

The Pd₄(dppm)₄(H)₂²⁺ Cluster: A Precatalyst for the Homogeneous Hydrogenation of Alkynes

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The catalytic properties of the title cluster toward the homogeneous hydrogenation of phenylacetylene, diphenylethyne and phenyl-1-propyne have been investigated as a function of temperature, pressure, solvents, substrate and cluster concentrations, and counterions. The title cluster is a precatalyst that exhibits a good catalytic activity under mild conditions (1 atm of H₂ at 20 °C) for the hydrogenation of alkynes and alkenes. For the alkyne substrates, the turnover frequencies (tof's) range between 200 and 500 h⁻¹, and the product distribution varies as: *cis*-products, 75–90%; *trans*-products; 0–8% after 3 h of reaction. Based on the graphs $-d[\text{substrate}]/dt$ vs $[\text{Pd}_4]^{1/2}$, the mechanism indicates a cluster dissociation into two dimers (presumably of the type Pd₂(dppm)₂(H)(solvent)⁺). The variations of tof (or $-d[\text{substrate}]/dt$) as a function of [substrate] and pressure of H₂ are linear. At 1600 psi of H₂, the tof can reach 2500–3000 h⁻¹ (in THF). The tof also increases with temperature reaching a maximum at ~35 °C (tof: 1000–1300 h⁻¹), but at higher temperatures cluster decomposition begins to occur, leading to a rapid decrease in rates of catalysis. At 50 °C, no catalysis is observed. The hydrogenation reaction can be stopped at the corresponding *cis*-alkenes with ~95% yields, depending on the substrate and experimental conditions used. The tof's also vary with the solvent, where stronger coordinating solvent molecules give higher tof's. In addition, the tof's do not change with the nature of the counterion, which acts as "spectator" in the catalysis.

Introduction

The synthesis of a purple compound active for the catalytic hydrogenation of alkynes and alkenes was reported by Kirss and Eisenberg over 10 years ago² but was of an unknown composition for several years until it was confidently identified as the title cluster as characterized by our teams using various spectroscopic tools.³ The structure consists of a cyclic Pd₄ frame supported by four bridging dppm ligands (dppm = bis(diphenylphosphino)methane), in which the two hydrides are bonded to the Pd centers; in solution the complex exhibits a rapid fluxional process at room temperature, keeping a C₄-symmetry of the molecule. A closer look at the structure suggests that two cavities described by the 16 dppm-phenyl groups are formed above and below the Pd₄

plane, resembling picket fences.⁴ This cyclic structure has been confirmed from X-ray crystallography for a close derivative issued from the redox reaction between the title cluster and the reducing tetraphenylborate anion to form the diamagnetic [Pd₄(dppm)₄(H)]BPh₄ species.⁵ The title cluster is also a precursor of the electrocatalytic reduction of H⁺ into H₂ and oxidative formate decomposition.⁶ Homogeneous catalyzed hydrogenations are clearly important processes,⁷ but for Pd-catalyzed reactions, the number of published works appears to be relatively smaller than for other active transition metal complexes.⁸ A close look at the known

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(1) (a) Université de Bourgogne. (b) Université de Sherbrooke.
(2) Kirss, R. U.; Eisenberg, R. *Inorg. Chem.* **1989**, *28*, 3372.
(3) Gauthron, I.; Gagnon, J.; Zhang, T.; Rivard, D.; Lucas, D.; Mugnier, Y.; Harvey, P. D. *Inorg. Chem.* **1998**, *37*, 1112.

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(5) Evrard, D.; Meilleur, D.; Drouin, M.; Mugnier, Y.; Harvey, P. D. *Z. Anorg. Chem.* **2002**, *628*, 2286.
(6) Meilleur, D.; Rivard, D.; Harvey, P. D.; Gauthron, I.; Lucas, D.; Mugnier, Y. *Inorg. Chem.* **2000**, *39*, 2909.
(7) (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (b) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 51. (c) Chaloner, P. A.; Esteruelas, M. A.; Joo, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic: Dordrecht, Netherlands, 1994.

homogeneous Pd catalysts indicates that the active species all appear to be mononuclear,⁸ except for one material, a species formulated as {Pd₅(PPh)₂}_n. In this case, no structural characterization is available, but this catalyst turns out to be very efficient.^{8b} To our knowledge, besides this material, the title cluster and Pd₂(dppm)₃,⁹ there is no other polynuclear palladium species that has been investigated for its homogeneous catalyzing hydrogenation properties. One wonders what the effects of the presence of more than one metal atom in the active catalysts are, with respect to cooperativity.

We now report the catalytic properties of the title cluster toward the homogeneous hydrogenation of phenylacetylene, diphenylethyne, and phenyl-1-propyne as a function of temperature, pressure, solvents, cluster and substrate concentrations, and counterions. The mechanism involves the cluster dissociation into active d⁹–d⁹ dimers.

Experimental Section

Materials. The title cluster as BF₄⁻, Cl⁻, and BPh₄⁻ salts has been prepared according to literature procedures.^{3,6} The phenylacetylene, diphenylethyne, 1-phenyl-1-propyne, cyclohexene, and methylcyclohexane starting substrates and the corresponding hydrogenated products styrene, *cis*- and *trans*-stilbene, *cis*- and *trans*-phenyl-1-propene, ethylbenzene, 1,2-diphenylethane, and propylbenzene used to calibrate the GC/MS instrument, were purchased from Aldrich, and were used as received. The solvents THF (Anachemia), acetonitrile (Fisher), acetone (Fisher), CH₂Cl₂ (ACP), pyridine (Aldrich), and DMF (Aldrich) were purified according to literature procedures.¹⁰ The cluster was kept under inert atmosphere at all times, even in the solid state, for best results and reproducibility.

