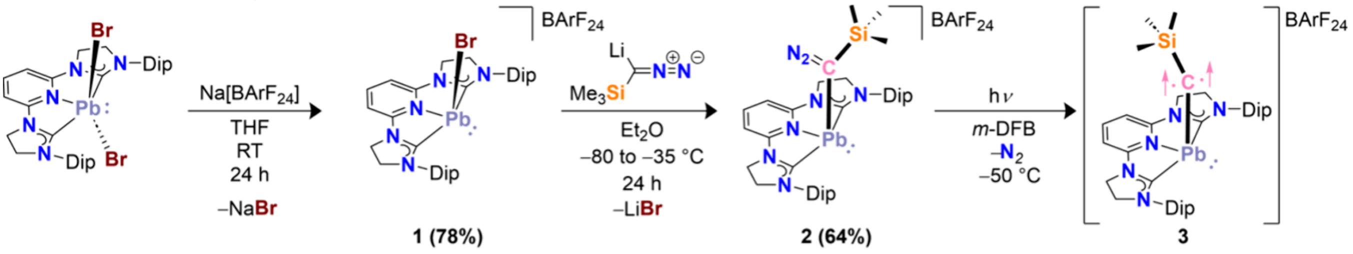
Targeting 3d metal-supported carbynes, we contributed iron[68] and cobalt[69] nitrilimides. Whereas these complexes are intermediates en route to terminal nitride (Fe) and isocyanoamides (Co), we did not succeed in obtaining the corresponding *C*-coordinated species. Here, we report that lead[70] forms such a formal plumba-alkyne. The heavy nature of lead prevents π-bonding with the carbon atom, thus rendering it a triplet carbene. Although persistent in solution up to −20 °C, it inserts into the benzylic C−H bonds of toluene when warmed to higher temperatures.

■ RESULTS AND DISCUSSION

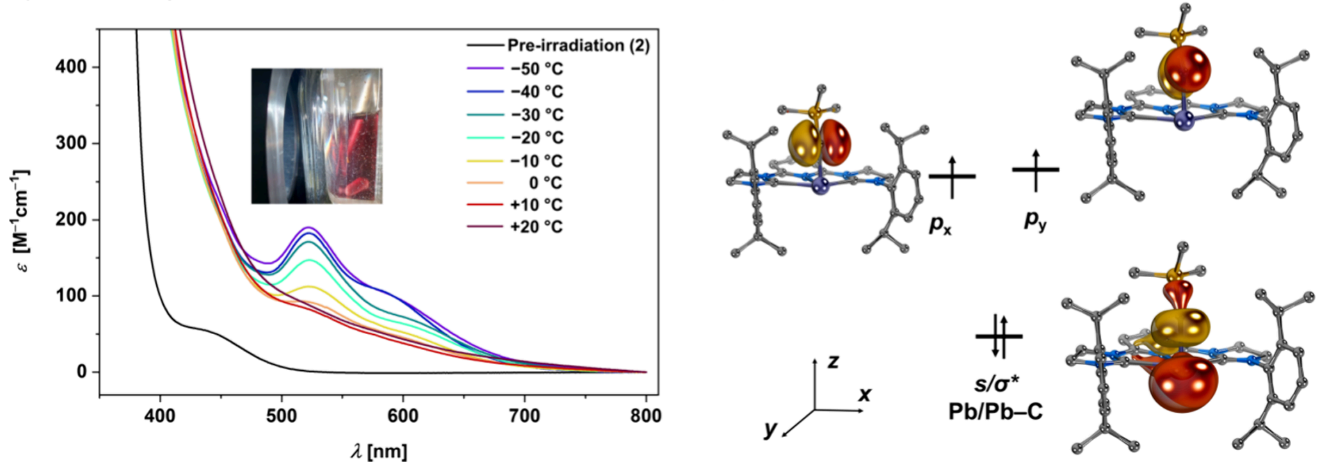
Treating $[L_3PbBr_2]$ (L_3 = CNC pincer-type ligand based on pyridine and two saturated NHCs (saNHC))[71] with $NaBArF_{24}$ at ambient temperature in tetrahydrofuran afforded $[L_3PbBr][BArF_{24}]$ (**1**) in 78% isolated yield (Scheme 1, a). Subsequent reaction of **1** with $Li[(C({=}N_2)TMS)]$ in diethyl ether furnished the trimethylsilyldiazomethylplumbylene $[L_3Pb(C({=}N_2)TMS)][BArF_{24}]$ (**2**) in 64% yield. Complex **2** can be recrystallized from various solvents (Et_2O, THF, toluene, fluorobenzene), thereby affording single crystals suitable for sc-XRD (single-crystal X-ray diffractometry; cf. Scheme 2). Irradiating **2** at room temperature in benzene, in which it is poorly soluble, using a Xe lamp induced N_2 release as visually apparent by gas bubbles. NMR and IR-spectroscopic measurements confirmed quantitative conversion within 2 h. However, an intractable mixture of compounds as well as a black precipitate formed, and partial deconstruction of the $BArF_{24}$ anion was evident in the NMR spectroscopic analysis. In stark

