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Reaction of $[Pt_2(dppp)_2(H)_3][BF_4]$ with Styrene or Phenylacetylene Gives the Same μ-Hydrido μ-Alkylidene Derivative, $[Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)][BF_4]$

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The reaction of the binuclear platinum hydride $[Pt_2(dppp)_2(H)_3][BF_4]$ with styrene or phenylacetylene gives the same μ-hydrido μ-alkylidene diplatinum complex, $[Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)][BF_4]$, under the same mild experimental conditions. Experiments with deuterium-labeled reagents show that the hydrogenation of phenylacetylene does not occur through the transfer of the acetylenic proton and suggest that the hydrogenation to styrene as an intermediate step is not implied. The ^{13}C NMR spectra of the reaction product of an equimolecular mixture of $[Pt_2(dppp)_2(H)_3][BF_4]$ and $[Pt_2(dppp)_2(D)_3][BF_4]$ with phenylacetylene suggest that fragmentation of the dimeric $Pt_2H_3^+$ core does not occur. Possible phenylacetylene hydrogenation pathways are discussed.

Introduction

Binuclear complexes containing both bridging hydrido and alkylidene ligands are of considerable interest, as they are involved in several conversions of hydrocarbyl fragments on polynuclear centers[1] and have been postulated as significant models for intermediates in catalytic processes such as olefin metathesis[2] and so on. These complexes are rather uncommon, particularly the homometallic species,[3] and their formation must be often rationalized a posteriori.

We have long been interested in the synthesis, structure, and reactivity of the 30e cationic diplatinum(II) hydrides $[Pt_2(P\text{-}P)_2(H)_3]^+$ (P-P = chelating diphosphine[4]),[5] promising precursors of different kinds of bimetallic complexes.[3a,e−f,5,6] Twenty years ago, we described the first example of a μ-hydrido μ-alkylidene diplatinum complex, $[Pt_2(dppe)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)][BF_4]$ (**1**), obtained as a unique product in the reaction of $[Pt_2(dppe)_2(H)_3][BF_4]$ and styrene under very mild conditions.[3a] More recently, three homologues of complex **1**, namely $[Pt_2(dppb)_2(\mu\text{-}H)(\mu\text{-}CHCH_2R)][BF_4]$ (R = Ph, **2**; R = H, **3**)[3e] and $[Pt_2(dfepe)_2(\mu\text{-}H)(\mu\text{-}CHCH_3)][O_2CCF_3]$ (**4**),[3f] have been similarly synthesized, i.e. by reaction of a binuclear hydrido complex, $[Pt_2(P\text{-}P)_2(H)_3][X]$, and styrene (**2**) or ethylene (**3**, **4**), respectively. Complex **4** was also obtained from a mononuclear platinum(II) species, as well as another known homologue, $[Pt_2(dppf)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ar)][Br]$ (Ar = $p\text{-}MeOC_6H_4$).[3d] The X-ray crystal structure determinations of compounds **1** and $[Pt_2(dppf)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ar)]$ show short Pt−Pt distances: 2.735(1)[3a] and 2.6540(8) Å,[3d] respectively.

The reaction affording complexes **1**−**4** from the appropriate binuclear hydride can be envisaged as an useful general way to synthesize these kinds of binuclear platinum complexes. In all cases satisfactory yields were obtained through a rather simple reaction, formally corresponding to H_2 loss from the bimetallic core and to a 1,2-hydrogen shift in the coordinated olefin. The former process seems to be the usual one in the reactions of these platinum(II) hydrides and various unsaturated molecules, provided that the binuclear structure is maintained.[3a,e−f,5,6] Despite the apparent simplicity, the reaction pathway is not straightforward, as shown by the cleavage of a P−C bond which occurs simultaneously with the syntheses of complexes **2** and **3**[3e] as well as by the different behavior of the cation $[Pt_2(dcype)_2(H)_3]^+$, recently observed.[7] On examination of the different diphosphines, i.e. dppb and dcype in comparison with dppe and dfepe, their features suggest that steric rather than electronic factors influence the reactions of $[Pt_2(P\text{-}P)_2(H)_3]^+$ cations with olefins.