Variable-Temperature Hydrogenation. The hydrogenation reactions at 1 atm of H₂ as a function of temperature were performed using two 250-mL round flasks connected to each other with a cannula. The first one contains 100 mL of THF, and H₂ bubbling was allowed to pass through this first flask to minimize the effect of evaporation with time. In these experiments, the level of solvent in the reaction flask never changed. The second flask contained 50 mL of THF, 0.002 mol of substrates ([substrate] = 0.04 M), and 0.002 mol of methylcyclohexane as internal standard ([methylcyclohexane] = 0.04 M). The whole system was allowed to reach the desired temperature and purged for 1 h prior to addition of 2 × 10⁻⁶ mol of Pd₄(dppm)₄H₂(BF₄)₂ ([Pd₄] = 4 × 10⁻⁵ M). The turnover frequency (tof) is defined as the number of moles of consumed starting alkyne (or alkene when it applies) per hour,

(8) See, for examples: (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995. (b) Moiseev, I. I.; Vargaftic, M. N. *New J. Chem.* **1998**, 1217. (c) van Asselt, R.; Elsevier, C. J. *J. Mol. Catal.* **1991**, 65, L13. (d) Tani, K.; Ono, N.; Okamoto, S.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1993**, 386. (e) Tour, J. M.; Pandalwar, S. L. *Tetrahedron. Lett.* **1990**, 31, 4719. (f) Suzuki, N.; Tsukanaka, T.; Nomoto, T.; Ayaguchi, Y.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 515. (g) Borriello, C.; Ferrara, M. L.; Orabona, I.; Panunzi, A.; Ruffo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 2545. (h) Pelagatti, P.; Bacchi, A.; Carelli, M.; Costa, M.; Fochi, A.; Ghidini, P.; Leporati, E.; Masi, M.; Pelizzi, C.; Pelizzi, G. *J. Organomet. Chem.* **1999**, 583, 94.

(9) Stern and Maples examined the catalytic activity of this complex with respect to homogeneous hydrogenation. Because the complex was handled in air, the true nature of the catalyst may be unknown. Stern, E.; Maples, P. K. *J. Catal.* **1972**, 27, 120.

(10) (a) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purifications of Laboratory Chemicals*; Pergamon Press: Oxford, 1966. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion, a Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972; p 436.

divided by the total number of moles of cluster. These values were extracted at the very beginning of the reaction where the graphs of tof vs time were fairly linear. The samples for GC/MS analyses were collected with an Ar-purged syringe, degassed with Ar-bubbling, and stored in the dark in the freezer (–5 °C) until analysis.

High-Pressure Hydrogenations. The hydrogenation reactions under high pressure were performed in a 200-mL Parr Instrument autoclave (4001 model) equipped with a gas inlet–outlet valve and a liquid sampling valve. Mechanical stirring provided agitation. In this contribution, no heating was provided when high-pressure experiments were performed. A 100-mL solution of THF (or other desired solvents) containing 4 × 10⁻⁶ mol of [Pd₄(dppm)₄H₂](BF₄)₂ (or other salts depending on the experiments), 0.004 mol of substrate, and 0.004 mol of methylcyclohexane was placed inside the reactor. The reactor was purged three times with H₂ gas at the desired pressure, while the stirring was activated. All the runs were 24 h.

Variable Concentration Hydrogenations. The hydrogenation reactions using various concentrations of cluster (4 × 10⁻⁶, 10⁻⁵, 2 × 10⁻⁵, 6 × 10⁻⁵, 8 × 10⁻⁵, 2 × 10⁻⁴, and 10⁻⁴ M) and substrates (4 × 10⁻³, 10⁻², 2 × 10⁻², 6 × 10⁻², 8 × 10⁻², 10⁻¹, 2 × 10⁻¹, and 4 × 10⁻¹ M) were performed at 20 °C and 600 psi of H₂. The procedure was the same as described above.

GC/MS Analyses. The GC/MS analyses were performed with a Hewlett-Packard 5890 series II spectrometer coupled with a selective mass detector HP 5971 series. The hydrogenated products were analyzed by temperature-programmed gas chromatography (10 °C/min) from 60 to 250 °C with a DB-5MS column. A 0.9 mL/min helium flow has been used. The instrument was calibrated using authentic samples of the substrates and their hydrogenation products.

NMR Experiments. Variable-temperature NMR spectra were recorded on a Bruker WM 300 spectrometer (¹H NMR: 300.15 MHz, ³¹P NMR: 121.497 MHz). The reference was the residual nondeuterated solvent. The chemical shifts are reported with respect to TMS (¹H NMR) and H₃PO₄ (³¹P NMR).

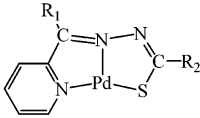
UV–Visible Experiments. UV–visible spectra were recorded on a Hewlett-Packard (HP 8452A) diode array spectrophotometer.

Space-Filling Model and Simulations. The space-filling model shown in Figure 3 was generated using the commercially available PC-model 7.0 (Serena software) which uses the MMX empirical parameters, and using ORTEP 32 and POV-Ray 3.5. The former software is used to compute the skeleton for Pd₄, while ORTEP and POV-Ray generate the space-filling drawing. For the PC-model computations, no particular constraint on bond lengths or angles was applied, but comparisons with known structures containing the same Pd₂(dppm)₂ skeleton from the literature were made, to ensure the validity of the results. Simulated curves of Figures 2 and 5 were obtained from the regression function of the commercially available Sigma Plot 2001 (Version 7.0) software.