Scheme 1. (a) Stepwise Synthesis of 2 and Structure of Intermediate 3. (b) Variable-Temperature UV/Vis Spectroscopic Analysis of 3 in 1,3-Difluorobenzene. (c) Pertinent Occupied Frontier Orbitals of 3 as Obtained by ZORA-CASSCF(10,11)/def2-TZVPP//r^{2}SCAN-3c

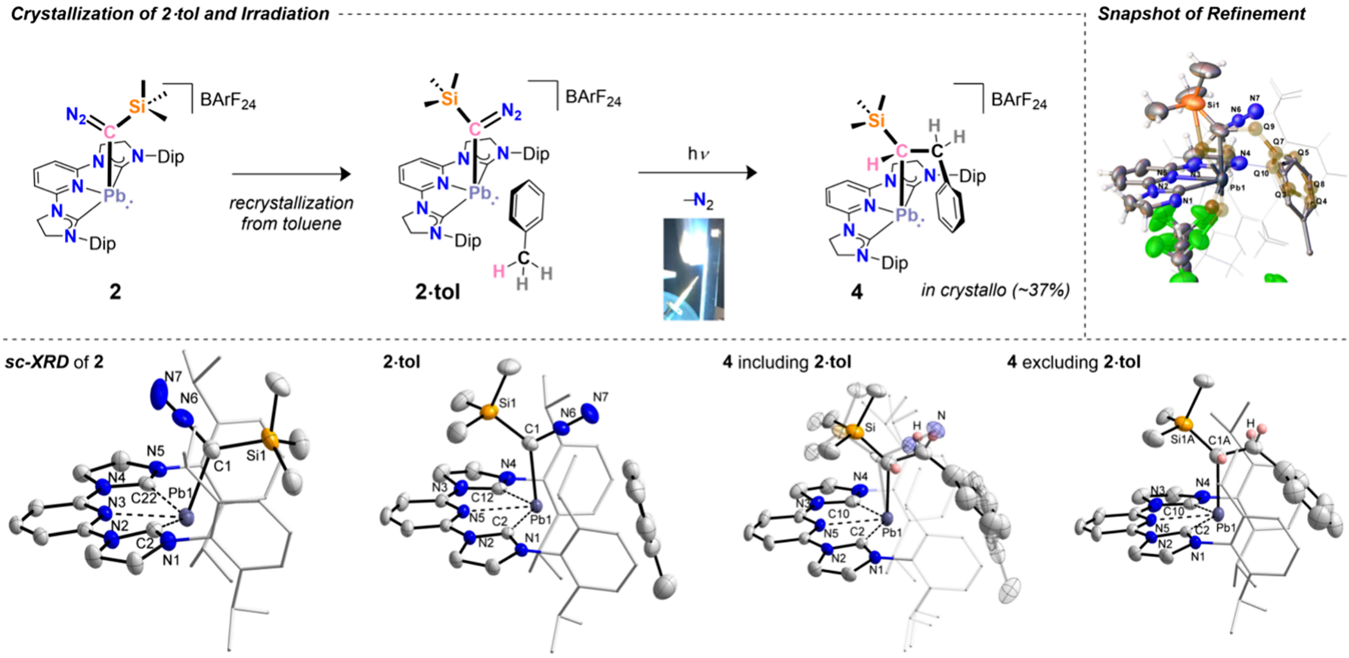
a) Stepwise Precursor Synthesis and Irradiation



b) VT-UV/Vis Capture of 3 **c) Pertinent Frontier Orbitals of 3**



Scheme 2. Synthesis of 2·Tol (Top Left), Photocrystallography Including a Snapshot of the Crystallographic Refinement Showing Suitable Electron Density for a Flipped Benzyl Moiety (Top Right) and Solid-State Structures (Bottom)[a]