To better understand the influence of the phosphino ligands on the synthesis of diplatinum μ-hydrido μ-alkylidene complexes and acquire suggestions for an easy synthetic route of these uncommon complexes, we have carried out the reaction of styrene and the complex $[Pt_2(dppp)_2(H)_3][BF_4]$: i.e. a hydride bearing a diphosphinoalkane with a bite intermediate between those of the previously examined dppe[3a] and dppb.[3e]

In addition, we have extended our investigations to the reaction of the same complex, $[Pt_2(dppp)_2(H)_3][BF_4]$, and phenylacetylene. Taking into account the aforementioned facile

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[1] E.g.: Zaera, F. *Chem. Rev.* **1995**, *95*, 2651 and references therein.

[2] E.g.: Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; Chapter 9.

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[4] Throughout this paper the chelating diphosphino ligands are indicated as follows: dcype, 1,2-bis(dicyclohexylphosphino)ethane; dfepe, 1,2-bis-[bis(perfluoroethyl)phosphino]ethane; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino)butane; dppf, 1,1′-bis(diphenylphosphino)ferrocene.

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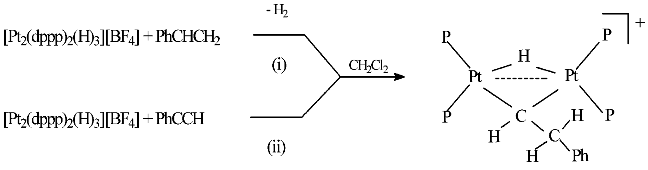
10.1021/om050801g CCC: $33.50

H_2 loss, we expected to obtain the new complex $[Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CCHPh)][BF_4]$, recalling the first μ-vinylidene diplatinum species described by Lukehart and co-workers.[8] Moreover, a previously examined reaction between a trihydrido bimetallic complex, $[(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(PPh_3)_2(CH_3CN)]$, and terminal alkynes showed the synergy exerted by two close metal centers, leading to an unusual styrene intermediate, described as the last step of hydrogenation of an alkyne to a coordinated alkene.[9]

Here we report the unexpected formation of the same μ-hydrido μ-alkylidene species, $[Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)][BF_4]$ (**5**), in both of the examined reactions. Different experiments with deuterium-labeled species, namely $[Pt_2(dppp)_2(H)_3][BF_4]$ with phenylacetylene-*d* (PhCCD), $[Pt_2(dppp)_2(D)_3][BF_4]$ with PhCCH, and a mixture of $[Pt_2(dppp)_2(H)_3][BF_4]$ and $[Pt_2(dppp)_2(D)_3][BF_4]$ with PhCCH, are discussed.

Results and Discussion

The reactions of $[Pt_2(dppp)_2(H)_3][BF_4]$ with styrene (reaction i) or phenylacetylene (reaction ii), carried out under the same experimental conditions, afforded as a unique compound the μ-hydrido μ-alkylidene species $[Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)][BF_4]$ (**5**). In both cases complex **5** was obtained after 1 week from CH_2Cl_2 (or acetone) solutions of the hydride and a large excess of the appropriate substrate, maintained with stirring and gentle reflux.



(**5**)

Complex **5** is a pale yellow powder, stable as a solid and in solution, but in the phenylacetylene reaction ii the crude product appears misleadingly brick red. Despite repeated purification attempts, the analytical sample color ranges from a pale red color to pink, but the analytical and spectroscopic data are unaffected.

The unexpected results and the deceptive color compelled us to carry out a full characterization of both reaction products in solution, in the solid state and in the vapor phase. Anyhow, the nature and the identity of the products of both reactions were undoubtedly shown by the identity of multinuclear NMR and FAB-MS data and by two independent X-ray crystal structure determinations.

On the whole the NMR features well agree with those of the known homologues.[3a,d−f] In particular in the ^1H NMR spectra a triplet of triplets with satellites (approximate ratios 1:8:18:8:1) at −2.6 ppm is diagnostic of the hydride bridging two equivalent platinum atoms in a rigid $Pt_2(\mu\text{-}H)(\mu\text{-}X)$ core, while an unresolved multiplet at 4.9 ppm can be ascribed to the bridging C*H* group. Owing to the large overlap of the signals in the region of methylene groups, the C*H*$_2$ resonance of the μ-alkylidene ligand (1.89 ppm) had to be identified by $^1H/^{13}C$ heterocorrelated spectra. In contrast, the same group can be observed in the $^{13}C\{^1H\}$ NMR spectra (46.5 ppm), while the weak and highly split resonance of the bridging *C*H has been unequivocally identified by means of $^1H/^{13}C$ heterocorrelated and $^{13}C\{^{31}P\}$ experiments. The shift value (135.9 ppm) lies in the typical range of sp^3-hybridized carbon atoms in binuclear transition-metal μ-alkylidene complexes.[10]

As expected from the presence of two couples of nonequivalent P donors, the $^{31}P\{^1H\}$ NMR spectra show two distinct signals at values in agreement with the ring contribution (Δ_R) of dppp ligands. The coupling constant ($^1J_{P-Pt}$) values reflect the greater trans influence of the alkylidene ($^1J_{Pt-P} = 2104$ Hz) as compared to that of the bridging hydride ($^1J_{Pt-P} = 4291$ Hz).