Results and Discussion

Hydrogenation under Mild Conditions. The [Pd₄(dppm)₄(H)₂](BF₄)₂ cluster catalyzes the homogeneous hydrogenation of phenylacetylene, diphenylethyne, and phenyl-1-propyne at 20 °C and 1 atm of H₂ in THF with tof's 500, 200, and 500 h⁻¹, respectively, to form the semi- (*cis*- and *trans*- when it applies) and fully hydrogenated corresponding products (the definition for tof is provided in the Experimental Section). These values are good when compared with literature data for other catalysts (Table 1).^{11–13} However, the values still fall short when compared with the best known

Table 1. Literature of Comparison for Homogeneous Hydrogenation of Phenylacetylene^a

Catalyst	t.o.f. (h ⁻¹)	Ref.
[(PP ₃)FeH(N ₂)]BPh ₄ and [(PP ₃)FeH(H ₂)]BPh ₄		
(PP ₃ = P(CH ₂ CH ₂ PPh ₃) ₃)	0.32	20 °C/1 atm H ₂ 13a
	4	20 °C/1 atm H ₂ 15a
[Ru(η ⁶ -p-cymene)(Cl)(biisoq)]ClO.5Et ₂ O (biisoq = 1,1'-biisoquinoline)	7.6	60 °C/100 atm H ₂ 13b ^b
Pt ₃ Ru ₆ (CO) ₂₀ (μ ₃ -PhCCPh)(μ ₃ -H)(μ-H)	47	20 °C/1 atm H ₂ 11b
Pd ₄ (dppm) ₄ H ₂ ²⁺	500	20 °C/1 atm H ₂ this work
{Pd ₅ (PPh) ₂ } _n	7200	20 °C/1 atm H ₂ 8b,12

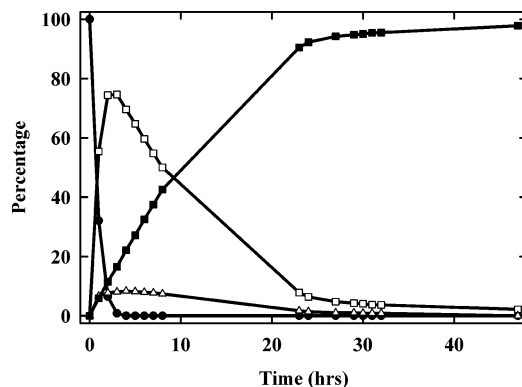
^a Other works reporting the homogeneous hydrogenation of phenylacetylene under mild conditions exist (see, for a recent example: Bacchi, A.; Carcelli, M.; Gabba, L.; Ianelli, S.; Pelagatti, P.; Pelizzi, G.; Rogolino, D. *Inorg. Chim. Acta* **2003**, *342*, 229), but the tof values are not reported. ^b The tof value at 1 atm of H₂ is not reported.

Pd catalyst, a species formulated as {Pd₅(PPh)₂}_n.^{8b,12} Other reports on efficient catalytic conversion of phenylacetylene in ethylbenzene at 20 °C/1 atm of H₂ by palladium species (where complete reaction occurs within 3 h, for example) also exist,¹³ but the lack of experimental data for tof does not allow making any meaningful comparison.

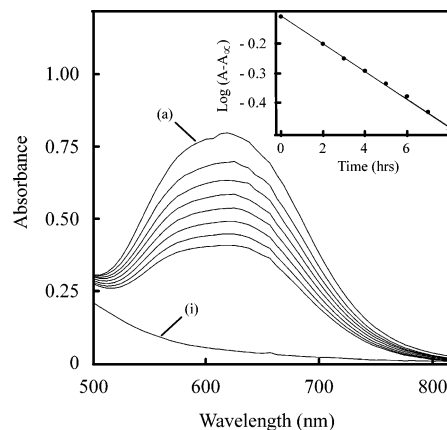
The evolution of the products as a function of time (see Figure 1 as an example for phenylacetylene) shows that styrene and the kinetic products, *cis*-stilbene and *cis*-1-phenyl-1-propene, are the first products to be observed, reaching a maximum concentration within ~3 h. This maximum value (or yield at a given time) varies from 75 to 90% and is somewhat, at first glance, similar or better than other mononuclear M(0) catalysts¹⁴ but falls shorter than that found for some other mononuclear Pd(0) complexes of bidentate nitrogen-containing donors, and thiosemicarbazone- and thiobenzoylhydrazone-containing Pd(II) catalysts (≥90%).¹⁵

The presence of observable alkenes is consistent with the greater reactivity of the alkynes,¹⁶ and the favored *cis*-stereochemistry agrees with Kirss and Eisenberg's findings

- (11) See, for examples: (a) Castiglioni, M.; Deabate, S.; Giordano, R.; King, P. J.; Knox, S. A. R.; Sappa, E. *J. Organomet. Chem.* **1998**, *571*, 251. (b) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 9103. (c) Adams, R. D.; Li, Z.; Swepson, P.; Wu, W.; Yamamoto, J. *J. Am. Chem. Soc.* **1992**, *114*, 10657.
- (12) Berenblyum, A. S.; Aseeva, A. P.; Lakham, L. I.; Petrovsky, V. V.; Moiseev, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1227 (in Russian).
- (13) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediani, P. *Organometallics* **1989**, *8*, 2080. (b) Frediani, P.; Giannelli, C.; Salvini, A.; Ianelli, S. *J. Organomet. Chem.* **2003**, *667*, 197.
- (14) See, for example: (a) van Laren, M. W.; Duin, M. A.; Klerk, C.; Naglia, M.; Rogolino, D.; Pelagatti, P.; Bacchi, A.; Pelizzi, C.; Elsevier, C. J. *Organometallics* **2002**, *21*, 1546. (b) Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1985**, *50*, 1147.

