

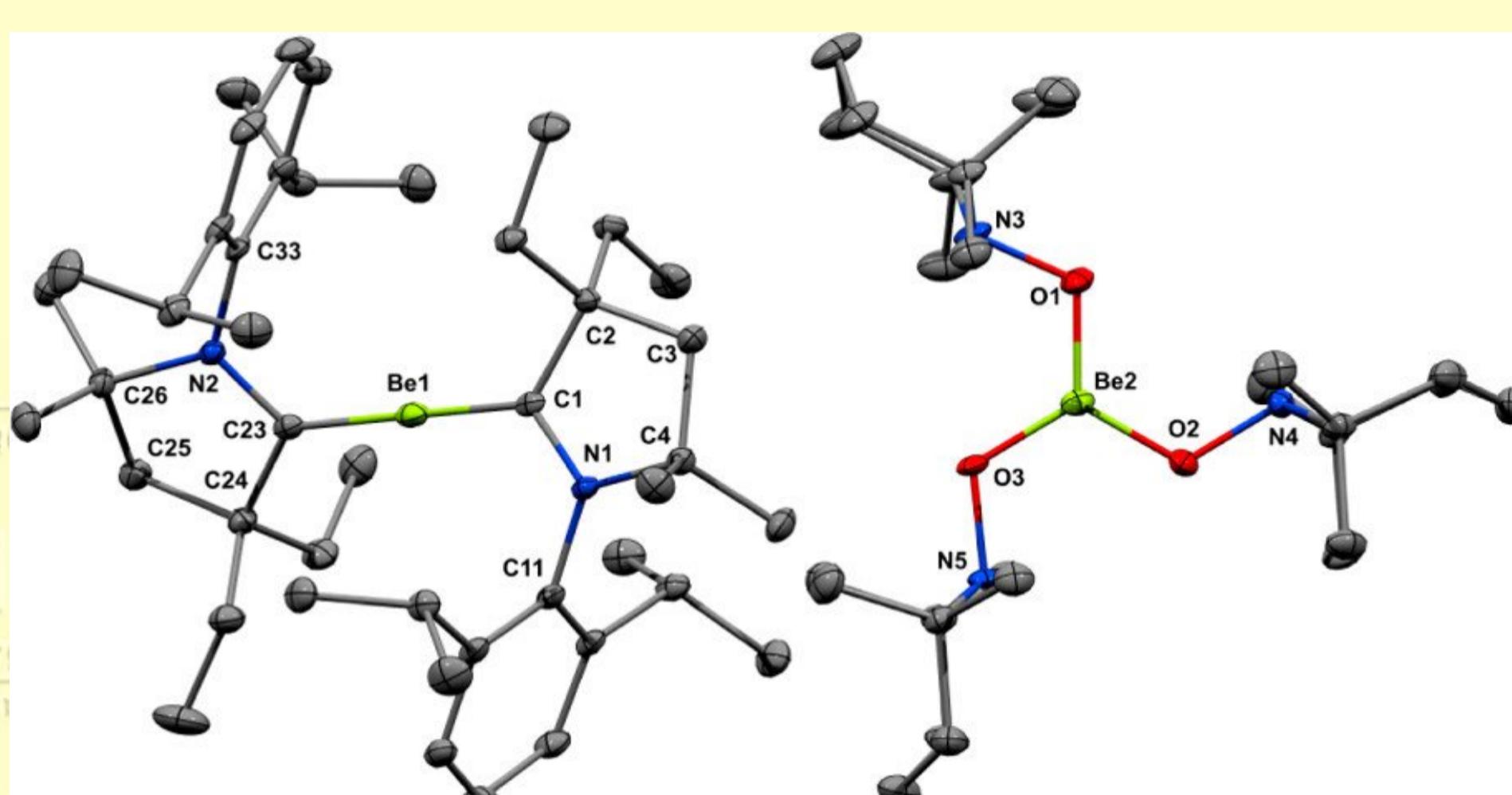
Notícies Inorgàniques

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<http://www.ub.edu/inorgani/dqi.htm>

