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*Original*

Semi-Reduction of Internal Alkynes with Prototypical Subnanometric Metal Surfaces: Bridging Homogeneous and Heterogeneous Catalysis with Trinuclear All-Metal Aromatics / Monfredini, Anna; Santacroce, Veronica; Marchio', Luciano; Maggi, Raimondo; Bigi, Franca; Maestri, Giovanni; Malacria, Max. - In: ACS SUSTAINABLE CHEMISTRY & ENGINEERING. - ISSN 2168-0485. - 5:(2017), pp. 8205-8212. [10.1021/acssuschemeng.7b01847]

*Availability:*

This version is available at: 11381/2829561 since: 2017-10-10T14:51:36Z

*Publisher:*

American Chemical Society

*Published*

DOI:10.1021/acssuschemeng.7b01847

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13 August 2025

# Semi-Reduction of Internal Alkynes with Prototypical Subnanometric Metal Surfaces: Bridging Homogeneous and Heterogeneous Catalysis with Trinuclear All-Metal Aromatics

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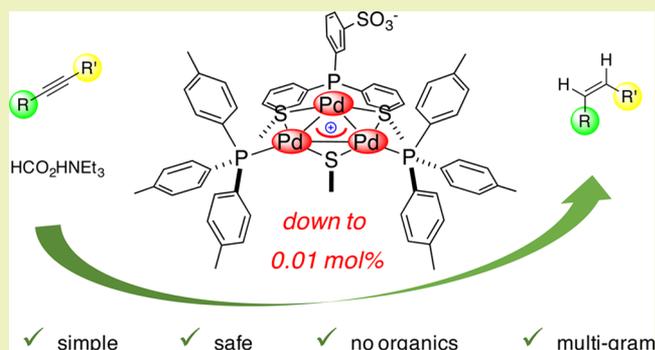
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## S Supporting Information

**ABSTRACT:** Suitably delocalized metal–metal bonds can stabilize a particular class of discrete trinuclear complexes that are the transition-metal counterparts of carbon-based aromatics. This chemical stability has pivoted the development of an advantageous catalytic method for the semireduction of internal alkynes under transfer hydrogenation condition. The reaction does not require any additional solvent and a simple workup delivers pure products. This combines with broad functional group tolerance, complete cis-selectivity and catalytic charges down to 100 ppm on multigram scale.

**KEYWORDS:** Catalysis, Alkynes, Transfer hydrogenation, Palladium, Aromaticity



## INTRODUCTION

All-metal aromatics are highly symmetric cyclic molecules that involve metal atoms in their cores and present delocalized molecular orbitals as regular aromatics.<sup>1,2</sup> Accordingly, this can represent a strategy to stabilize particular oligometallic species of discrete nuclearity, which in turn could potentially be of high interest for catalysis.<sup>3</sup> Depending on the coordination properties and formal oxidation states of their constituents, a metal-aromatic behavior has been observed in trinuclear complexes that have differently charged cores.<sup>4–7</sup> All these complexes are accompanied by the presence of a precise number of electrons and holes that are evenly delocalized in the prototypical metal surface represented by their kernel. Unfortunately, experimental studies on the promising opportunities<sup>8</sup> of these fascinating molecules are often restricted by synthetic limitations.<sup>9</sup> Wondering to explore this domain, we recently developed a simple synthetic route to access in one-pot from commercial reagents a family of  $M_3^+$  complexes incorporating palladium or platinum nuclei<sup>10</sup> upon observation of the metal aromatic character of  $Pd_3^+$  complexes<sup>11</sup> laboriously assembled from acylisothiouras.<sup>12</sup> This greatly simplified route enabled to elicit their promising activity and selectivity in the semireduction of internal alkynes to *cis*-alkenes under transfer hydrogenation conditions.<sup>13</sup> These reactions have vast synthetic interest and allow to avoid the use of explosive dihydrogen, as witnessed by

the variety of approaches developed in recent years.<sup>14–17</sup> Most research on homogeneous methods to afford *cis*-alkenes involves the use of mononuclear palladium complexes. State-of-the-art systems can indeed attain complete chemo and stereo control,<sup>18–25</sup> but their activity comes with an inherently low chemical stability, which often impose 1 mol % as the lower bound for catalytic charge. On the other hand, several elegant heterogeneous materials can trigger this reaction too, although this often comes at the cost of issues with catalyst preparation to minimize undesired over-reduction of the starting alkyne to alkane.<sup>26–30</sup>