As mentioned above, the FAB-MS spectra show a quasi-molecular peak at *m/z* 1317 ($[M - 2H]^+$) and identical fragmentation pathways; similarly, the single-crystal X-ray diffraction structures determined for two samples obtained from reactions i and ii are identical.[11]

The styrene reaction (i) supports our synthetic approach as a useful way to obtain these uncommon platinum derivatives, considering the diphosphine steric requirements. Moreover the acetylene reaction (ii) was unexpected, even though a simple explanation could be found in the hydrogenation of the coordinated alkyne to a styrene intermediate, as is usually the case in the hydrogenation of alkynes to alkanes in homogeneous processes.[12]

To better understand the course of the reaction leading to **5** from phenylacetylene, in particular to ascertain whether the intermediate step could be the hydrogenation to styrene, we have carried out two different experiments with deuterium labeled species, namely $[Pt_2(dppp)_2(H)_3][BF_4]$ with phenylacetylene-*d* (PhCCD) (reaction iii) and $[Pt_2(dppp)_2(D)_3][BF_4]$ with PhCCH (reaction iv). Both of the reactions were carried out under the same experimental conditions as in (ii) and the isolated compounds, **5a** and **5b**, respectively, were purified and characterized by the usual analytical and spectroscopic techniques.

$$[Pt_2(dppp)_2(H)_3][BF_4] + PhCCD \rightarrow [Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CDCH_2Ph)][BF_4] \quad \text{(iii)}$$

5a

$$[Pt_2(dppp)_2(D)_3][BF_4] + PhCCH \rightarrow [Pt_2(dppp)_2(\mu\text{-}D)(\mu\text{-}CHCD_2Ph)][BF_4] \quad \text{(iv)}$$

5b

The most interesting indications have been obtained on comparing the ^1H, ^2H, and ^{13}C NMR spectral data. In particular, the resonances of the bridging hydrido ligands have been observed in the ^1H spectrum of **5a** and in the ^2H spectrum of **5b**. Moreover, the ^1H spectrum shows the resonance of the μ-C*H* group (4.93 ppm) in the latter compound, while in the former the corresponding signal is observed only in the ^2H spectrum. With respect to the resonance of the methylene group in the aliphatic alkylidene chain, this is easily detectable in the ^2H spectrum of the product **5b**, obtained from the trideuteride, while the CH_2 isotopomer in the product **5a**, obtained from the trihydride, had to be inferred from $^{13}C\ \{^1H,^{31}P\}$ DEPT spectrum (46.3 ppm).

Briefly, each of these reactions produces only one compound, among the possible isotopomers, namely one that formally

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originated from a double β-hydrogen transfer from the metal centers, with anti-Markovnikov addition. The isotopic transfer direction is then defined from the hydrido core to the coordinated substrate.

This result suggests that the alkylidene formation from phenylacetylene does not imply a hydrogenation step leading to coordinated styrene at the bimetallic core, from which mixtures of various isotopomers are expected, whatever the mechanism of alkyne insertion considered.[13]

In addition, the absence of isotopic exchange between the α-CH group of the organic substrate and the hydrido ligands excludes activation of the CH bond of phenylacetylene to give alkynyl or vinylidene species.[9,14] This picture together with the overall behavior of the binuclear trihydrides suggests that mechanisms involving separation and recombination of the binuclear core, i.e. reaction pathways through mononuclear intermediates, could be unlikely. In particular, the fragmentation of the dimeric $Pt_2H_3^+$, induced by unsaturated substrate coordination, was excluded in the process giving the μ-ethylidene complex **4**, and a binuclear cationic intermediate was proposed as a key step in the formation of the same complex from mononuclear species.[3f]

With regard to this subject, we have carried out a further experiment[15] by using an equimolecular mixture of $[Pt_2(dppp)_2(H)_3][BF_4]$ and $[Pt_2(dppp)_2(D)_3][BF_4]$ reacting with PhCCH. If mononuclear intermediates were involved in the reaction pathway, the mixed alkylidene ligand (μ-CHCHDPh), as hydride and deuteride, would be expected as the most abundant component in the isotopomer mixture.

