



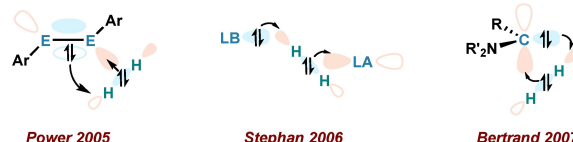
Dihydrogen and Ethylene Activation by a Sterically Distorted Distibene

Yue Pang, Markus Leutzsch, Nils Nöthling, and Josep Cornella*

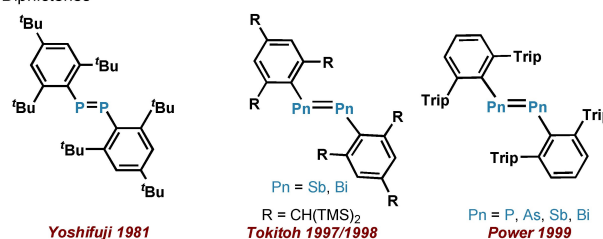
Abstract: Herein, we report the synthesis of a sterically distorted distibene (**[4]₂**) and its transition-metal-like reactivity towards two fundamental feedstock chemicals: H₂ and ethylene. Although **[4]₂** exhibits an unusually long Sb=Sb distance and noticeable backbone distortion in the solid state, NMR data suggest that **[4]₂** remains predominantly as a dimer in solution, even at high temperatures. However, it was proposed that the elusive reactivity of **[4]₂** toward H₂ and ethylene results from reversible dissociation of **[4]₂** into the transient stibinidene (**[4]**), which could be observed by NMR spectroscopic techniques.

The study of coordination and activation modes of small molecules at transition-metal (TM) centers is crucial to understanding the mechanistic aspects of catalytic cycles.^[1] One of the classical examples is the TM-catalyzed hydrogenation reaction, where the coordination and activation of both H–H and C=C bonds are involved.^[2] For years, activation of these molecules was considered the exclusive domain of *d*-block elements (frequently referred to as “transition-metal-like reactivity”^[3]); yet, this apparent dogma has been challenged during the past two decades (Figure 1A). In 2005, Power et al. reported the activation of H₂ by a digermene at ambient conditions.^[4] Later, splitting of H₂ was also unlocked using frustrated Lewis pairs (FLPs) and (alkyl)(amino)carbenes, by Stephan and Bertrand groups, respectively.^[5] In these systems, H₂ cleavage occurs through the interaction of H₂ with a filled and an empty frontier orbitals of main-group elements, reminiscent of that of TMs.^[3a] Ever since, a variety of main-group systems exhibiting diverse TM-like reactivity appeared, such as main-group multiple bonds^[6], group 13 carbene analogues^[7] tetrylenes^[8] and low-valent alkaline compounds^[9]. In the first category of main-group systems, the polar dative nature of heavier group 13 and 14 multiple bonds leads to modest

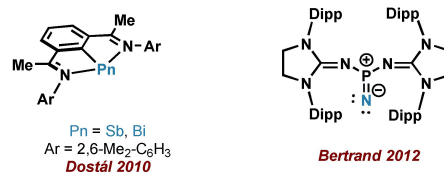
A. TM-like activation modes of main-group compounds



B. Dipnictenes



C. Singlet pnictinidenes



D. Well-characterized triplet nitrene and bismuthinidene

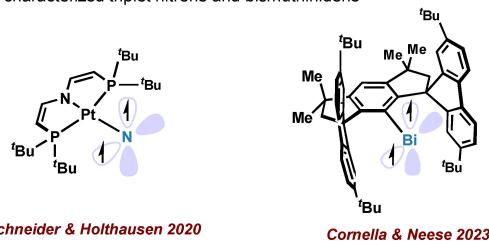


Figure 1. (A) Pioneering work of TM-like reactivity of main-group compounds; (B) Selected examples of dipnictenes; (C) Selected examples of singlet nitrenes and pnictinidenes; (D) Emerging triplet nitrenes and pnictinidenes.

energetic separation of the frontier orbitals, rendering efficient interaction with substrates, such as H₂.^[3a]

In contrast to group 13 and 14 systems, the TM-like reactivity for low-valent pnictogen (Pn) compounds remains underdeveloped. For dipnictenes, the Pn=Pn bonds have a classical bonding situation with a significant orbital overlap, which makes the interaction with small molecules difficult. Representative examples of these compounds are Yoshifuji's diphosphene,^[10] and Tokitoh's and Power's distibenes and dibismuthenes^[11] (Figure 1B).