**Figure 1.** Typical example of product evolution during a homogeneous hydrogenation. Here the reaction is for diphenylethyne in THF at 20 °C and 1 atm of H₂ using the [Pd₄(dppm)₄(H₂)](BF₄)₂ cluster as catalyst (● = alkyne; ■ = alkane; □ = *cis*-alkene; △ = *trans*-alkene).**Table 2.** Product Distribution in THF after 24 h at 20 °C/1 atm H₂

substrate	alkyne (%)	<i>cis</i> -alkene (%)	<i>trans</i> -alkene (%)	alkane (%)
PhC≡CH	0	35.2	—	64.8
PhC≡CMe	0	56.4	16.4	27.2
PhC≡CPh	0	6.4	1.4	92.2

**Figure 2.** Evolution of the UV-vis spectra of [Pd₄(dppm)₄(H)₂](BF₄)₂ in THF at 20 °C, monitoring its stability over a period of 24 h (curve a = 0, progressing by intervals of 1 h until 8 h, curve i = 24 h).

where the addition of H₂ onto PhC≡CD led to the *cis*-addition PhCH=CHD product.² However, the thermodynamic *trans*-alkene products are also observed in this work, but always in a smaller quantity. At room temperature, the maximum *trans*/*cis*-ratio is about 1/4 after 24 h (Table 2), but is generally smaller for most other experiments. The quantity of alkanes increases with reaction time, while the amount of alkenes decreases, consistent with a stepwise mechanism. No reactivity is observed between the cluster and the substrate under Ar as monitored by ¹H NMR.

The Pd₄ Thermal Stability. The graph of tof as a function of temperature (see Figure 2 as an example) shows an increase between 20 and 35 °C and then a decrease down to zero at 50 °C. Above 40 °C, a rapid cluster decomposition

- (15) (a) Pelagatti, P.; Venturini, A.; Leporati, A.; Carcelli, M.; Costa, M.; Bacchi, A.; Pelizzi, G.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **1998**, 2715. (b) van Laren, M. W.; Elsevier, C. *J. Angew. Chem., Int. Ed.* **1999**, *38*, 3715.
- (16) Trost, B. M.; Braslau, R. *Tetrahedron. Lett.* **1989**, *30*, 4657.

is observed in the presence or absence of any substrate. This high-temperature decomposition is accompanied by the deposition of a black Pd-containing precipitate; a material that does not further hydrogenate alkynes or alkenes in our experimental conditions. No solid deposit is observed in experiments where the temperature does not exceed 40 °C within 24 h, but a slow decomposition occurs over a period of a few days at 20 °C. Again this solid is not active for the hydrogenation reactions investigated in this work. The bell-shape curve (Supporting Information) is approximately the same for all three substrates.

The monitoring of this decomposition process by UV-vis spectroscopy (Figure 2) allows the extraction of the rates of decomposition. The graph of $\log(A - A_\infty)$ vs time (Figure 2, see inset) indicates a first-order reaction. The slopes extracted from the graphs $\log(A - A_\infty)$ vs time are -1.0×10^{-3} , -1.9×10^{-3} , -5.8×10^{-3} , -1.6×10^{-2} , and $-4.6 \times 10^{-2} \text{ h}^{-1}$ for MeCN, DMF, THF, Py, and CH_2Cl_2 , respectively. MeCN, DMF, and THF exhibit slower rates of decomposition, while for Py and CH_2Cl_2 , reactivity with Pd_4 is noticed, and the observed slopes are 1 order of magnitude greater. CH_2Cl_2 reacts with the title cluster to form $\text{Pd}_2(\text{dppm})_2\text{Cl}_2$ (minor) and $\text{Pd}(\text{dppm})\text{Cl}_2$ (major product) agreeing with Kirss and Eisenberg's previous findings.² The pyridine solvent (Py) also reacts with the cluster to form a new, but uncharacterized species, which is discussed further below.

In the presence of H_2 (instead of Ar), cluster decomposition occurs more rapidly (based on ^1H NMR and UV-vis; Supporting Information), which suggests reactivity between H_2 and the title cluster, presumably producing unstable Pd-H intermediates. From ^1H and ^{31}P NMR, no intermediate could be detected under all experimental conditions used in this work at 1 atm of H_2 .¹⁷

The monitoring by GC/MS of the products' distribution with time at high temperatures (i.e., ~ 45 °C) shows a rapid substrate consumption ($< 2-3$ h), but the complete production of the corresponding alkanes is never observed, even after 24 h. Instead, the typical bluish color of the solutions changes to yellow (with a small black Pd-containing suspension), witnessing the catalyst's decomposition. The maximum amount of intermediate alkenes is observed after 2 h in all cases. For styrene, this peak amount fluctuates between 80 and 90%, while for *cis*- and *trans*-stilbenes, their corresponding values are 80 ± 5 and about 10%, respectively.