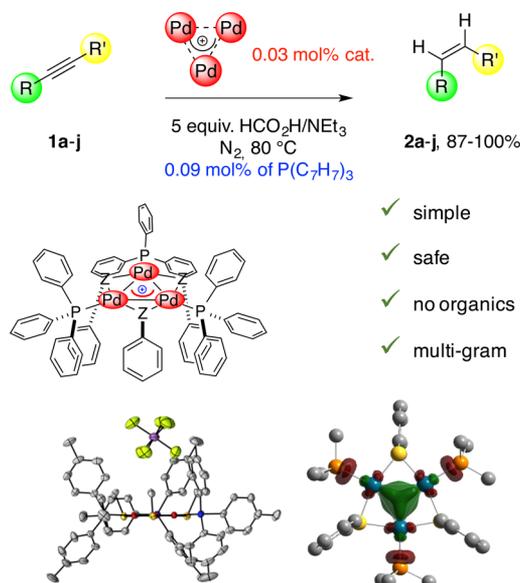
We report herein a simple catalytic method for the *cis*-selective semireduction of internal alkynes using triethylammonium formate as reductant (Scheme 1). Taking advantage of our studies on the mechanism of formation of all-metal aromatic  $Pd_3^+$  complexes,<sup>31</sup> we were able to develop an optimized catalyst that merges chemical stability for up to ten thousand turnovers with surgical *cis*-alkene selectivity. We exploited these complexes to perform reactions without any additional organics. This combines with a simple workup procedure to recover almost quantitatively desired products

Received: June 9, 2017

Revised: August 2, 2017

Published: August 10, 2017

**Scheme 1. Catalytic Application of Metal-Aromatic Pd<sub>3</sub><sup>+</sup> Complexes for Semi-reduction of Internal Alkynes (Top) and the X-ray Structure of These Complexes and Their Delocalized HOMO (Bottom)**



minimizing formation of wastes and catalyst consumption. Taken together with further mechanistic probes, these results highlight the potential of tailor-made stable metal–metal bonds as original strategy to develop greener and more sustainable alternatives for synthesis involving transition-metal based catalysts.

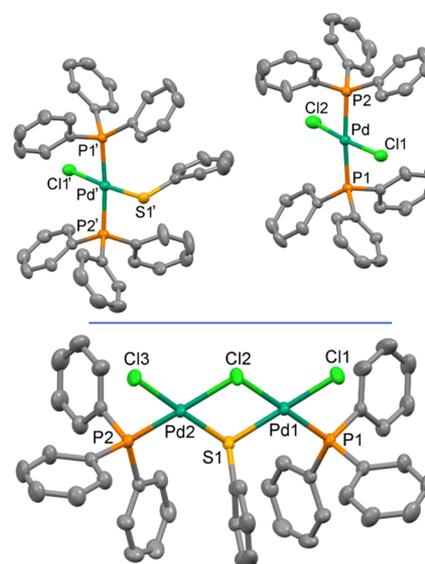
## EXPERIMENTAL DETAILS

Reagents were purchased from commercial sources and used as received. Liquids were degassed by bubbling N<sub>2</sub> for at least 20 min prior to use. Reactions and filtrations were carried out under N<sub>2</sub> using standard Schlenk technique. Trinuclear complexes were prepared in one step from commercial reagents. Pd(dba)<sub>2</sub> (115 mg, 0.2 mmol, 1.0 equiv), 3-(diphenylphosphino)benzenesulfonic acid sodium salt (24 mg, 0.066 mmol, 0.33 equiv), and tri(*p*-tolyl)phosphine (40 mg, 0.132 mmol, 0.66 equiv) were sequentially added to a 50 mL Schlenk, which then underwent at least three vacuum/N<sub>2</sub> cycles. Twenty milliliters of freshly degassed CHCl<sub>3</sub> and dimethyl disulfide (9 μL, 0.1 mmol, 0.5 equiv) were sequentially syringed under N<sub>2</sub>, and the mixture was stirred at room temperature for 3 h. Traces of black metals were removed via Schlenk filtration through a Celite pad and volatiles were removed under vacuum. The solid residue was purified by CHCl<sub>3</sub>/hexane washings (1/60 v/v, 6 × 30 mL), affording the pure cluster as an orange solid (71 mg, 76%). For catalytic semireductions, the trinuclear complex (2.0 mg, 0.0014 mmol, 0.03 mol %) and tri(*p*-tolylphosphine) (1.3 mg, 0.0042 mmol, 0.09 mol %) were introduced in a Schlenk, which then underwent at least three vacuum/N<sub>2</sub> cycles. Freshly degassed triethylamine (3.3 mL, 23.6 mmol, 5 equiv) and formic acid (0.9 mL, 23.6 mmol, 5 equiv) were then syringed under N<sub>2</sub>, and the mixture was stirred for few minutes at room temperature. The desired alkyne (4.7 mmol, 1 equiv) was then added and the resulting mixture warmed at 80 °C under stirring. Reagents do not require any anhydrication. Conversion and selectivity were monitored by <sup>1</sup>H NMR. Upon alkyne consumption, the crude mixture was adsorbed over a short pad of silica and washed with the minimum amount of solvent to recover pure *cis*-alkenes. CCDC 1542232 and 1542233 contain the crystallographic data for complexes II and III, respectively.