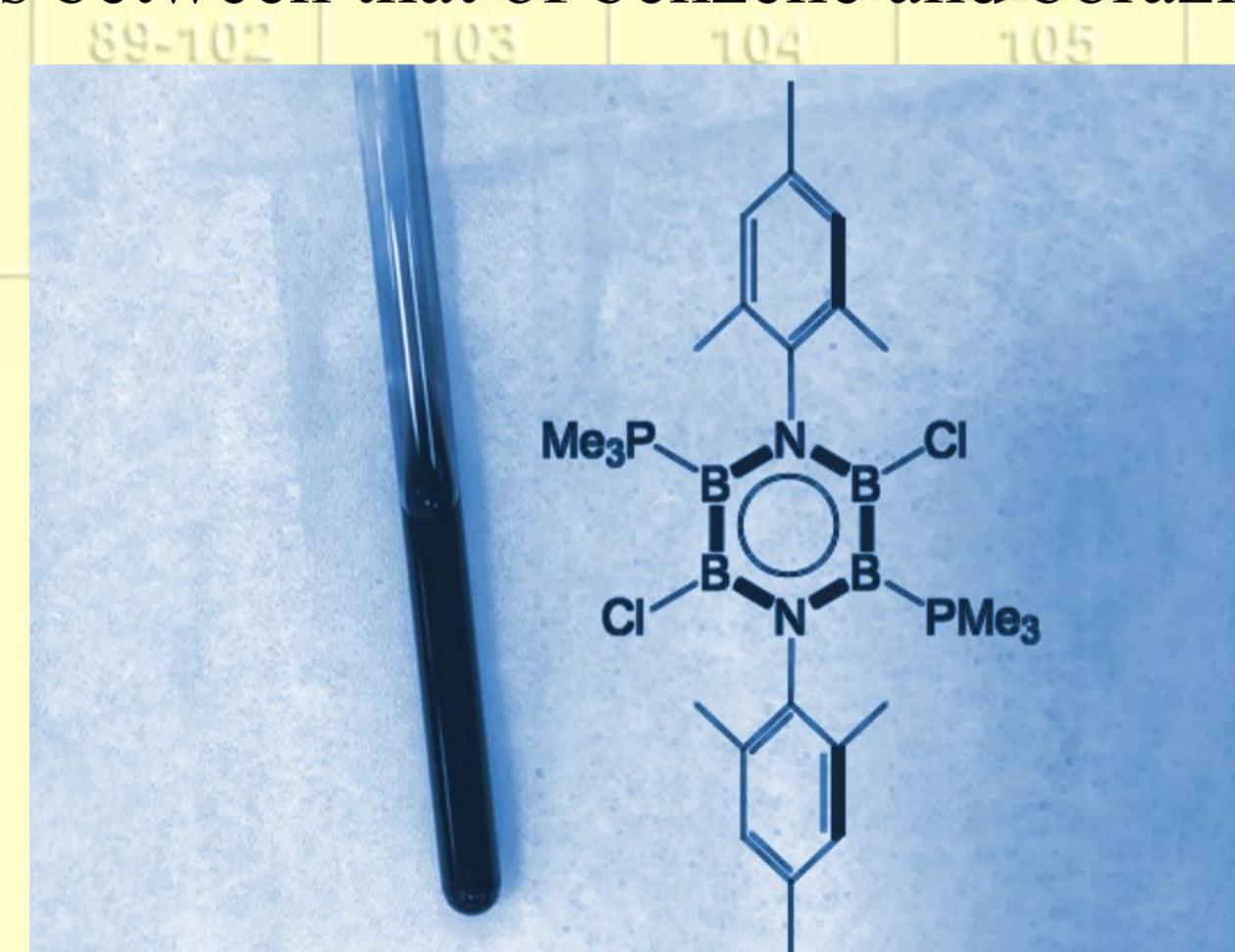
Beril·li(І) estable

Main-group elements in low oxidation states have the potential to carry out chemistry that's usually reserved for transition metals. For example, at low oxidation states, atoms like beryllium might be able to carry out oxidative addition and reductive elimination. But coming up with stable forms of such low-valent compounds is challenging. A team (R.J. Gilliard et al., *J. Am. Chem. Soc.*, **2020**; DOI: 10.1021/jacs.9b13777) has synthesized, isolated, and characterized the first known stable beryllium radical cation. Beryllium in compounds is usually in the +2 oxidation state, and the beryllium radical cation is in the +1 oxidation state. The new compounds have been obtained by oxidation of the Be(0) compound, reported in 2016 [vegeu: *Not. Inorg.* **15**, 76, setembre-2016], with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl). They isolated two compounds containing the same beryllium radical cation but different anions. Though the radical cation looks similar on paper to the neutral compound reported, the electronics are completely different because it's a radical cation; the C–Be–C angle in the radical cation is twisted and slightly bent, whereas it's linear in the neutral compound.



Un altre benzè inorgànic

The first inorganic version of benzene was reported almost a century ago. Borazine ($B_3N_3H_6$) contains a flat six-membered ring and a delocalized cloud of six π electrons but is only moderately aromatic. Since borazine's discovery, a handful of other inorganic benzenes have been created, none of which seem to have much aromaticity. Now, a cunningly modified ring of boron and nitrogen atoms is the closest inorganic analog of benzene yet created (R. Kinjo, et al., *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.201915790); 1,4,2,3,5,6-diazatetraborinine derivative that is much more benzene-like than its predecessors. Unlike borazine's alternating pattern of elements, diazatetraborinine's ring includes four boron atoms that sit in pairs and bond to either chlorine or trimethylphosphine. X-ray crystallography shows that the molecule is flat and has a perfectly hexagonal central ring, while nuclear magnetic resonance measurements demonstrate the magnetic deshielding effects typical of aromatic rings. Theoretical calculations show that the molecule's six π electrons are highly delocalized and that its aromaticity lies between that of benzene and borazine.