Homogeneous System. The presence of cluster decomposition at high temperatures calls into questions the nature of the catalysis (homogeneous vs heterogeneous). Attempts to hydrogenate cyclohexene were made, knowing that this substrate is not or only very slowly hydrogenated by homogeneous Pd species but is readily hydrogenated by colloidal or heterogeneous Pd.^{15b} Indeed, cyclohexene is not at all hydrogenated by Pd_4 in THF (600 psi of H_2 at 20 °C) after several hours, demonstrating the likely homogeneous character of this catalyst.¹⁸

(17) High pressure ^1H NMR experiments (pression = 1000 bar of H_2 using acetone- d_6 at 20 °C) performed at the University of Lausanne, also did reveal any intermediates.

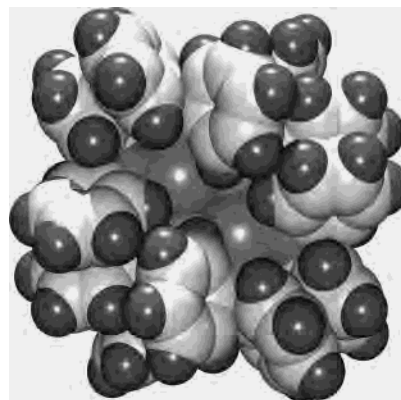


Figure 3. Space-filling model for the $\text{Pd}_4(\text{dppm})_4(\text{H})_2^{2+}$ cluster showing the cavity giving access to the Pd atoms. This is one possible conformation as an example, due to the multiple relative conformations of the dppm ligands and orientations of the phenyl groups.

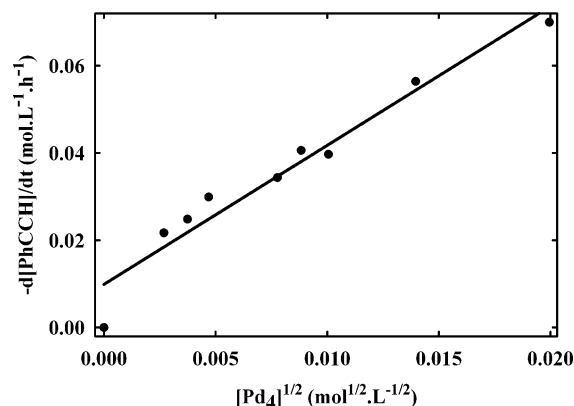


Figure 4. Graph of $-\text{d}[\text{phenylacetylene}]/\text{dt}$ vs $[\text{Pd}_4]^{1/2}$ showing a linear dependence. Experimental conditions: THF at 20 °C and 600 psi of H_2 using the $[\text{Pd}_4(\text{dppm})_4(\text{H})_2](\text{BF}_4)_2$ cluster as catalyst.

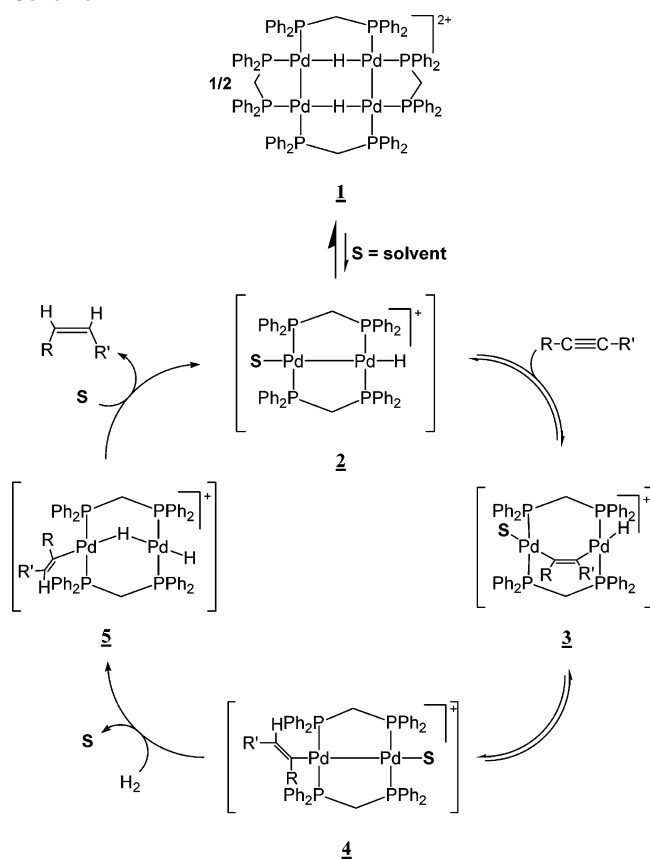
Mechanism. The space-filling model for $\text{Pd}_4(\text{dppm})_4(\text{H})_2^{2+}$ (Figure 3) shows a cavity that is clearly too small to allow any efficient interactions between the metal atoms and the substrates in a side-on geometry, as verified from modeling. However, the relatively impressive *tof* value of 500 h^{-1} at room temperature for both $\text{PhC}\equiv\text{CH}$ and $\text{PhC}\equiv\text{CPh}$ strongly suggests that $\text{Pd}_4(\text{dppm})_4(\text{H})_2^{2+}$ is not the active catalyst.

This observation leads one to investigate the dependence of the cluster and substrate concentrations, and H_2 pressure on *tof* (or $-\text{d}[\text{alkyne}]/\text{dt}$), and to propose a mechanism in which the first step involves the dissociation of the title cluster **1** into less sterically demanding d^9-d^9 dimers of the type $\text{Pd}_2(\mu\text{-dppm})_2(\text{H})(\text{S})^+$ (**2**), where **S** = solvent (Scheme 1: mechanism adapted for alkynes).¹⁹ The graphs $-\text{d}[\text{alkyne}]/\text{dt}$ versus $[\text{Pd}_4]^{1/2}$ are indeed linear (see Figure 4 for $\text{PhC}\equiv\text{CH}$

(18) (a) The mercury test^{18b} was not suitable in this case, since the title cluster reacts rapidly with Hg. In fact, reactivity between a Pd species and Hg has been observed before.^{18c} (b) Fusi, A.; Ugo, R.; Psaro, R.; Braunstein, P.; Dehand, J. *J. Mol. Catal.* **1982**, *16*, 217. (c) Harvey, P. D.; Aye, K. T.; Hierso, K.; Isabel, E.; Lognot, I.; Mugnier, Y.; Rochon, F. D. *Inorg. Chem.* **1994**, *33*, 5981.