## RESULTS AND DISCUSSION

During our preliminary studies,<sup>31</sup> we noticed that the solvent played a role in the reaction leading to the desired complex. A better understanding of these phenomena could prove determinant to achieve a clear picture at the molecular level on factors governing the assembly of small metal surfaces and higher nuclearity aggregates, such as small nanoclusters. We performed additional experiments to gain insights on the mechanism of formation of Pd<sub>3</sub><sup>+</sup> complexes, seeking to understand clues that would be pivotal to future incorporation of different nuclei and organic fragments.

Addition of a 2-fold excess of phosphine to our standard method for the synthesis of Pd<sub>3</sub><sup>+</sup> clusters inhibited their formation. In this case it has been possible to isolate and characterize both a mono- and dimeric Pd(II) complexes that could give insights on intermediates of the reaction leading to Pd<sub>3</sub><sup>+</sup> clusters (Figure 1). In [Pd(PPh<sub>3</sub>)<sub>2</sub>(PhS)Cl][Pd-

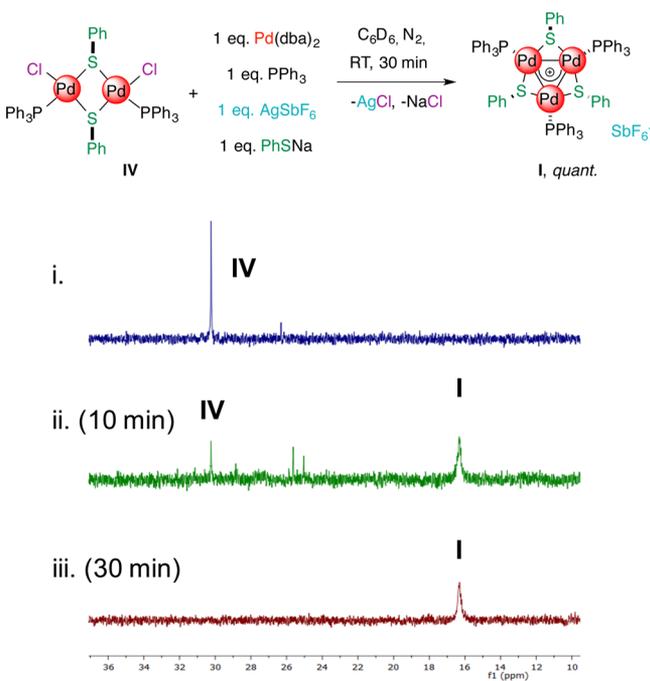


**Figure 1.** Molecular structure of [Pd(PPh<sub>3</sub>)<sub>2</sub>(PhS)Cl][Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] II (top) and of [Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(PhS)Cl<sub>3</sub>]·CHCl<sub>3</sub> III (bottom) with thermal ellipsoids depicted at the 30% probability level. The CHCl<sub>3</sub> molecule and hydrogen atoms were removed for clarity.

(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (II) the asymmetric unit comprises two cocrystallized square planar Pd(II) complexes, namely [Pd-(PPh<sub>3</sub>)<sub>2</sub>(PhS)Cl] and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], (Figure 1, top). In both systems, the phosphorus atoms are in trans positions. In one complex molecule, a thiolate group is in trans to the chloride anion, whereas the second complex is more symmetric since two chloride anions complete the first metal coordination sphere (selected bond distances and angles in Supporting Information (SI)). The related dimer [Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(PhS)Cl<sub>3</sub>]·CHCl<sub>3</sub> (III) exhibits a symmetric dinuclear structure (Figure 1, bottom), in which the Pd atoms show a square planar geometry with a terminal chloride anion a terminal PPh<sub>3</sub> group, a bridging thiolate, and a bridging chloride anion. The Pd–Cl<sub>bridge</sub> bond distance are approximately 0.1 Å longer than the Pd–Cl<sub>terminal</sub> ones. The molecular structure is analogous to similar dinuclear systems with bridging thiolates and chloride anions.<sup>32–34</sup> Nevertheless, in the present case, the assembly involving the metal coordination is planar, at variance with the structure reported in the literature where the two coordination planes are not coplanar. Both complexes represent the proof

that the chlorinated solvent is actually a reagent, confirming the preliminary hypothesis that the oxidation of Pd(0) likely occurs via single electron transfers involving both the disulfide and a chlorinated solvent with suitable C–H BDE.<sup>35,36</sup>

We wondered whether the delocalized three-centers-two-electrons bond that is peculiar of all-metal aromatic Pd<sub>3</sub><sup>+</sup> could result from the formal addition of a Pd(0) fragment onto a coordinatively unsaturated Pd(II) dimer. This would represent a strategy to assemble trinuclear all-metal aromatics complementary to those reported in the literature, which rely on the addition of an oxidized mononuclear complex (such as Au(I) or Zn(II) fragments) on a reduced metal dimer that formally provides the two electrons to the metal-aromatic complex (either Au(0) or Zn(I), respectively).<sup>5,6</sup> In order to check if dimeric Pd(II) complex IV<sup>37</sup> represents an intermediate in the reaction leading to Pd<sub>3</sub><sup>+</sup> species, we mixed it with 1 equiv of Pd(dba)<sub>2</sub> in a nonchlorinated redox-neutral solvent.<sup>31</sup> Addition of 1 equiv of triphenylphosphine, sodium thiolate and silver salt in benzene at RT enable complete conversion of the dimer within 30 min, as followed via multinuclear NMR analyses. Figure 2 shows the <sup>31</sup>P spectra of this reaction. The reagent