Grignards: una mica més de llum

Chemistry students and bench chemists alike rely on the Grignard reaction, a relatively simple way to make carbon-carbon bonds. But even though the reaction was first described 120 years ago, chemists have only now uncovered the details of its complex mechanism. In a Grignard reaction, a carbon-bonded magnesium halide adds to a carbonyl group to form an alcohol. Textbook explanations describe the reaction's mechanism as a nucleophilic addition or mention a possible radical mechanism. Now, a team (O. Eisenstein, et al., *J. Am. Chem. Soc.* **2020**; DOI: 10.1021/jacs.9b11829), using ab initio molecular dynamics simulations has shed light on the topic. They simulated the reactions of CH_3MgCl with acetaldehyde and fluorenone in tetrahydrofuran (THF), revealing a complicated mechanistic landscape involving competing nucleophilic and radical pathways that differ in energy by just 1 kcal. Although magnesium typically accepts only four ligands, they found that THF can act as a fifth, changing the metal's electronic symmetry and helping bonds break and form. The research shows that whichever pathway the reaction takes, it's not just the reactant and substrate that matter: The number and movements of attached solvent molecules play a supporting role in the mechanism.



Grafè bé de preu

Although graphene can be made in many ways, such as via organic synthesis, chemical-vapor deposition, or exfoliation from graphite, these methods don't produce large amounts of high-quality graphene. A team (J.M. Tour, et al., *Nature* **2020**, DOI: 10.1038/s41586-020-1938-0), discovered they could use flash Joule heating, a low-cost, energy-efficient process, to transform coal, food waste, and plastic into multigram quantities of high-quality graphene in less than 1 s. The process involves lightly compressing virtually any carbon-based material inside a quartz or ceramic tube between two electrodes. This apparatus is then zapped with a high-voltage electrical discharge from a capacitor bank, which heats the carbonaceous material to temperatures in excess of 3,000 K in less than 1 s. The process converts the amorphous carbon into graphene while all other chemicals escape as volatile material. Because the graphene is produced so quickly, its layers don't have time to align via electrostatics, making it easy to extract individual graphene sheets.



Breus

- Com és ben sabut la millor profilaxi contra el SARS-CoV-2, causant de la COVID-19, és rentar-se les mans. En els següents articles trobareu les bases químiques de l'eficàcia de l'aigua i el sabó (www.vilaweb.cat/noticies/coronavirus-mans-sabo-aigua-rentar/) i dels gels hidroalcohòlics (*C&EN*, **2020**, 98 (12), pp 24–25; March 30, 2020). Si voleu saber més del coronavirus, aquí hi trobareu alguns estudis estructurals (*C&EN*, **2020**, 98 (8), pp 7–7; February 24, 2020. *C&EN*, **2020**, 98 (10), pp 6–6; March 16, 2020).
- Des de fa més de 85 anys, diversos estudis han predit l'existència d'hidrogen metàl·lic, sense que cap d'ells hagi estat confirmat a hores d'ara. Recentment s'ha fet una altra proposta, però els resultats també són qüestionats, començant per si conté molècules o àtoms d'hidrogen (*Nature*, **2020**, DOI: 10.1038/s41586-019-1927-3).
- S'ha descrit un metallaborà pla que conté reni, $[ReB_4]^-$, amb aromaticitat de Möbius, (*J. Am. Chem. Soc.* **2020**. doi.org/10.1021/jacs.9b13417).

Avui recomanem

- El podcast cenm.ag/apollo13, de la sèrie Stereo Chemistry, que explica la història –amb final feliç– i la química que hi ha al darrera de l'explosió a la nau Apol·lo 13, camí de la lluna, ara tot just fa 50 anys.

L'element

L'element número 91, **protoactini**, fou identificat per primera vegada l'any 1931, per K. Fajans i O.H. Göhring –mitjançant l'isòtop ^{234}Pa , molt inestable– estudiant la descomposició radioactiva de l'urani, i li digueren *brevium*. Posteriorment, l'any 1918, Otto Han i Lisa Meitner –a Alemanya– i Frederic Soddy i John Cranston –a Anglaterra– van obtenir, independentment, l'isòtop ^{231}Pa , molt més estable ($t_{1/2} = 32.000$ anys). Li posaren *protoactinium*, ja que forma part de la cadena de descomposició radioactiva de l'urani i és el precursor de l'actini. L'any 1949 la IUPAC escurçà el nom a *protactinium*, nom que manté en l'actualitat l'anglès i altres llengües. Mendeléiev l'any 1871, predigué l'existència d'un element entre el tori i l'urani. En aquell moment no es coneixien als actínids, i el tori estava col·locat sota el zirconi en el grup IV, i l'urani sota el tungstè en el grup VI, deixant un posició en blanc, sota el tàntal en el grup V. És un dels elements naturals més rar i car. Es troba en minerals d'urani, com la pechblenda, en una proporció de entre 0.3 i 3 ppm, pràcticament només com ^{231}Pa . Contràriament als seus veïns, tori i urani, el protoactini no té cap aplicació, per la seva raresa, radioactivitat i toxicitat. Recentment, comença a emprar-se el ^{231}Pa , com a traçador en geologia i paleoceanografia; la relació $^{231}Pa/^{230}Th$, ha permès la datació de sediments de 175.000 anys d'antiguitat que ha millorat els estudis sobre la formació de minerals.