It is worth noting that in the present case the distinction among the three different methylene groups, i.e. CH_2, CD_2, and CHD, can be actually achieved only by ^{13}C NMR spectra, but the broadness and closeness of labeled group resonances preclude their observation in an unique NMR experiment, preventing a reliable quantitative determination. In fact, the CH_2 and CHD resonances are clearly observed in $^{13}C\{^1H,^{31}P\}$ DEPT spectra, while the CD_2 signal is unequivocally detected only by APT experiments (see the Experimental Section). The unavoidable presence of all different isotopomers (PtD_3, PtD_2H, $PtDH_2$, and PtH_3) in the starting trideuteride cation must give a negligible amount of **5a** and of mixed-alkylidene species, in addition to compound **5b** (reaction iv). If this is true, as it is, the $^{13}C\{^1H,^{31}P\}$ DEPT spectrum of **5b** in the alkylidene region must show both CH_2 and CHD resonances in the relative abundance "naturally" occurring in the isotopomer mixture. As a consequence, we took the alkylidene region of the ^{13}C NMR spectrum (Figure 1) of a saturated solution of **5b** (ca. 200 mg/mL) as a reference for comparison with the same spectral region of the isotopomer mixture obtained from the equimolecular $[Pt_2(dppp)_2(H)_3][BF_4]$ and $[Pt_2(dppp)_2(D)_3][BF_4]$ mixture.

If the reaction occurs by mononuclear intermediates, the relative amount of mixed alkylidenes, $[Pt_2(dppp)_2(\mu\text{-}X)(\mu\text{-}CHCHDPh)][BF_4]$ (X = H, D), must increase, being produced by both of the precursors. In contrast, the mixture spectrum shows an increase in the CH_2 resonance, which indicates a greater formation of **5a** from $[Pt_2(dppp)_2(H)_3][BF_4]$. If not definitive, owing to intrinsic experimental limits, this result strongly indicates that the fragmentation of the dimeric $Pt_2H_3^+$ is unlikely.

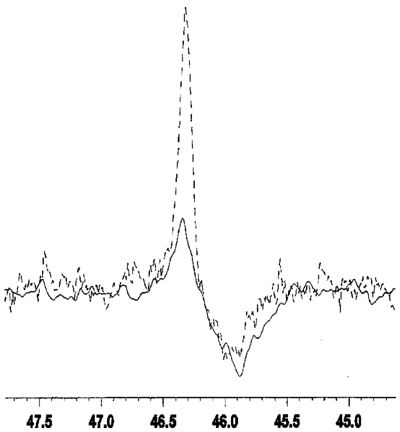

Figure 1. $^{13}C\{^1H,^{31}P\}$DEPT NMR spectra (β-C resonances of alkylidene ligand: CH_2 up, CHD down) of saturated solutions of complex **5b** (solid line) and of the isotopomeric mixture (dotted line) produced by the reaction of $[Pt_2(dppp)(H)_3][BF_4]$ and $[Pt_2(dppp)(D)_3][BF_4]$ with PhCCH.

While we cannot give a definitive explanation on the detailed mechanism affording complex **5** from phenylacetylene, some considerations can be given on the basis of reactions iii and iv. The above results suggest a direct regiospecific insertion of the coordinated substrate into a Pt−H bond (Scheme 1) leading to a σ-bonded vinyl intermediate, through a four-center transition state: i.e., the most common intermediate proposed for the formation of carbene or vinylidene species, from either mono-[16] or binuclear complexes.[17]

The next step, i.e. the final transfer of the second hydrogen in the hydrogenation process, can be briefly described as β-hydride transfer from the closest hydrogen-rich platinum atom on the coordinated vinyl ligand. For this latter point different possibilities must be considered.