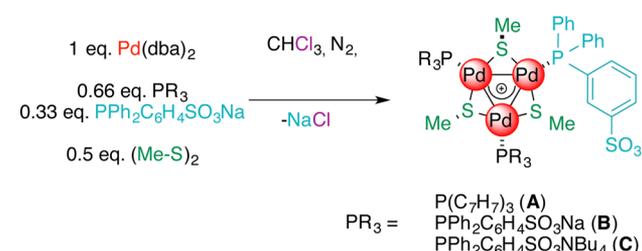
**Figure 2.** Formation of metal-aromatic Pd<sub>3</sub><sup>+</sup> complex I from a Pd(II) dimer and Pd(0).

(blue line) reacts swiftly and the diagnostic broad peak of trinuclear complex I becomes the main species already after 10 min (green line). At the end of the reaction a single resonance remains, witnessing the selectivity of the process (red line). <sup>1</sup>H NMR confirmed this trend (spectra in SI).

This result shows that trinuclear all-metal aromatics can be accessed through addition on oxidized dimers of mononuclear fragments that can formally undergo two-electrons oxidation to access trinuclear complexes with delocalized three-center-two-electrons bonds. This is complementary to existing literature<sup>4–7</sup> and might thus represent a valuable addition for future developments. The assembly of novel discrete clusters with aromatic metal–metal bonds could indeed extend the panel of readily available prototypical metal surfaces.

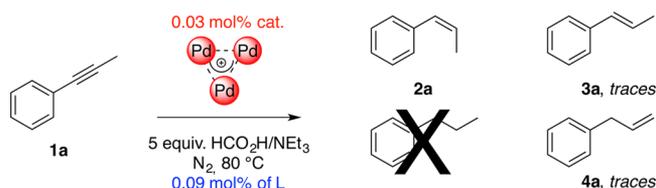
These platforms can show interest catalytic applications, as witnessed by the selectivity toward *cis*-alkenes displayed by highly symmetric Pd<sub>3</sub><sup>+</sup> complex I in the semireduction of internal alkynes under transfer-hydrogenation conditions, even despite large molar excess of hydrogen donor. Among a variety of substrates, reactions never displayed the least trace of over-reduction, namely alkane formation.<sup>13</sup> Intrigued by this unique selectivity, we developed a second generation catalytic system that works without additional solvents, enabling in turn to minimize both formation of wastes and the catalytic charge. These features are unique among mononuclear homogeneous catalysts, and proved possible exploiting zwitterionic Pd<sub>3</sub><sup>+</sup> complex A.<sup>31</sup> Complexes A–C were thus synthesized (Scheme 2) and used as tool to further study the properties of these clusters as catalyst for the semireduction of internal alkynes to *cis*-alkenes.

### Scheme 2. Synthesis of Catalysts Used in This Study



Under optimized conditions, phenylpropyne can be converted almost quantitatively to *cis*-alkene **2a** in few hours consuming as low as 0.03 mol % of catalyst in combination with 0.09 mol % of an additional phosphinic ligands. This proved determinant to minimize the odds of complex decomposition when the substrate concentration faded, as determined through UV–vis titrations. To check the generality of this trend, we repeated our model reactions with various combination of complexes A–C and additional ligands. Results are summarized in Table 1.

**Table 1.** Screening of Catalyst for Semi-reduction of Phenylpropyne<sup>a</sup>



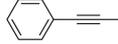
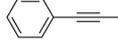
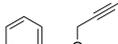
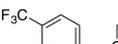
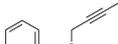
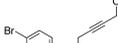
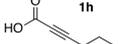
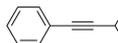
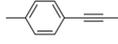
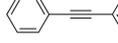
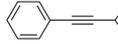
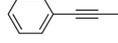
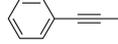
entry	Pd complex	L	<i>t</i> (h) <sup>b</sup>	conv. 1a (%)	sel. 2a (%) <sup>c</sup>
1	Pd <sub>3</sub> <sup>+</sup> A	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	6	quant.	98
2	Pd <sub>3</sub> <sup>+</sup> A	C <sub>6</sub> H <sub>5</sub> -SNa	5	36	100
3	Pd <sub>3</sub> <sup>+</sup> B	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	6	quant.	94
4	Pd <sub>3</sub> <sup>+</sup> B	P(Ph) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	6	94	97
5	Pd <sub>3</sub> <sup>+</sup> C	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	8	96	96
6	Pd II	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	8	72	92
7	Pd <sub>2</sub> III	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	8	24	98
8	Pd <sub>2</sub> IV	P(4-Me-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	6	45	94

<sup>a</sup>Reaction conditions: **1a** (4.7 mmol, 1 equiv), Pd<sub>3</sub><sup>+</sup> complex A (2 mg, 0.0003 equiv), trip-tolylphosphine (1.3 mg, 0.0009 equiv), NET<sub>3</sub> (3.3 mL, 5 equiv) HCO<sub>2</sub>H (0.9 mL, 5 equiv), under N<sub>2</sub> at 80 °C. <sup>b</sup>Time to reach full conversion. <sup>c</sup>Determined by <sup>1</sup>H NMR.