(19) d^9-d^9 dimeric species axially functionalized by good coordinating solvent molecules have already been reported in the past. See, for examples: (a) Maekawa, M.; Munakata, M.; Kudora-Sowa, T.; Suenaga, Y. *Polyhedron* **1998**, *17*, 3657. (b) Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Suenaga, Y. *Inorg. Chim. Acta* **1998**, *281*, 116. (c) Hill, R. H.; De Mayo, P.; Puddephatt, R. J. *Inorg. Chem.* **1982**, *21*, 3642.

Scheme 1



CH as an example), while the graphs $-d[\text{alkyne}]/dt$ versus $[\text{Pd}_4]$ are not (see one example in the Supporting Information), hence demonstrating the dissociation of the cluster into active species.

The graph of $-d[\text{phenylacetylene}]/dt$ vs $[\text{phenylacetylene}]$ is also linear (Supporting Information), illustrating the first-order dependence. This result is consistent with the second step of the mechanism where one molecule of substrate inserts onto the Pd–Pd bond of the active catalyst to give species **3**.^{20,21} The related $[\text{Pt}_2\text{H}(\text{S})(\text{dppm})_2(\mu\text{-RCCR})]^+$ complexes ($\text{S} = \text{MeCN}, \text{MeC}(\text{O})\text{Me}; \text{R} = \text{CF}_3$) have already been reported in the literature by Puddephatt and Thompson.²²

Then, the coordinated alkyne migration-insertion onto the Pd–H bond of **3** produces another d^9-d^9 intermediate, **4**, which undergoes an oxidative addition with H_2 to form a suspected species $\text{Pd}_2(\mu\text{-dppm})_2(\text{H})(\eta^1\text{-CR}=\text{CHR}')(\mu\text{-H})^+$ **5**.²³ Figure 5 shows tof vs H_2 pressure for the hydrogenation

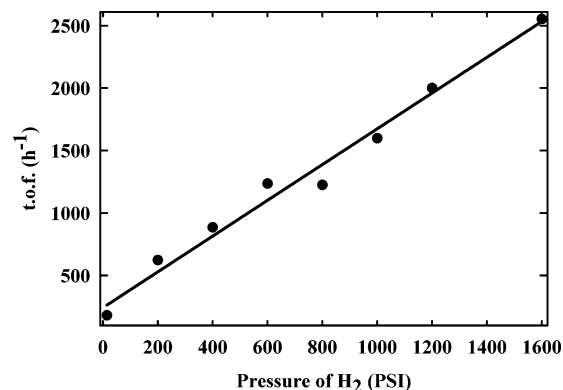


Figure 5. Graph of the tof as a function of pressure of H_2 for phenyl-1-propyne in THF at 20°C using $[\text{Pd}_4(\text{dppm})_4(\text{H})_2](\text{BF}_4)_2$ as catalyst.

of phenyl-1-propyne (as an example) where an increase of about 10-fold is observed (from 200 to 2500 h^{-1}) between atmospheric pressure and 1600 psi at 20°C . This figure exhibits a first-order dependence on the pressure of H_2 , which is consistent with the oxidative addition step of H_2 on **4** to give **5**.²⁴ As a result of high pressures, the corresponding alkane products are generated far more rapidly, and all the reactions reach completion (i.e., 100% of alkanes) within 2 or 3 h instead of 24 h for 1 atm of H_2 . The tof vs H_2 pressure graphs exhibit slopes of 1.06, 1.43, and 1.57 h^{-1}/psi for phenylacetylene, 1-phenyl-1-propyne, and diphenylethyne, respectively. Intermediate **5** reductively eliminates the alkenes, and regenerates the active dimer **2**. By ^1H and ^{31}P NMR, no new species has been detected under catalytic conditions, indicating that the concentration of the intermediates must be very small, which indicates a small displacement of the first equilibrium from **1** to **2** in the mechanism of Scheme 1.

The kinetic analysis allows us to formulate the following rate law:

$$r = k[\text{alkyne}] [\text{Pd}_4]^{1/2} P(\text{H}_2) \quad (1)$$

The addition of a 10-fold excess ($/[\text{Pd}_4]$) of PPh_3 to the solutions strongly slows down the catalysis. A long induction period of 15 min where no hydrogenation occurs is observed, and after 1.5 h the distribution of products is phenylacetylene: 95% and styrene: 5%. This result is consistent with PPh_3 competing for the coordination site otherwise occupied by a solvent molecule on the intermediates **2–4**, where the

(20) Addition of alkynes onto Pd–Pd bonds is well documented. See, for examples: (a) Davies, J. A.; Pinkerton, A. A.; Syed, R.; Vilmer, M. *J. Chem. Soc., Chem. Commun.* **1988**, 47. (b) Davies, J. A.; Kirschbaum, K.; Kluwe, C. *Organometallics* **1994**, *13*, 3664. (c) Kluwe, C.; Muller, J.; Davies, J. A. *J. Organomet. Chem.* **1996**, *526*, 385. (d) Kluwe, C.; Davies, J. A. *Organometallics* **1995**, *14*, 4257. (e) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22. (f) Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2498. (g) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1988**, 457. (h) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1629.