Nucleophilic attack on unsaturated intermediates was demonstrated,[18] and very recently a new hydrogenation mechanism implying the hydride (H^-) transfer from a late-transition-metal center has been proposed.[19]

However, the β-carbon in metal−vinyl intermediates is considered the electron-rich site,[16c] so that this step is regarded as an electrophilic attack of a proton often supplied from an "external" H^+ source.[16c,17a,20] In the present case this is excluded by the isotopic distribution in complexes **5a** and **5b**, even considering the solvent or a second molecule of PhCCH[20b] as possible H^+ sources. In the absence of an "external" H^+ source, its formation "in situ" from the starting compound, e.g. HCl

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(13) E.g.: Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62 and references therein.

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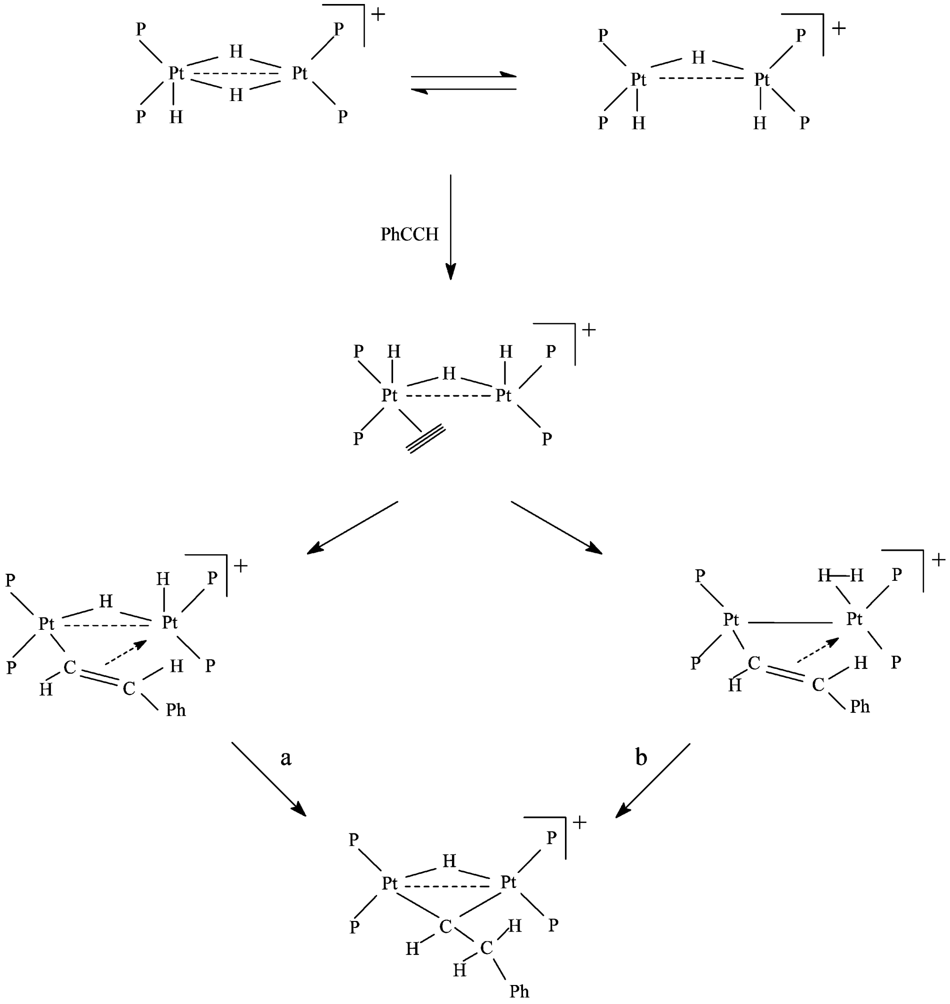
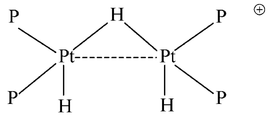
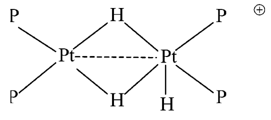
Scheme 1



from $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$,[16a] or a slightly positively charged hydride ($Pt^{\delta-}-H^{\delta+}$),[21] have been proposed as "internal" sources of H^+.