The combination of complex A and tritylphosphine provided the best result (entry 1). The reagent was fully consumed upon warming the mixture for 6 h, delivering 98% of *cis*-alkene **2a**. Traces of *trans*-product **3a** and allylbenzene (**4a**) were barely visible with GC analyses (1% each). Replacement of the additional phosphine with a thiolate quenched reactivity (entry 2) and conversion remained stuck at 36% upon the first 5 h. This result suggest that a phosphine could stabilize the complex in the reducing medium while an excess of thiolate did not have a meaningful effect to this end. On the contrary, the apparent rate of the semireduction slows down, suggesting that this species could compete with formate anions. Decoration of the Pd<sub>3</sub><sup>+</sup> kernel with three anionic phosphines (complex B, entry 3) provided **2a** in 94% yield upon 6 h, showing therefore a limited erosion of the selectivity. Replacing the added neutral phosphine with the sodium salt of a sulfonated one increased the selectivity to 97% (entry 4), although conversion ceased at 94%. Wondering whether this might be due to solubility issues, we prepared complex C in which alkali counteranions were replaced by tetrabutylammonium ones. The resulting complex is soluble even in strongly apolar media, but did not provide a further boost of either activity or selectivity (entry 5). We then tested monomeric complex II (entry 6). Under best conditions, alkyne consumption ended upon 8 h (72% conversion), delivering *cis*-alkene with 92% selectivity. Dinuclear complexes III and IV followed suit (entries 7–8). Conversion ceased at 24% and 45% respectively. No further changes were observed prolonging warming for 24 additional hours. During these experiments (entries 6–8), black metal colloids started forming from the beginning despite a high concentration of substrate. Selectivity remained high in all cases, suggesting that these heterogeneous aggregates are fairly active at most either for alkyne semireduction or alkene isomerization under these conditions (vide infra). Taken together, these results confirm that zwitterionic Pd<sub>3</sub><sup>+</sup> complexes with delocalized metal–metal bonds are efficient catalyst for solvent-free semireduction of internal alkynes to *cis*-alkenes. We thus tested the scope of this reaction (Table 2).

In general, an ample mix of internal alkynes can be converted to the corresponding *cis*-alkene **2** in excellent to quantitative yields. Beside **2a** (entry 1), hindrance close to the triple bond requires longer reaction time to quantitatively convert the alkyne to alkenes **2–3b** (entry 2, in 90/10 ratio upon 15 h). This represent nonetheless an improvement over first generation cationic complexes, which delivered a 78/21/1 ratio of **2b–4b** upon 24 h.<sup>13</sup> Various propargylic ethers can be smoothly converted, portraying the tolerance to benzylic substituents (entries 3–4, 93% and 96% yields of **2c** and **2d** respectively). Similarly, substitution of butyndiol with various fragments enabled to access *cis*-diethers **2e–2g** quantitatively. Remarkably, the C–Br bonds of **1g** remain untouched, leaving a valuable handle for further functionalization. All these ethers present propargylic C–H bonds that could easily undergo homolytic cleavage. To perform reactions with these low catalyst loadings (0.03 mol %) these reagents require purification on silica gel or distillation prior to use. This is no longer required using higher loadings instead (1 mol %), indicating that the purity of reagents can become an important issue to preserve chemical stability over several thousand turnovers. Substituted propiolic acids could be employed (entry 8, 100%), showing that conjugated carboxylic acids did not hamper the reaction. Diarylacetylenes, including heteroaryl ones followed suit (**2i–l**, entries 9–12). Both 3- and 2-pyridyl

Table 2. Reaction Scope<sup>a</sup>


Entry	Alkyne	t (h) <sup>a</sup>	Sel. <b>2</b> (%) <sup>b</sup>	Yield <sup>c</sup>
1		6	98	98
2		15	90	99 <sup>d</sup>
3		6	93	99 <sup>d</sup>
4		4	96	99 <sup>d</sup>
5 <sup>e</sup>		13	100	94
6		5	100	99
7		5	100	99
8		6	100	99
9		3	100	99
10 <sup>f</sup>		7	100	87
11 <sup>g</sup>		15	100	95
12		6	100	99
13		4	100	99
14		6	94	85 <sup>d</sup>

<sup>a</sup>Time to reach full conversion of **1**. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Products **2** were purified by filtration on a silica pad eluting with 5 mL of solvent. <sup>d</sup>Isolated with traces of *trans*-olefin **3**. <sup>e</sup>Conversion ceased at 95%, recovered with residual donor for its volatility. <sup>f</sup>Conversion ceased at 87%. <sup>g</sup>Conversion ceased at 95%. Reaction conditions as in Table 1.

fragments afforded exclusively the *cis*-product. Conversion was stuck at 87% with the former (entry 10), while the latter delivered 95% of **2k** upon 15 h. Thiophene rings are similarly tolerated, as witnessed by the smooth semireduction of **1l** that gave quantitatively **2l** in 6 h. Hindered propargylic alcohols are efficient reagents too (**1m–n**, entries 13–14). Taken together these results shows that present complex displays chemical stability for at least 3300 turnovers over an ample mix of functionalized substrates, combined with high activity and often complete selectivity.