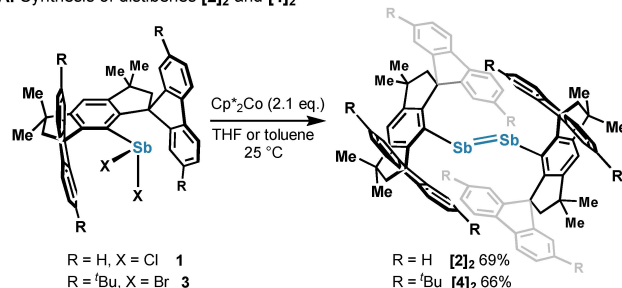
[*] Dr. Y. Pang, Dr. M. Leutzsch, Dr. N. Nöthling, Dr. J. Cornella
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
E-mail: cornella@kofo.mpg.de

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By analogy to carbenes, however, monomeric pnictinidenes are expected to exhibit similar TM-like reactivity via dual orbital interaction (SOMO and SOMO for the triplet, or HOMO and LUMO for the singlet).^[12] To date, coordination of Lewis bases to one of the np orbitals of pnictinidenes is required for their isolation in the stable singlet state, which can prevent interaction with substrates. Dostál's N,C,N -pincer stibinidenes and bismuthinidenes represent landmark examples (Figure 1C, left),^[13] where the catalytic reactivity arises from the HOMO-orbital on the pnictinidene center, via either two- or single-electron processes.^[14] Paradigmatic examples that elude external Lewis-base stabilization are Bertrand's phosphino-nitrene (Figure 1C, right) and -phosphinidene,^[15] where the pnictinidene center in these two compounds form a double bond with the phosphino-ligand and no additional supporting ligands were required. Yet, in 2020, Schneider and Holthausen reported the characterization of a triplet platinum metallonitrene under the *in situ* single crystal X-ray diffraction (SC-XRD) condition or in solution at low temperatures (Figure 1D, left).^[16] Later, a palladium analogue was also reported and found application in photocatalytic amidation of aldehydes.^[17] Very recently, our group reported a triplet bismuthinidene^[18] by using a rigid and bulky hydrindacene ligand (Figure 1D, right), coined by Tamao group^[19] and modified by Tan group^[20]. In light of the prestigious candidacy of group 15 elements in redox catalysis,^[21] the genuine pnictinidenes, especially stibinidenes and bismuthinidenes, might unlock unexplored catalytic reactivity.

In our recent study on a triplet bismuthinidene, it was concluded that a remarkable effect of spin-orbit coupling (SOC) is responsible for its high stability and intriguing magnetic properties.^[18] During our investigations, it became obvious that the lighter group 15 analogue, stibinidene, embedded in the same scaffold would aid in understanding of such effect derived from relativity.^[22] To this end, we attempted the reduction of $M^{\text{Fluind}}\text{-SbCl}_2$ (**1**) and $^t\text{Bu-M}^{\text{Fluind}}\text{-SbBr}_2$ (**3**) with 2.1 equiv. Cp^*_2Co in THF or toluene at ambient temperature under argon (Figure 2A). Contrary to the bismuthinidene, air-sensitive dark purple and brown *distibenes* (**[2]₂** and **[4]₂**) were isolated in 69% and 66% yields. As revealed by SC-XRD analysis (Figure 2B),^[23] these two *distibenes* have $\text{Sb}=\text{Sb}$ bond lengths of 2.6731(3) and 2.7046(4) Å, being the latter amongst the longest $\text{Sb}=\text{Sb}$ bond lengths reported for *distibenes* thus far (Figure S64).^[11b,24] The influence of the rigidity and bulkiness of the M^{Fluind} backbones can be inferred from structural comparisons. Similar to the corresponding $[\text{M}^{\text{Fluind}}\text{-Bi}]_2$,^[18] the monomeric fragments of **[2]₂** and **[4]₂** dimerize by adopting an unusual geometry, as revealed by the torsion angles of $\text{C}_{\text{ipso}}\text{-Sb1-Sb2-C}_{\text{ipso}}$ (144.80° and 154.31°), as well as a non-parallel arrangement of the aryl planes of the ligand scaffolds. More importantly, the ligand backbones in **[2]₂** and **[4]₂** are bent to certain degree, suggesting a tension in these dimeric structures (Figure S75). The remarkable distortion in **[4]₂** renders all aromatic rings of the fluorenyl arms non-identical in the ^1H NMR (Figure S8), with significant signal broadening at elevated temperatures (Figure S9).