With regard to the possible "internal" sources, it is worth mentioning that in the solid state two different structures of the hydrido cations $[Pt_2(P\text{-}P)_2(H)_3]^+$ have been determined with one[5,22] or two[23] hydrides as bridging ligands, respectively:





It was previously suggested that these structural differences involve small energy changes, in agreement with the fluxional behavior observed in solution (at least down to 183 K). Even though the dynamic process has not yet been rationalized, it seems possible that classical and "nonclassical" hydrides are involved as intermediate core configurations, in agreement with the facile H_2 loss previously observed in various reactions with unsaturated molecules.[3a,e−f,5,6] Therefore, an elusive η^2-H_2 intermediate can be envisaged as an "internal" proton source, according to Esteruelas' hypothesis on the hydrogenation of the alkynyl intermediate $OsCl(CyC{\equiv}C)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ to the vinylidene compound $OsCl(H)(CyCH{=}C)(CO)(Pi\text{-}Pr_3)_2$.[20a]

Whatever the nature of the internal hydrogen source, the synthesis of the alkylidene **5** is accomplished through a concerted intramolecular process in which a vinyl intermediate, σ-bonded to a platinum center, is maintained close to a second hydrogen-rich platinum atom, possibly but not necessarily through an η^2 bond.

In conclusion, relevant points on the unexpected formation of complex **5** from PhCCH that should be emphasized are (i) the unprecedented behavior of a binuclear platinum hydride as a hydrogenating reagent, (ii) the unprecedented formation of the same compound from a binuclear metal complex and styrene or phenylacetylene under the same mild experimental conditions, (iii) the formation of a saturated hydrocarbon skeleton from an alkyne without the intermediate hydrogenation step to the corresponding olefin, usually considered in homogeneous processes[12] and recalling more the direct hydrogenation concept used in heterogeneous catalysis,[24] and (iv) the synergy exerted

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by two interlocked metal centers to accomplish the hydrogenation process.

Experimental Section

General Considerations. Styrene and phenylacetylene (Fluka) were distilled and their purity was checked by GC-MS before use. Phenylacetylene-*d* (98% D) and sodium borodeuteride (98% D) were purchased from Aldrich. The platinum complexes $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ and $[\mathrm{Pt_2(dppp)_2(D)_3}][\mathrm{BF_4}]$ were prepared as previously reported.[23a] Solvents were distilled prior to use. Diethyl ether was dried over sodium. Evaporation was always carried out under reduced pressure. The analytical samples were pumped to constant weight (room temperature, ca. 0.1 Torr). The elemental analyses were performed by the Microanalytical Laboratories of the University of Milan. IR spectra were recorded on a Jasco FT/IR 420 spectrometer. NMR spectra and HMQC (heteronuclear multiple quantum correlation spectroscopy), APT (attached proton test), and DEPT (distortionless enhancement by polarization transfer) experiments were recorded at ambient temperature on a Bruker DRX 300 Avance spectrometer operating at 300 (^{1}H), 75.4 (^{13}C), 121.5 (^{31}P), 46.07 (^{2}H), and 64.5 MHz (^{195}Pt), respectively. The shift values are given in ppm from the usual standards; ^{195}Pt NMR spectra are referenced to external $\mathrm{Na_2PtCl_6}$ aqueous solution. Mass spectra were recorded on a VG-7070 EQ spectrometer equipped with a PDP 11/73 data system and operating under FAB conditions with 3-nitrobenzyl alcohol (from Fluka) as matrix, bombarding the solutions with 8 keV Xe atoms; the *m*/*z* values are referenced to ^{195}Pt.

Synthesis of $[\mathbf{Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CHCH_2Ph)}][\mathbf{BF_4}]$ (5). (a) From Styrene. (1) In Dichloromethane. A stirred solution of $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ (175 mg, 0.134 mmol) and freshly distilled styrene (1.0 mL, $d = 0.906$ g/mL, 8.71 mmol) in dichloromethane (10 mL) was gently refluxed for 1 week. Addition of diethyl ether to the pale yellow solution gave the crude product. The analytically pure sample was obtained as a pale yellow solid by crystallization from dichloromethane and diethyl ether (131 mg, 69% yield). Anal. Calcd for $\mathrm{C_{62}H_{61}P_4Pt_2BF_4}$: C, 52.92; H, 4.33. Found: C, 52.97; H, 4.24. Mp: 213 °C dec.

(2) In Acetone. On carrying out the reaction as described above but in acetone solution ($[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ (207 mg, 0.160 mmol) and styrene (4 mL, 35 mmol) in 30 mL of solvent) and crystallizing the crude mixture from acetone and diethyl ether, higher yields were obtained (80%).