In all these cases reactions mixtures remain clean solutions without traces of black metal colloids until complete alkyne

conversion. This feature is obtained thanks to the addition of the extra phosphine and enables to quench undesired isomerization of *cis*-alkenes, which was instead partially observed with first generation catalysts (1 mol % in THF).<sup>13</sup> The partial decomposition of the latter can be monitored via ESI-MS analyses on samples collected from reaction mixtures at regular intervals, which present a fading ionic concentration of Pd<sub>3</sub><sup>+</sup> complex through time. We reasoned that this partial decomposition might generate palladium species that are the actual isomerization catalyst responsible for the formation of isomerized olefins and which might have different nuclearity. This can be consistent with the observation of 10% of **3b** (Table 2, entry 2) employing the least reactive alkyne of the series. In this case, the prolonged warming has likely caused partial complex decomposition. Addition of a phosphinic ligand (3 equiv. compared to **A**) prevented formation of *trans*- and isomerized alkenes, delivering 98% of **2a** upon 4 h in THF. The stability of **A** can be proved by UV-vis analyses on reaction samples collected at regular intervals. The diagnostic bands of complex **A**, between 350 and 450 nm,<sup>31</sup> did not change throughout the reaction. This means that the complex is stable under reaction conditions and that its average concentration did not change significantly until **1a** is completely semireduced to **2a**. On the other hand, the reductive reaction environment can cause partial decomposition through time of complex **A**. This is clearly witnessed by visible formation of black colloids prolonging warming upon full alkyne conversion. Many palladium species are able to reduce alkynes under transfer-hydrogenation conditions.<sup>38–40</sup> For comparison, commercial Pd(*dba*)<sub>2</sub> (1 mol %) becomes no longer active upon 24 h warming, delivering 82% conversion of **1a** and 13% alkane. Addition of ligands as phosphines and thiolates in semi-reduction with Pd<sub>3</sub><sup>+</sup> complexes has an impact on the formation of undesired products (Table 1). Addition of 10 equiv of phosphine compared to **A** slows the reaction (24 h) and **2a** exclusively forms (98%). Phosphines and thiolates can become efficient poisons, especially for higher nuclearity aggregates whose surface to volume ratio sinks compared to mononuclear complexes and discrete clusters. Thanks to this, stoichiometric amounts can already quench reactivity.<sup>40</sup> Performing the Sheldon hot filtration test by pouring the crude on a short Celite pad in a Schlenk filter, did not hamper the model reaction of **1a** and conversion of the latter proceeded linearly. Taken together, these results suggest that the catalyst of present reactions is a homogeneous species.

The aromatic metal–metal bond of **A** should grant him a relative stabilization in respect to nucleation processes.<sup>1–8</sup> We cannot rule out that the trinuclear complex can enter equilibria with species of either lower or higher nuclearity. They could actually be the most active palladium particles in reaction mixtures and clear-cut identification of the actual catalyst is often very difficult.<sup>38,39</sup>

Figure 3 present the series of <sup>1</sup>H NMR spectra collected during the semireduction of **1f** (purple line). Beside triethylammonium formate, no other organic except **1f** and **2f** appears throughout the experiment. Copies of <sup>1</sup>H NMR spectra clearly present this outcome, comparing samples collected upon 1 (blue line), 2 (green), 3 (yellow), and 5 h respectively (red). It is worth noting that upon full conversion of alkyne **1f** (violet line), the crude mixture is essentially a pure solution of *cis*-alkene **2f**.

These results confirm the hypothesis that Pd<sub>3</sub><sup>+</sup> complexes **A** do not catalyze any alkene isomerization. To further check this