[a]Thermal ellipsoids (if given) represent the 50% (**2**, **2·tol**) and 30% (**4**) probability level. For selected atom distances and close contacts, see the SI. Dip-groups are rendered as wireframe, and H-atoms are attached using a riding model.

contrast, switching to fluorinated aromatic solvents such as *m*-DFB (1,3-difluorobenzene) or TFB (1,2,3,4-tetrafluorobenzene) afforded at −50 °C (−40 °C, respectively) homogeneous solutions of persistent pink reddish color. Elevating the temperature induced a color change to yellow with concomitant formation of a brownish precipitate. Following the reaction by in situ UV/Vis spectroscopy in the cold captured the intermediate **3** with an absorption maximum at 524 nm and a shoulder around 600 nm (Scheme 1, b).

Intermediate **3** decays with appreciable rate upon raising the temperature to −20 °C. It is interesting to note that the platina-analogue **Vb** exhibits an essentially equivalent absorption spectrum with bands centered at 490 and 584 nm. Albeit complicated due to partial precipitation upon warming, the irradiation in an NMR tube allowed us to study **3** by ^{1}H NMR spectroscopy in the cold. In line with the spectra reported for a lead(I) radical,[70f] we do not find strong paramagnetic shifting yet line-broadening (Figure S31). *Evans* NMR measurements (Table S1) corroborate paramagnetism and suggest a magnetic moment of ~1.6 μ_B for **3**, which vanishes upon warming the sample to room temperature. As expected in the presence of a heavy *p*-block element with strong spin−orbit coupling as well as in line with the platinum-substituted triplet carbene **Vb**, no signals were observed by neither X-band nor Q-band EPR spectroscopy at 10 K, including in situ irradiation in solution as well as of single crystals. Quantum chemical calculations (r^{2}SCAN-3c, ZORA-TPSSh, ZORA-PBE0, ZORA-PBE, NEVPT2//CASSCF, and DLPNO−CCSD(T)) were conducted to pinpoint the electronic nature of **3** (Scheme 1, c). All methods predict a slightly bent Pb−C−Si linkage (157°−171°; Table S4) and favor a triplet ground state (Table S8). For instance, NEVPT2//ZORA-saCASSCF(10,11) affords a vertical singlet/triplet energy gap $\Delta E^{s/t}$ of 1.04 eV. At this level of theory, the calculated zero-field splitting exhibits low rhombicity (E/D = 0.006), hence approaching axial symmetry as is expected for a triplet carbene. The calculated D values >37 cm^{-1} (DFT predicts D = 112−309 cm^{-1}; Table S9) are in the same order of magnitude as for **Vb** (D = 65 cm^{-1}; E/D = 0.008) and too large to render EPR suitable for characterizing **3**. The zero field splitting is though significantly smaller than for a stibinidene and a bismuthinidene.[72,73] The two unpaired electrons reside in the two perpendicular carbon-centered p-orbitals without significant π-interaction with the metal (Scheme 1, c). These two SOMOs neither profit from conjugation (as is the case for diarylcarbenes) nor mix with metal-based orbitals (as is the case for compounds **Va** and **Vb**), yet profit from hyperconjugation with the trimethylsilyl group (Löwdin's atomic spin density on Si: 0.21 au; Mayer's bond order C−Si: 1.02). The lead's lone pair is located in the 5s orbital, which admixes lead *p*- and carbon *sp*-character (Löwdin's atomic spin density on Pb: 0.13 au; Mayer's Bond Order Pb−C: 0.55), thus inferring weakly σ*-antibonding character with the carbene, and consequently suggesting that the Pb−C bond is labile. Population analyses using DFT afford consistent results (Table S6) and corroborate the absence of stabilizing electronic interactions with the supporting pincer ligand (Figure S41). The SOC-NEVPT2//ZORA-saCASSCF calculations match the experimental UV/Vis spectrum (Tables S13 and S14). The two bands at λ = 600 and 524 nm (λ^{calc} = 633, 439 nm) are rationalized as the spin-forbidden SOMO → SOMO transition and the spin-allowed transitions from the lead atom's 5s orbital into the two quasidegenerate SOMOs. In short, the computations describe transient plumba-alkyne **3** as a bona fide triplet carbene, which is persistent in the cold thanks to steric protection. Irradiating **2** in fluoroarenes in the cold under dinitrogen atmosphere led to predominant intramolecular C−H insertion of the carbene into one of the benzylic positions of the Dip substituents (~50%, Figures S17 and S18), similarly as observed by Kira and colleagues for compound **IV**.[45] To trap the transient carbene **3**, irradiation experiments (Figures S23−S30) were conducted in the presence of sulfur, carbon monoxide, styrene, hydridic reagents (pinacolborane, triphenylsilane, dihydrogen), and an alkyl halide (dichloromethane). Dichloromethane cleanly generated the chloride analogue of **1**, thus highlighting the labile nature of the Pb−C bond.