(21) No 1,2-shift reaction^{20b,c} was observed either by ^1H NMR or the appearance of other peaks in the GC/MS.

(22) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chem.* **1982**, *21*, 725.

(23) The lack of literature precedent for this complex **5**, or related compounds, is likely due to the well-known fragility of Pd–H species.^{24a} However, the presence of stable species such as $\text{Pd}_2(\mu\text{-dppm})_2(\text{aryl})_2(\mu\text{-H})^+$ (aryl = various substituted benzenes),^{23a} $\text{Pd}_2(\text{dppm})_2(\text{aryl})(\text{Et})(\mu\text{-H})^+$,^{23b,c} and $\text{Pt}_2(\text{dppm})_2(\text{H})_2(\mu\text{-H})^+$,^{23d,e} suggests that such a formulation is reasonable. (a) Grushin, V. V. *Chem. Rev.* **1996**, *96*, 2011. (b) Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *J. Am. Chem. Soc.* **1999**, *121*, 7945. (c) Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *Inorg. Chim. Acta* **2000**, *300*, 395. (d) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L33. (e) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516.

(24) Attempts to synthesize intermediates **2–5** stubbornly failed. For instance, addition of one equivalent of NaBH_4 to $\text{Pd}_2(\text{dppm})_2\text{Cl}_2$ in the presence of a 10-fold excess of phenylacetylene resulted in a 1:1 mixture of starting material and $[\text{Pd}_4(\text{dppm})_4\text{H}_2](\text{Cl})_2$. The alkyne substrate acted as a spectator and **2** was never observed.

Pd–PPh₃ bond is stronger. This PPh₃ molecule greatly slows down the oxidative addition of H₂ onto intermediate **4** to give **5**.²⁵

Properties at High Pressure. The products' evolution with time for the hydrogenation reaction of phenylacetylene at high pressures (200–1600 psi of H₂) is similar to that of Figure 1. Styrene appears and disappears faster with higher pressures (i.e., within 2 h), but the relative amount of styrene at its maximum concentration, generally observed after 1 h, remains fairly constant at around 65 ± 10% for all experiments. This result indicates that the relative rates of hydrogenation of phenylacetylene and styrene remain very similar to each other, for all investigated pressures.

For diphenylethyne, similar observations are made. The maximum amount observed for *cis*-stilbene fluctuates between 50 and 65% for all pressures. Similarly, the maximum quantity of the intermediate *trans*-stilbene product also stays the same at about 4%. This observation reinforces the hypothesis that the apparent regioselectivity is not lost at high pressures.

The same observations are drawn for the phenyl-1-propyne substrate, except that the *trans*-product is never observed at more than 8%. These experiments above indicate that the complete production of the corresponding alkanes is best carried out at higher pressures. Pressure at 200 psi, which is the lowest investigated pressure in this work, is fully adequate for this purpose. For the generation of *cis*-alkenes, best results are obtained after 2 h using THF as the solvent at 30–40 °C and at 1 atm of H₂ (> 75%).

***cis*- vs *trans*-Products.** Occasional amounts of minor *trans*-alkene products were observed as stated. Pd₄ does not induce the *cis*–*trans* isomerization, or at least not efficiently (in the absence of H₂ as monitored by ¹H NMR and GC/MS) using both *cis*- and *trans*-alkenes as starting materials. This result is interesting since it implies that a second mechanism, involving different intermediates, must operate to explain the presence of the *trans*-alkene products. Speculatively, **1** and **2** in Scheme 1 have not been considered to add H₂ to form the corresponding Pd₄(dppm)₄(H)₂²⁺ (**1**–H₂) and Pd₂(dppm)₂(H)₃⁺ (**2**–H₂) potential intermediates. The former (**1**–H₂) has already been suspected in the past to be one of the active intermediates in the H₂-evolution reaction catalyzed by **1**.⁶ The second potential intermediates (**2**–H₂) are not known, but the corresponding platinum analogue Pt₂(dppm)₂(H)₃⁺ is.²⁶ For such reactive H-rich species, atom or hydride transfer to uncoordinated alkenes

(or alkynes) may be possible. For alkene substrates, such a process renders *cis*–*trans* isomerization possible. All in all, this proposal is highly speculative, and the presence of the minor transient *trans*-product must be explained by another mechanism which constitutes a separate study from this work.

Both the *cis*- and *trans*-stilbene in THF 20 °C/600 psi of H₂ are converted into 1,2-diphenylethane with nearly comparable rates, considering the uncertainties (tof = 1000 and 800 h⁻¹; for *cis*- and *trans*-, respectively), indicating that Pd₄ is able to hydrogenate *trans*-alkenes as well. A similar mechanism as shown in Scheme 1 may apply for the hydrogenation of olefins (Supporting Information).

