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Addition of Nucleophiles to Phosphanido Derivatives of Pt(III): Formation of P–C, P–N, and P–O Bonds

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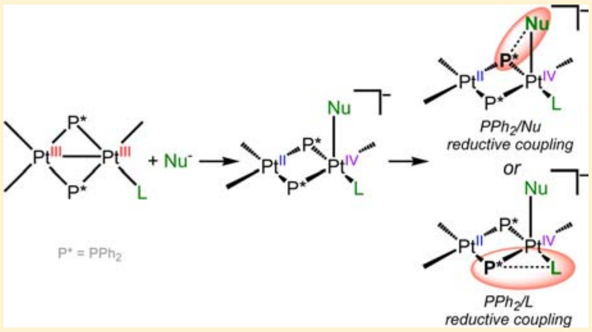
Ⓢ *Supporting Information*

ABSTRACT: The reactivity of the dinuclear platinum(III) derivative $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(R_F)_2]$*(Pt–Pt)* ($R_F = C_6F_5$) (**1**) toward OH^-, N_3^-, and NCO^- was studied. The coordination of these nucleophiles to a metal center evolves with reductive coupling or reductive elimination between a bridging diphenylphosphanido group and OH^-, N_3^-, and NCO^- or C_6F_5 groups and formation of P–O, P–N, or P–C bonds. The addition of OH^- to **1** evolves with a reductive coupling with the incoming ligand, formation of a P–O bond, and the synthesis of $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**3**). The addition of N_3^- takes place through two ways: (a) formation of the P–N bond and reductive elimination of PPh_2N_3 yielding $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**4a**) and (b) formation of the P–C bond and reductive coupling with one of the C_6F_5 groups yielding $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$ (**4b**). Analogous behavior was shown in the addition of NCO^- to **1** which afforded $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**5a**) and $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$ (**5b**). In the reaction of the trinuclear complex $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*$(Pt^{III}–Pt^{III})$* (**2**) with OH^- or N_3^-, the coordination of the nucleophile takes place selectively at the central platinum(III) center, and the PPh_2/OH^- or PPh_2/N_3^- reductive coupling yields the trinuclear $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$ (**6**) and $[NBu_4]$-$[(R_F)_2Pt^1(\mu_3\text{-}Ph_2PNPPh_2)(\mu\text{-}PPh_2)Pt^2(\mu\text{-}PPh_2)Pt^3(R_F)_2]$*$(Pt^2–Pt^3)$* (**7**). Complex **7** is fluxional in solution, and an equilibrium consisting of Pt–Pt bond migration was ascertained by ^{31}P EXSY experiments.

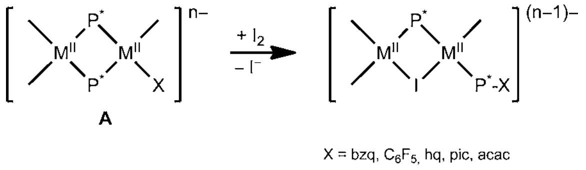


■ INTRODUCTION

Oxidation of platinum(II) and palladium(II) derivatives is the usual way to prepare complexes in high oxidation states (III and IV) which undergo easy reductive elimination processes which produce new M(II)/M(IV)/M(II) or M(II)/M_2(III)/M(II) cycles and provide transformations that are difficult to achieve otherwise. Despite the fact that platinum and palladium chemistry display rather similar trends in reactivity, the unambiguous characterization and isolation of dinuclear Pd(III) and mononuclear Pd(IV) intermediates in these cycles have been carried out only in the past 10 years.[1−18]

In the course of our current research on diphenylphosphanido derivatives of palladium(II) and platinum(II), we have reported (Scheme 1) that complexes of the type $[(R_F)_2M(\mu\text{-}PPh_2)_2M'XL]^{n-}$ (type **A**, $R_F = C_6F_5$) add I_2 affording new complexes $[(R_F)_2M(\mu\text{-}PPh_2)(\mu\text{-}I)M'(PPh_2X)L]^{(n-1)-}$ showing (a) the "$M(\mu\text{-}PPh_2)(\mu\text{-}I)M'$" fragment; (b) a new PPh_2X ligand, and (c) both metal centers in formal oxidation state (II).[19−22] Thus, oxidative addition of I_2 to the dinuclear phosphanido complexes of M(II) (type **A**) is followed by a reductive coupling process between a diphenylphosphanido bridged ligand and a pentafluorophenyl, benzo[*h*]quinolinate (bzq), 8-hydroxyquinolinate (hq), piccolinate (pic), or acetylacetonate (acac) groups with formation of P–C and P–O bonds (Scheme 1).

Scheme 1



These reductive couplings have been demonstrated to take place either via the dinuclear M(III)–M′(III) (type **B**) or from the mixed oxidation state M(II),M′(IV) (type **C**) intermediates (Scheme 2).[20−23] It has been concluded that both the