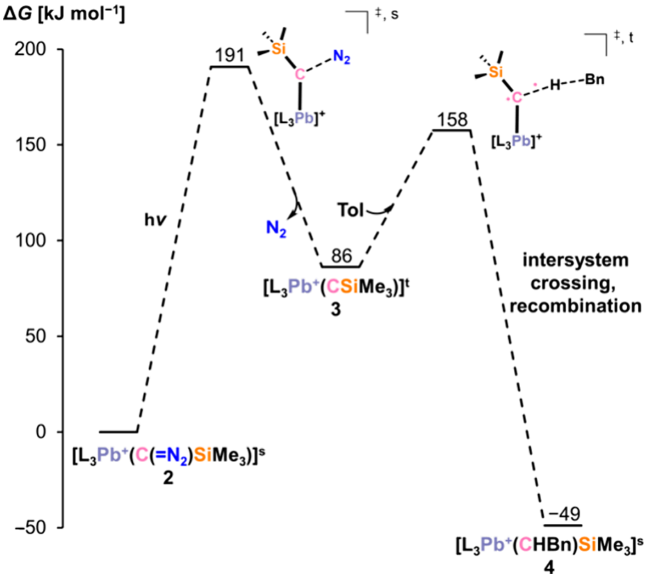
Dihydrogen formed a mixture of compounds yet with only a minor amount (~7%) of the intramolecular C−H insertion product, thus pointing as well at metal-centered reactivity and Pb−C bond cleavage. Carbon monoxide, styrene, and triphenylsilane afforded a mixture of compounds of very similar composition to the irradiation in the absence of an additive. Sulfur and pinacolborane led to instantaneous metal-centered reactivity under the loss of the diazomethanide even without irradiating the sample.

We thus turned our attention toward in-crystallo transformations.[74] The solid-state structure of **2** (Scheme 2, bottom), obtained through crystallization from fluorobenzene, revealed the Pb(II) center in 4-fold, yet asymmetric coordination with the saNHC and the diazomethanide ($d(C_{carbene}{-}Pb)$ = 255.3(4), 263.4(3) pm; $d(C_{N2C}{-}Pb)$ = 228.6(4) pm; d(N−Pb = 252.3(3) pm) ligands. A contact to a CF_3 group adjacent to the Pb center is noted (d(F···Pb) = 362.9(5) pm). Due to the packing of $[BArF_{24}]^-$, the $[L_3Pb(C(=N_2)TMS)]^+$ units form dimers with R−N−N··· H−C contacts (Figure S37). Akin to $[L_3Pb(OTf)_2(tol)]$,[71] the flanking Dip groups create a peculiar void. Driven by dispersive interactions with these arenes, this cavity may host aromatic solvent molecules.[71] Crystallization in the presence of toluene afforded $[L_3Pb(C(=N_2)TMS)(tol)][BArF_{24}]$ (**2·tol**), in which the void is occupied by toluene. Drying single crystals of **2·tol** in vacuo leads to desolvation, hence corroborating that the interaction with the lead complex is weak and reversible. The $Pb{-}C_{tol}$ atom distances in the single crystal are accordingly long (363 pm in average). The $Pb{-}C_{carbene}$ distances suit the ones in **2** ($d(C_{carbene}{-}Pb)$ = 257.8(3), 263.1(3) pm; $d(C_{N2C}{-}Pb)$ = 228.6(4) pm), whereas the $Pb{-}N_{py}$ bond is slightly elongated d(N−Pb = 259.5(7) pm). Irradiating single crystals of **2** excluding solvent in between the Dip-tweezers on the goniometer of the diffractometer in the cold led to darkening of the crystals, followed by cracking upon loss of approximately 10% of N_2, thus preventing the collection of high-quality data (Figure S40), yet substantiating the formation of a carbene. Irradiation of **2·tol**, which includes cocrystallized toluene, at 153 K gave though access to a new species **4** in about 37% conversion in respect to the starting material according to free refinement of the relative proportions of **2·tol** and **4** on split positions (Scheme 2, top). This species **4** relates to the insertion of the carbene into the benzylic position of the cocrystallized toluene molecule. Whereas a detailed discussion of the structural metrics is challenging due to restraints used in the refinement, a few pertinent observations may be noted. Both mean planes of the crystallographically observed benzyl groups are tilted 27° against each other. The centroid of the phenyl ring in the insertion product is thereby ~32 pm closer to the lead center than in the starting material (354 pm in **4** vs 386 pm in **2·tol**).