(b) From Phenylacetylene. A stirred solution of $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ (176 mg, 0.135 mmol) and phenylacetylene (1,0 mL, $d = 0.928$ g/mL, 9.11 mmol) in dichloromethane (10 mL) was gently refluxed for 1 week. The resulting deep red solution was filtered, and the crude product was precipitated as a brick red powder by addition of diethyl ether. The pale orange analytical sample was obtained as a more soluble fraction (124 mg, 65% yield) by two fractional crystallizations from dichloromethane and diethyl ether. Anal. Calcd for $\mathrm{C_{62}H_{61}P_4Pt_2BF_4}$: C, 52.92; H, 4.33. Found: C, 53.13; H, 4.22. Mp: 213 °C dec.

Spectroscopic Data for 5. IR (Nujol, cm^{-1}): 1050 vs $\nu_{\mathrm{BF_4}}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, δ): -2.60 tt ($^2J_{\mathrm{P}trans-\mathrm{H}} = 74$ Hz,$^2J_{\mathrm{P}cis-\mathrm{H}} = 9.6$ Hz, with satellites (ca. 1:8:18:8:1), $^1J_{\mathrm{Pt-H}} = 561$ Hz, 1H, μ-H); 3.0−1.7 m (14H, CH_2); 4.94 m (1H, μ-CHCH$_2$Ph); 7.6−6.8 m (45H, Ph). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, δ): 4.0 m ($^1J_{\mathrm{Pt-P}} = 4291$ Hz; $^3J_{\mathrm{Pt-P}} = 181$ Hz; from satellites: apparent $J_{\mathrm{P-P}} = 20$ Hz, $\mathrm{P}_{trans-\mathrm{H}}$); -7.0 m ($^1J_{\mathrm{Pt-P}} = 2104$ Hz, $\mathrm{P}_{trans-\mu-\mathrm{CH}}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_3COCD_3}$, δ): 4.8 m ($^1J_{\mathrm{Pt-P}} = 4287$ Hz; $^3J_{\mathrm{Pt-P}} = 179$ Hz; from satellites: apparent $J_{\mathrm{P-P}} = 20$ Hz, $\mathrm{P}_{trans-\mathrm{H}}$); -6.2 m ($^1J_{\mathrm{Pt-P}} = 2104$ Hz, $\mathrm{P}_{trans-\mu-\mathrm{CH}}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, δ): 146.2, 135−125 m (Ph); 46.0 s (μ-CHCH$_2$Ph); 28.3 m ($J_{\mathrm{P-C}} = 29$ Hz), 26.8 m ($J_{\mathrm{P-C}} = 37$ and 5 Hz), 19.8 m (P(CH$_2$)$_3$P). ^{1}H/^{13}C HMQC ($\mathrm{CDCl_3}$, δ): 1.89 (μ-CHCH_2Ph); 135.9 m ($^1J_{\mathrm{Pt-C}} = 489$ Hz, μ-CHCH$_2$Ph). ^{195}Pt{^{1}H} NMR ($\mathrm{CDCl_3}$, δ): -5436 (ddd, $^1J_{\mathrm{Pt-P}trans-\mathrm{H}} = 4290$ Hz, $^1J_{\mathrm{Pt-P}trans-\mu\text{-}\mathrm{CH}} = 2105$ Hz, $^3J_{\mathrm{Pt-P}trans-\mathrm{H}} = 181$ Hz). FAB MS: *m*/*z* 1317 [M − 2H]$^+$.

Synthesis of $[\mathbf{Pt_2(dppp)_2(\mu\text{-}H)(\mu\text{-}CDCH_2Ph)}][\mathbf{BF_4}]$ (5a) and $[\mathbf{Pt_2(dppp)_2(\mu\text{-}D)(\mu\text{-}CHCD_2Ph)}][\mathbf{BF_4}]$ (5b). 5a and **5b** were synthesized by following procedure b from $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ with phenylacetylene-*d* and from $[\mathrm{Pt_2(dppp)_2(D)_3}][\mathrm{BF_4}]$ with phenylacetylene, respectively.