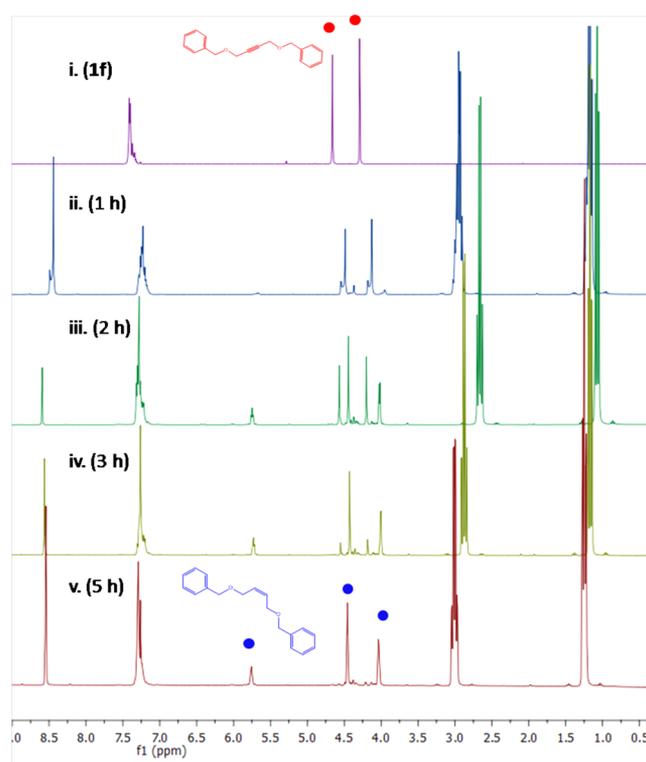
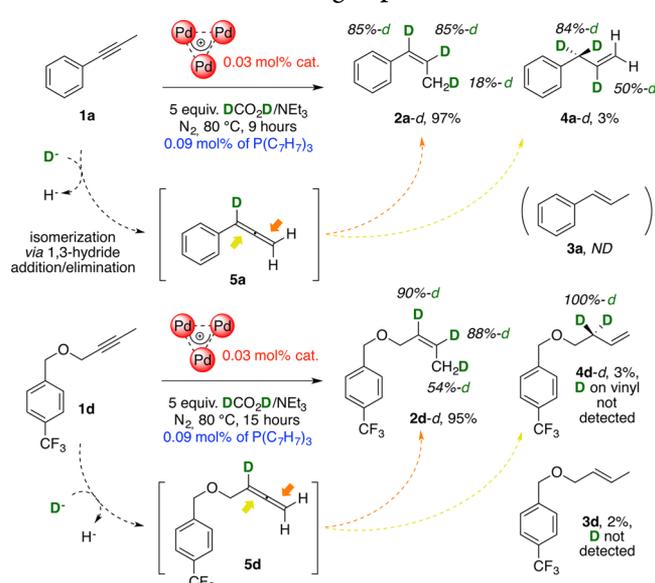


Figure 3. Quantitative conversion of alkyne **1f** to *cis*-alkene **2f** through time.

feature, we performed deuterium labeling experiments. Using first generation cationic complexes without addition phosphine ligands, deuterium was nonselectively retrieved on the three nonaromatic carbons of **2a** in a roughly 2:2:1 ratio with DCOOD as hydride source. Traces of **3a** and **4a** (3% and 4% respectively) behave similarly. In this case, 24 h were necessary to consume **1a**, while the reaction was completed within 10 h using unlabeled formic acid. This is consistent with a relevant primary kinetic isotopic effect and, in turn, likely caused partial complex decomposition over the longer experiment, which we speculate as the root of both double bond isomerization and H/D scramblings.<sup>41</sup> Repeating this model reaction with zwitterionic complexes under solvent-free conditions enabled the consumption of **1a** within 9 h (Scheme 3). This combines with a higher selectivity for *cis*-alkene (**2a-d**, 97%). The *trans*-alkene **3a** no longer forms, and **4a-d** is observed in traces (3%). Regarding deuterium incorporation, an average of two D nuclei for each molecule is observed. In particular, significant incorporation on the terminal carbon of **2a** is observed (18%). Furthermore, the methylene group of **4a** is almost completely deuterated (84%). These findings have no precedent<sup>18–25</sup> among homogeneous Pd-based catalysts and suggest that **1a** can isomerize to phenylallene **5a**, via sequential 1,3-hydride addition/elimination during the reaction.<sup>42–44</sup> These results support the hypothesis that Pd<sub>3</sub><sup>+</sup> complexes **A** can catalyze both alkyne/allene isomerization and reduction<sup>45</sup> and neither alkene isomerization nor over-reduction. We could not rule out at present stage that this distribution of olefins **2a** and **4a** stems from hydrogenolysis of a palladium allyl intermediate, which would favor formation of the aryl-conjugated *cis*-olefin. We repeated deuterium labeling experiments on alkyne **1d**, which features a nonconjugated triple bond flanked by a methyl and a methylene substituted by an

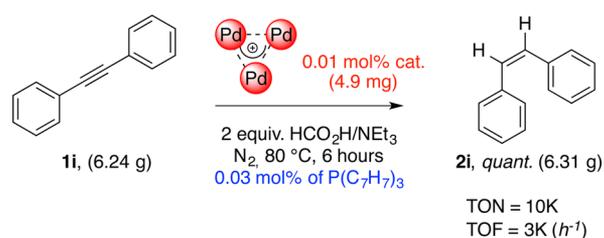
## Scheme 3. Deuterium-Labeling Experiments



electron-donating oxygen (lower part of Scheme 3, copies of NMR spectra in SI). Full conversion occurred upon 15 h, confirming the impact of primary kinetic isotope effect. Products 2–4d were retrieved in a 95:2:3 ratio. The amount of D on the terminal methyl of 2d was 58%, thus even more than the 18% value observed in 2a. We were unable to quantify deuterium incorporation on 3d. The allylic methylene of isomerized olefin 4d is fully deuterated. None of 2–4d displayed deuterium incorporation on the ethereal methylene of 1d. This could correlate with an unfavorable hydride 1,3-addition/elimination leading to an allene different from 5d caused by the presence of the electron-donating ethereal oxygen.