Diazomethanide **2** was eventually irradiated in a toluene:*m*-DFB 1:1 mixture at −50 °C, whereupon again a pink reddish color was obtained, which faded to yellow when raising the temperature. The NMR spectroscopic analysis confirmed in combination with mass spectrometry that two major compounds formed, whereof the major is the benzylic insertion product **4** (~35%), whereas the minor one (~25%) relates to the intramolecular C−H insertion product (vide supra; Figures S16−S22).

To put the in-crystallo transformation into context with the solution-phase chemistry, calculations were performed at the ZORA-DLPNO−CCSD(T)/def2-TZVPP//r^2SCAN-3c level of theory under the implicit consideration of solvation (Scheme 3). The calculations confirm that N_2 release is light-driven (ΔG = +86 kJ mol^{-1}) and irreversible in the cold. The C−H bond insertion proceeds via H atom abstraction and with a barrier of $\Delta G^{\ddagger}$ = (158−86) = +72 kJ mol^{-1}. This value confirms a slow reaction at −50 °C ($t_{1/2}$ > 3 h), hence corroborating the stability of **3** in the cold even in the presence of toluene. Accordingly, it is in line with the formation of mixtures including **4** upon elevating the temperature and suggests that the in-crystallo transformation profits from spatial confinement. H atom abstraction is followed by barrierless intersystem crossing and radical recombination (ΔG = −49 kJ mol^{-1}).

Scheme 3. Mechanism for C−H Insertion into the Benzylic Position of Toluene[a]



[a] Superscripts s and t designate the singlet and triplet multiplicities. For details and the equilibrium between two conformers of **2** and **3**, see Figures S43 and S44.

CONCLUSIONS

We have presented the synthesis, characterization, and low-temperature photolysis of trimethylsilyldiazomethylplumbylene **2**. Low-temperature NMR and UV/Vis measurements in combination with computational studies reveal upon irradiation the formation of formal plumba-alkyne **3**, which is electronically identified as bona fide triplet carbene. It is persistent in fluoroarene solutions up to −20 °C. In-crystallo reactivity studies, complemented by quantum chemical calculations, provide a snapshot of benzylic C−H insertion with toluene, which also occurs in solution. This contribution describes a new approach toward stabilizing triplet carbenes and thus provides impetus to discovering carbene/carbyne catalysis with heavy *p*-block metals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c10205.

Synthetic procedures, spectroscopic data, and computational and crystallographic details (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 2366283–2366285 and 2366288 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

$BArF_{24}$, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; CAAC, Cyclic (Alkyl)(Amino) Carbene; DFT, Density Functional Theory; Dip, 2,6-diisopropylphenyl; EPR, Electron Paramagnetic Resonance; ^{i}Pr, isopropyl; *m*-DFB, 1,3-difluorobenzene; NHC, *N*-Heterocyclic carbene; NMR, Nuclear Magnetic Resonance; Mes, mesityl; saNHC, saturated *N*-heterocyclic carbene; sc-XRD, single-crystal X-ray diffractometry; SOC, Spin–Orbit Coupling; Tip, 2,4,6-triisopropylphenyl; THF, tetrahydrofuran; TFB, 1,2,3,4-tetrafluorobenzene; TMS, trimethylsilyl; VT, variable temperature

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