A. Synthesis of *distibenes* **[2]₂** and **[4]₂**



B. SC-XRDs of **[2]₂** and **[4]₂**

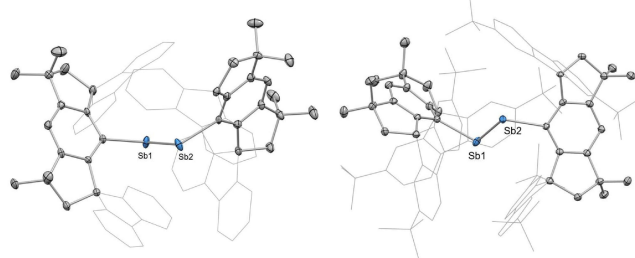


Figure 2. (A) Preparation of *distibenes* **[2]₂** and **[4]₂** by Cp^*_2Co reduction of the corresponding antimony(III) halides **1** and **3**; (B) The solid state structures of **[2]₂** (left) and **[4]₂** (right), with ellipsoids drawn at the 50% probability level, H atoms and *n*-pentane in **[4]₂** are omitted for clarity.

Some rotational processes can be observed by the EXSY correlations in ROESY NMR data (Figure S14). Despite the dramatic distortion in **[2]₂** and **[4]₂**, DOSY NMR data qualitatively suggest that these compounds remain dimeric in solution (Table S2).

Under 1.2 bar atmosphere of H_2 or ethylene and at 60°C , *distibene* **[4]₂** was converted into the corresponding antimony dihydride **5** or stibacyclopropane **6**, respectively (Figure 3A). In sharp contrast, no reactivity was observed for **[2]₂** under the same conditions. The activation of H_2 and ethylene by **[4]₂** is irreversible, and **5** and **6** were isolated in 85% and 80% yield, respectively. Their structures were determined by the SC-XRD analysis (Figure 3B), showcasing the Sb centers in a trigonal pyramidal geometry in both cases.^[23] In structure **5** (Figure 3B, left), two hydrogen atoms, H17A and H17B, could be clearly found in the Fourier difference map and freely refined on their positions (Figure S59) [Sb1-H17A : 1.54(2) Å, Sb1-H17B 1.63(2) Å, H17A-Sb1-H17B : $90.8(12)^\circ$]. Additionally, the hydride signal was found at 1.24 ppm in ^1H NMR, and a medium intense IR band at 1885 cm^{-1} can be attributed to the stretching vibration of the Sb-H bond (Figure S21), agreeing with the previous reports.^[25] Stibacyclopropane **6** (Figure 3B, right) represents a unique heavy pnictacyclopropane (from As to Bi). The C17A-C17B distance of 1.477(2) Å falls between that of a C=C bond in ethylene [$1.3142(3)\text{-}1.3180(5)$]^[26a] and the C-C bond in ethane [$1.532(2)\text{ Å}$]^[26b]. This bond length is noticeably longer than that in TM-ethylene coordination complexes,^[27] but is shorter than in the reported main-group cyclopropanes (eg. Al,^[28] Si,^[29] Ge^[30]; Figure S72). The protons in the stibacyclopropane core are diastereotopic ($\delta_{\text{H}} = -0.37$ and -0.66 ppm), showing

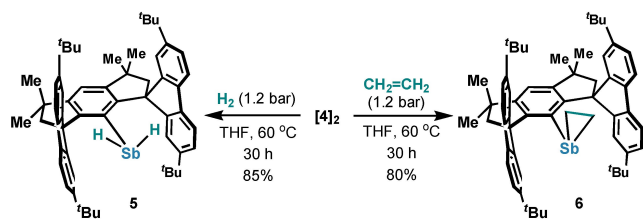
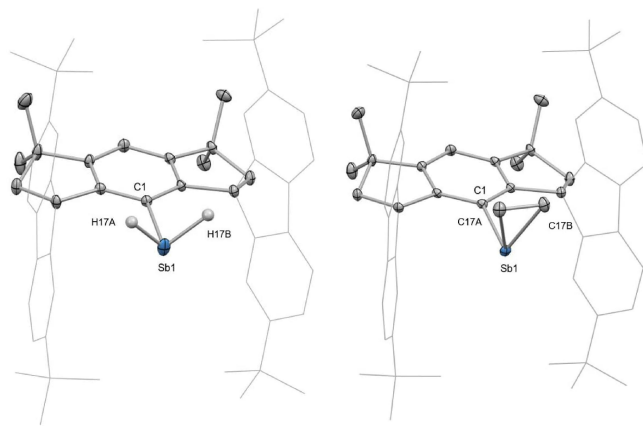
A. The reactivity of **[4]₂** toward H₂ and ethyleneB. SC-XRDs of **5** and **6**