Isomerization of 1–5 liberates a hydride. This could in principle contribute to catalyst decomposition, possibly altering its nuclearity and eventually leading to visible black metal colloids in the reductive reaction medium. Reasoning that 1,3-hydride addition/elimination on internal alkynes requires a propargylic C–H group, we wondered whether it would have been possible to further push reaction conditions using diphenylacetylene 1i as model.

Scheme 4 presents the summary of a brief dedicated optimization (further details in SI). It is possible to keep a

Scheme 4. Multi-gram Scale Synthesis of *cis*-Stilbene (2i) with 0.01 mol % of Pd<sub>3</sub><sup>+</sup> Catalyst

practical reaction times (6 h) and complete selectivity for *cis*-alkene 2i reducing both the molar excess of hydrogen donor (down to 2 equiv) and the catalyst amount (0.01 mol %). This minimizes the consumption of chemicals en route to pure product.<sup>46–51</sup> The reaction can be performed on multigram

scale (6.24 g, 35 mmol) consuming few milligrams of catalyst and phosphine (4.9 and 3.2 mg respectively) and 10.3 g of hydrogen donor.<sup>52</sup> Pure 2i can be quantitatively recovered (6.31 g) pouring the crude on short silica pad (4.0 g) and eluting with 12.5 g of pentane (20 mL). This clearly highlights the synthetic viability of the method.<sup>53</sup> Although Pd<sub>3</sub><sup>+</sup> complexes can be purified by flash chromatography on silica gel,<sup>10</sup> this recovery method is not feasible with present multigram-scale reactions. This approach would also yield a large increase of the amount of wastes. With present simple purification, palladium remains mostly adsorbed on the short silica pad. On the other hand, even assuming that it quantitatively contaminates 2i, this would result in a heavy metal content equal to 174 ppm only.

Table 3 presents a selection of calculated green metrics comparing this procedure with four representative ones, which

Table 3. Calculated Green Metrics

entry	yield (%)	E-factor	PMI
this procedure	100	4.24	5.24
Furstner procedure <sup>19</sup>	82	45.8	46.8
Elsevier procedure <sup>21</sup>	99	31.7	32.7
Copéret procedure <sup>29</sup>	99	24.4	25.5
Studer procedure <sup>30</sup>	99	52.9	53.9

make use of organic solvents and require workup or chromatographic purifications. We calculate E-factor and PMI index to quantify a possible benefit coming from the absence of unnecessary organics in our model reaction combined with its simple purification methods. The use of solvents, workup extractions, or column chromatography usually results in values above 20 even for most efficient methods, either based on homogeneous catalysts<sup>18–25</sup> or heterogeneous ones.<sup>26–30</sup> On the contrary, a meaningful enhancement on viability is found in this case, E-factor, and PMI being 4.24 and 5.24, respectively. These results further suggest the promising role of small metal surfaces as tool to devise new sustainable catalytic methods.

## CONCLUSIONS

We reported a study clarifying the mechanism of formation of all-metal aromatic M<sub>3</sub><sup>+</sup> complexes. This enabled to devise an alternative route for the assembly of these prototypical noble-metal surfaces. These frameworks can be tailored at the molecular level, like most homogeneous catalysts. Similarly, remarkable selectivity is shared too. Internal alkynes can be easily converted under transfer hydrogenation conditions to the corresponding *cis*-alkenes without any unnecessary organics. This is accompanied by chemical stability for several thousand turnovers, which is often an exclusive feature of heterogeneous materials granted however by nanometric metal aggregates at least. Although implementation of smart methods for M<sub>3</sub><sup>+</sup> recovery are still an open issue, we hope that present study will witness the potential of subnanometric low-nuclearity metal species in catalysis.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01847.

Experimental procedures and details, synthesis of complexes, substrates and catalytic reactions, single crystal X-ray data, and copies of all NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank MIUR, UniPR, UPCM, and CNRS for funding. Research on metal aromaticity is funded through SIR Project "AROMA-TriP" (Grant No.: RBSI14NKFL, GM) and FIL Project "RADICAT" (GM).

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(52) Unreacted triethylammonium formate and trimethylamine could be in principle recovered too at the end of the reaction via distillation, allowing one to further shrink green parameters.

(53) To prevent overheating of large-scale reaction, neutralization of formic acid with trimethylamine can be carried out in advance using an ice bath and the resulting solution can be then stored and later syringed to the reaction flask. Repeating model experiments, this alternative did not impact on the reaction outcome.