(a) 5a. $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ (231 mg, 0.177 mmol) and phenylacetylene-*d* (1.0 mL, 9.03 mmol) were dissolved in dichloromethane (30 mL). The crude product was washed with diethyl ether, leading to the analytical sample (205 mg; yield 82%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): -2.58, tt ($^2J_{\mathrm{P}trans-\mathrm{H}} = 75$ Hz,$^2J_{\mathrm{P}cis-\mathrm{H}} = 9.8$ Hz, with satellites (ca. 1:8:18:8:1), $^1J_{\mathrm{Pt-H}} = 562$ Hz, 1H, μ-H); 2.9−1.9 m (14H, CH_2); 7.8−6.9 (m, 45H, Ph). ^{2}H NMR ($\mathrm{CDCl_3} + \mathrm{CHCl_3}$, δ): 4.94 m (μ-CDCH$_2$Ph). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, δ): 4.0 m ($^1J_{\mathrm{Pt-P}} = 4290$ Hz; $^3J_{\mathrm{Pt-P}} = 183$ Hz; from satellites: apparent $J_{\mathrm{P-P}}= 20$ Hz, $\mathrm{P}_{trans-\mathrm{H}}$); -6.7 m ($^1J_{\mathrm{Pt-P}} = 2108$ Hz, $\mathrm{P}_{trans-\mu}$ -CD). ^{13}C{^{1}H,^{31}P} DEPT NMR ($\mathrm{CDCl_3}$, δ): 135−125 m (Ph); 46.3 s (μ-CDCH$_2$Ph); 26.9 m, 28.2 m, 19.8 m (P(CH$_2$)$_3$P).

(b) 5b. $[\mathrm{Pt_2(dppp)_2(D)_3}][\mathrm{BF_4}]$ (110 mg, 0.084 mmol) and phenylacetylene (0.50 mL, 4.6 mmol) were dissolved in dichloromethane (22 mL). The crude product was washed with diethyl ether, leading to the analytical sample (106 mg; yield 89%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 2.9−1.8 m (12H, P(CH_2)$_3$P); 4.93 m, broad (1H, μ-CHCD$_2$Ph); 7.8−6.8 m (45H, Ph). ^{2}H NMR ($\mathrm{CDCl_3} + \mathrm{CHCl_3}$, δ): -2.51 t, broad ($J_{\mathrm{P-D}} \approx 11$ Hz, with satellites,$^1J_{\mathrm{Pt-D}} \approx 43$ Hz, μ-D); 1.87 m, broad (μ-CHCD_2Ph). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, δ): 4.0 m, broad ($^1J_{\mathrm{Pt-P}} = 4305$ Hz; $^3J_{\mathrm{Pt-P}} = 178$ Hz, $J_{\mathrm{P-P}}$ unresolved, $\mathrm{P}_{trans-\mathrm{D}}$); -6.9 m, broad ($^1J_{\mathrm{Pt-P}} = 2105$ Hz, $\mathrm{P}_{trans-\mu}$-CH). ^{13}C{^{1}H,^{31}P} ATP NMR ($\mathrm{CDCl_3}$, δ): 134−125 m (Ph); 45.5 m, broad (μ-CHCD$_2$Ph); 28.2 m, 26.9 m, 19.8 m (P(CH$_2$)$_3$P).

Reaction of the Mixture of $[\mathbf{Pt_2(dppp)_2(H)_3}][\mathbf{BF_4}]$ and $[\mathbf{Pt_2(dppp)_2(D)_3}][\mathbf{BF_4}]$ with Phenylacetylene. An equimolecular mixture of $[\mathrm{Pt_2(dppp)_2(H)_3}][\mathrm{BF_4}]$ (150 mg, 0.11 mmol) and $[\mathrm{Pt_2(dppp)_2(D)_3}][\mathrm{BF_4}]$ (150 mg, 0.11 mmol) was reacted with phenylacetylene (1 mL) by following the procedure b, and the crude product was washed with diethyl ether, leading to the analytical sample (245 mg; yield 79%). ^{13}C{^{1}H,^{31}P} DEPT NMR ($\mathrm{CDCl_3}$, δ): 135−125 m (Ph); 46.3 s (μ-CHCH$_2$Ph); 45.9 s,br (μ-CHCHD); 26.9 m, 28.2 m, 19.8 m (P(CH$_2$)$_3$P). ^{13}C{^{1}H,^{31}P} APT NMR ($\mathrm{CDCl_3}$, δ): 45.8 br (μ-CD$_2$).

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[24] E.g.: (a) Al-Ammar, A. S.; Webb, G. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 1900. (b) Sárkány, A.; Weiss, A. H.; Guczi, L. *J. Catal.* **1986**, *98*, 550. (c) Arafa, E. A.; Webb, G. *Catal. Today* **1993**, *17*, 411. (d) Jackson, S. D.; Shaw, L. A. *Appl. Catal. A: Gen.* **1996**, *134*, 91.