Figure 3. (A) The formation of **5** and **6** by the reactions of **[4]₂** with H₂ and ethylene; (B) The solid state structures of **5** (left) and **6** (right), with ellipsoids drawn at the 50% probability level. H atoms (except H17A and H17B in **5**) and THF molecule in **6** are omitted for clarity. Selected bond lengths (Å) and angles (°), for **5**: Sb1–C1 2.1660(13), Sb1–H17A 1.54(2), Sb1–H17B 1.63(2), C1–Sb1–H17A 94.0(9), C1–Sb1–H17B 93.0(8), H17A–Sb1–H17B 90.8(12); for **6**: Sb1–C1 2.1776(12), Sb1–C17A 2.2001(14), Sb1–C17B 2.1942(14), C17A–C17B 1.477(2), C1–Sb1–C17A 99.85(5), C1–Sb1–C17B 98.29(5), C17A–Sb1–C17B 39.27(5), C17B–C17A–Sb1 70.15(8).

a characteristic AA'BB' spin system (Figure S28). The C_{2v} symmetric set of NMR signals of the ligand is in line with free rotation around the C1–Sb1 bond, while the inversion of the pyramidal Sb center is not observed at room temperature (as no exchange between the diastereotopic protons is observed in the NOESY NMR data, Figure S27). Although nitrene and certain phosphinidene transfer agents are able to react with unactivated olefins^[31] and *N,C,N*-stibinidenes can react with activated double bonds via element-ligand cooperation^[32], the reactivity of molecular pnictogen compounds with ethylene is unprecedented. The formation of complex **5** represents a unique oxidative addition of H₂ by a heavier element of the group 15.^[3b] In addition, the formation of monomeric **6** represents complimentary reactivity to a recent distibirane synthesis by Schulz group using distibenes.^[24h]

A close inspection of the SC-XRD structure of the surrounding ligand environment of **[4]₂** suggested that an approach of H₂ or ethylene to the Sb=Sb moiety is rather difficult. This led to a speculation that the reactions might proceed through a transient stibinidene, *in situ* generated by Sb=Sb dissociation (Figure 4A). In spite of the well-known ability of group 13 and 14 double bonds to undergo

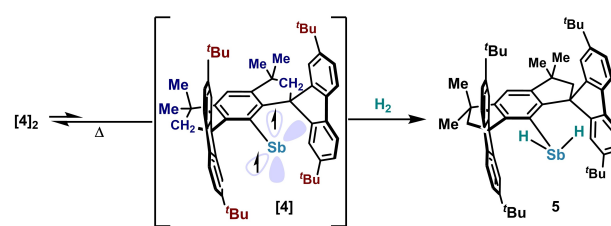
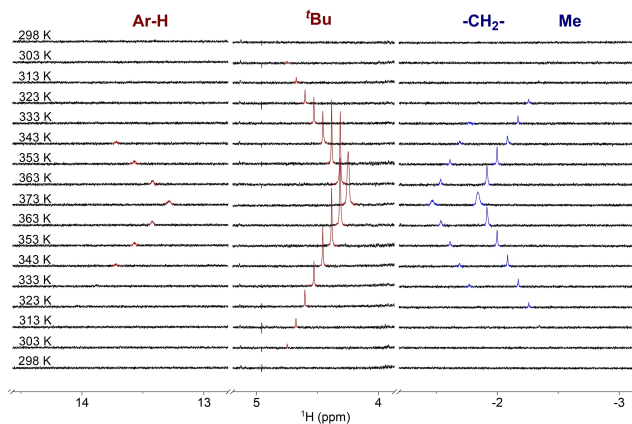
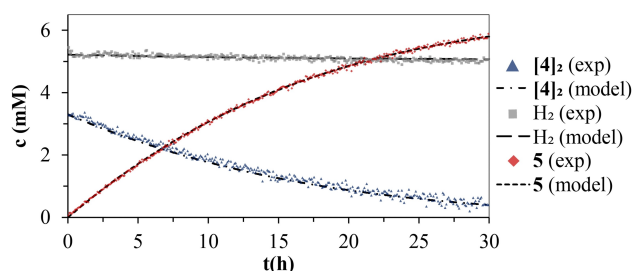
A. Oxidative addition of H₂ via transient stibinidene **[4]**B. Reversible formation of **[4]** from **[4]₂** - VT-NMR studyC. NMR concentration profile for H₂ oxidation addition of **[4]₂**