Solvent Dependence. The tof's for the hydrogenation of phenyl-1-propyne in various solvents at 20 °C and 600 psi of H₂ have been measured. These values can be divided into three groups: (1) large for DMF (1800), (2) medium for THF (1240), MeC(O)Me (1130), and MeCN (1060), and (3) small for Py (660 h⁻¹). Indeed, complete conversion of phenyl-1-propyne in propylbenzene (as an example) is performed within 4 h in DMF instead of, say, 12 h in THF. This result is not unprecedented for us, as a previous investigation on the electrocatalytic properties of the title cluster also indicated that better results are obtained for this solvent for the reduction of H⁺ and oxidative decomposition of HCO₂⁻.⁶ The medium-sized tof values for THF, MeC(O)Me, MeCN (which cannot be separated on the basis of the uncertainties) reflect a lower coordinating ability of the solvent molecules with respect to DMF (i.e. DMF > THF ≈ MeC(O)Me) on the intermediates **2**–**4** shown in Scheme 1.²⁷

Py exhibits a significantly lower tof (660 h⁻¹). The results are obscured by the presence of a reactivity with this solvent where a yellow coloration appears with time.²⁸ With this solvent, the hydrogenation of phenylacetylene at 600 psi of H₂ at 20 °C leads to 75% of styrene and 25% of ethylbenzene after 45 min. Except for the relatively rapid appearance of styrene, these proportions do not differ greatly from THF at the same pressure. However for 1,2-diphenyl-acetylene, *cis*- and *trans*-stilbene and diphenylethane were detected with a proportion of 80, 2, and 17%, respectively, after 24 h. Overall, these observations are consistent with catalyst poisoning; however, the *cis*–*trans*- ratio has greatly improved. For 1-phenyl-1-propyne, 97% of *cis*-1-phenyl-1-propene, and only 3% of propylbenzene are obtained after 4 h of catalysis. These results indicate that the hydrogenation can be stopped at the semihydrogenated products.²⁹

The Counterions. The counterions BF₄⁻, BPh₄⁻, and Cl⁻ exhibit no important effect on tof within the experimental uncertainties. For example, the tof's for phenyl-1-propyne in THF at 20 °C at 600 psi of H₂ are 1000, 1333, and 1000

- (25) (a) An additional experiment where two competitive substrates (i.e. [diphenylethyne] = [*cis*-stilbene] = 0.02 M, at 20 °C, and 600 psi of H₂) were inserted with the cluster was performed to demonstrate that the alkyne substrate is preferentially hydrogenated over the alkene. The alkyne substrate is hydrogenated first, resulting in an increase of the total [*cis*-alkene]. Then, [*cis*-alkene] starts decreasing after 20 min. (b) Addition of 7 equiv of PPh₃ to Pd₄(dppm)₄(H)₂²⁺ in (CD₃)₂CO leads to a new product that exhibits a peak at +8.3 ppm in the ³¹P NMR spectra. No attempt was made to identify the species. A structurally related compound, [Pd₂(dppm)₂(PPh₃)(C₆Cl₅)](BPh₄), has been reported in the literature.^{25c} (c) Espinet, P.; Fornies, J.; Fortunato, C.; Hidalgo, G.; Martínez, F.; Thomas, M.; Welch, A. J. *J. Organomet. Chem.* **1986**, *317*, 105.
- (26) Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516.

- (27) Cotton, F. A.; Wilkinson, G.; Gaus, P. *Basic Inorganic Chemistry*, 3rd ed.; Wiley: Toronto, 1987; p 208.
- (28) (a) Reactivity of pyridine with d⁹–d⁹ and d⁸–d⁸ Pd₂(dppm)₂ species is precedented.^{27b–d} (b) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764. (c) Uson, R.; Fornies, J.; Espinet, P.; Martínez, F.; Fortunato, C.; Menjon, B. *J. Organomet. Chem.* **1983**, *256*, 365. (d) Chin, C. C. H.; Yeo, J. S. L.; Loh, Z. H.; Vittal, J. J.; Henderson, W.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3777.

h^{-1} for BF_4^- , BPh_4^- , and Cl^- , respectively. This result is consistent with Scheme 1 where the counterion is a “spectator”.

Conclusions

The title cluster is one of the very good Pd-catalyst for the homogeneous hydrogenation of alkynes, despite the fact that decomposition is observed at temperatures exceeding 45 °C. The mechanism proceeds via a cluster dissociation, and depending on the experimental conditions, selectivity for *cis*–*trans* isomers and semi- and fully hydrogenated products is possible.

(29) (a) Another example where the hydrogenation is stopped at the alkene using Py as the solvent exists: Kerr, J. M.; Suckling, C. J.; Bamfield, P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 4, 887. (b) One possible explanation for this result is the relative lability of the donors. PPh_3 is not as labile as THF for instance (the commonly used solvent in this work), and its presence in the solution leads to a saturation of the active sites. This coordination strongly inhibits the catalyses. On the other hand, Py is less labile than THF but more than PPh_3 . As alkynes are more reactive than alkenes based on this work, it is possible that hydrogenation reactions for both alkynes and alkenes are slowed to the point that the hydrogenation of alkenes are too slow to be observed in the conditions used.

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Supporting Information Available: Graph of $-d[\text{phenylacetylene}]/dt$ vs $[Pd_4]$. Experimental conditions: THF at 20 °C and 600 psi of H_2 using the $[Pd_4(dppm)_4(H)_2](BF_4)_2$ cluster as catalyst, graph of $-d[\text{phenylacetylene}]/dt$ vs $[\text{phenylacetylene}]$ at 600 psi of H_2 at 20 °C, graphs of $\log A$ vs time for $[Pd_4(dppm)_4(H)_2](BF_4)_2$ in THF at 20 °C in the presence of 1 atm of H_2 and diphenylethyne, graph of the *tof* as a function of temperature for phenyl-1-propyne in THF at 1 atm H_2 using $[Pd_4(dppm)_4(H)_2](BF_4)_2$ as catalyst, and possible mechanism for the homogeneous hydrogenation of alkenes by $[Pd_4(dppm)_4(H)_2](BF_4)_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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