Figure 4. (A) Mechanistic proposal: reversible dissociation of **[4]₂** into the reactive stibinidene **[4]**; (B) VT NMR of **[4]₂** in THF-*d*₈ (3.30 mM) from 298 K to 373 K to 298 K; (C) NMR monitoring of **[4]₂** in THF-*d*₈ (3.30 mM) under 1.2 bar of H₂. For a complete picture of the mechanistic model, see Supporting Information.

dissociation^[6a] similar disconnection for Pn=Pn bonds has rarely been reported.^[33] To investigate this, VT NMR studies were conducted on a THF-*d*₈ solution of **[4]₂** (3.30 mM), ranging from 298 K to 373 K (Figure 4B). As the temperature increased, a minor species associated to **[4]** appeared and accumulated; while upon cooling (298 K), this species disappeared. Several cycles of temperature can be repeated without noticeable decomposition of **[4]₂**, thus confirming a reversible process. The intermediate **[4]** features paramagnetic ¹H NMR shifts (δ_H = 13.42, 4.31, –1.54 and –1.92 ppm at 363 K). The signals at 4.31, –1.54 and –1.92 ppm at 363 K can be assigned to ^tBu (H-16), CH₂ (H-7) and Me (H-6), based on the EXSY correlations with **[4]₂** in NOESY NMR data (Figure S32). Compared to our bismuthinidene, noticeably higher temperature-dependence of **[4]** was observed (Figure S34). This intriguing NMR behavior is in agreement with a triplet ground state species,

which has been observed for Holthausen and Schneider's triplet iridium imido and oxo compounds^[34] and our triplet bismuthinidene^[18]. Hence, we proposed that, **[4]** be the corresponding triplet stibinidene, which is in a slow and reversible equilibrium with distibene **[4]₂**. From van't Hoff analysis, the Gibbs free energy (ΔG^\ominus) of the dimerization at 333 K was estimated to be $-6.8 \pm 0.6 \text{ kcal} \cdot \text{mol}^{-1}$ ($\Delta H^\ominus = -25.6 \pm 0.7 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta S^\ominus = -56.3 \pm 2.0 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). In comparison, similar paramagnetic species in a THF-*d*₈ solution of **[2]₂** was not observed. Therefore we believe that the additional ^tBu group at C-11 increases ΔH^\ominus due to steric repulsion in the dimer **[4]₂**, which is also supported by the distorted structure and the elongated Sb=Sb bond in the solid state. The role of a monomeric intermediate **[4]** in the H₂ oxidative addition of **[4]₂** was also evaluated by NMR reaction monitoring at 333 K. Although the monomer **[4]** was not observed due to its low concentration, a kinetic model following the proposed mechanism was in excellent agreement with the observed experimental reaction profile (Figure 4C). Besides, in the presence of 2,3-dimethylbuta-1,3-diene, the corresponding cycloaddition product (**S2**) was obtained in high yields by heating **[4]₂** in THF to 60°C or reduction of **3** with Cp*₂Co. These results are consistent with the intermediacy of **[4]**, as previously also suggested by Tokitoh.^[33a,35]

In conclusion, the facile activation of two fundamental feedstock chemicals, H₂ and ethylene, by a sterically distorted distibene **[4]₂** is reported. Based on advanced NMR spectroscopic studies, *in situ* generation of a transient stibinidene (**[4]**) was proposed for the observed reactivity, which was previously unknown for group 15 systems. This study fills the gap of the canonical TM-like reactivity of group 15 species, thus adding to the known activation of H₂ and unactivated olefins by group 13 and 14 systems. Our work indicates that unlocking other elementary steps at the Sb centers might eventually lead to Sb^I/Sb^{III} redox catalytic systems, reminiscent of TM-catalyzed paradigms. Further investigations along this line are currently being conducted in our group.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Dihydrogen Activation · Distibene · Ethylene Activation · Main-Group Compounds · Stibinidene

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