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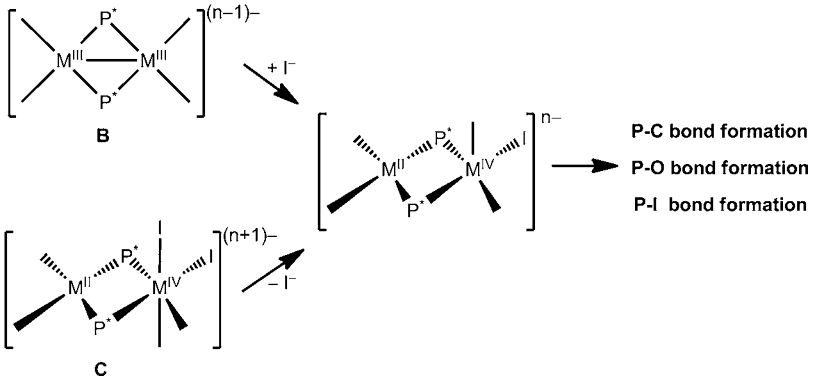
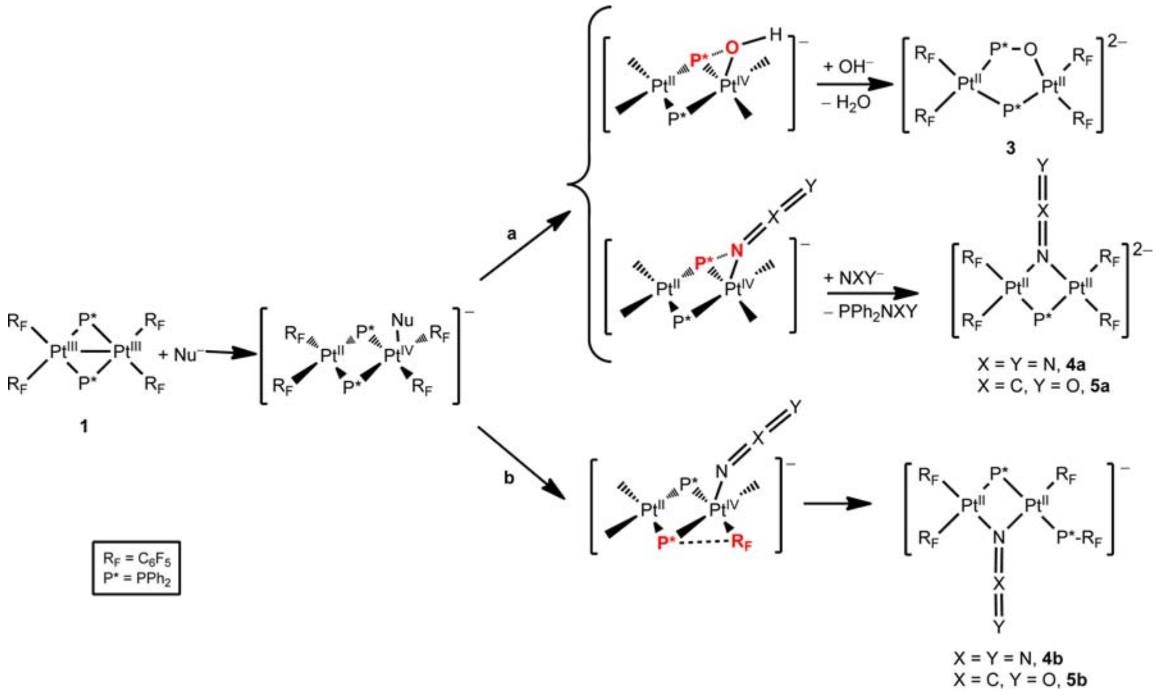
Scheme 2



Scheme 3



coordination of I^- to the M(III)−M′(III) type **B** complex[19,24,25] or the elimination of a I^- group from the M(II),M′(IV) type **C** complex[21,22] produces the unsaturated M(II),M′(IV) intermediate which evolves through a PPh_2/X reductive coupling with formation of P−C and P−O bonds. In this way complexes with $PPh_2C_6F_5$,[19,20,24−27] PPh_2bzq,[21] PPh_2hq,[22] PPh_2pic,[22] and PPh_2acac[22] ligands could be isolated. We have also identified in solution complexes with diphenyliodophosphine as a result of the reductive coupling between a diphenylphosphanido bridging ligand and the incoming ligand, the iodide group, with formation of a P−I bond.[22] Besides these studies, very little is known about the behavior of the M(III), M(III) phosphanido complexes and their role on the PPh_2/X reductive coupling.

Therefore, we have studied the reaction of several nucleophiles X^- with $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(R_F)_2]$*(Pt−Pt)* (**1**) and $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*($Pt^{III}$−$Pt^{III}$)* (**2**) (smoothly obtained by Ag^+ oxidation of $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$, and $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$, respectively) in order to establish the ability of these two complexes to produce PPh_2/X reductive coupling and to ascertain the nature of the final Pt(II) complexes.

RESULTS AND DISCUSSION

Reaction of $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(R_F)_2]$*(Pt−Pt)* (1) with OH^-, N_3^-, and OCN^-. Complex **1** shows the two Pt(III) centers in square planar environments, a Pt−Pt bond (30 valence electron count), and only one type of terminal ligand. The attack of a nucleophile to **1** is expected to occur at one of the two equivalent metal centers with rupture of the Pt−Pt bond and formation of an unsaturated Pt(II),Pt(IV) derivative.[3,28] Such a mixed-valence species can then evolve to the more stable Pt(II),Pt(II) system, via a reductive coupling.[29,30]

The addition of N^nBu_4OH to a CH_2Cl_2 solution of the Pt(III),Pt(III) **1** complex (2:1 molar ratio) gives the platinum(II) derivative $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**3**) in which the two metal centers with formal oxidation state (II) are bridged by a phosphanido and a phosphinito ligand (Scheme 3). Despite several attempts at crystallization we were not able to complete X-ray studies of the structure of complex **3** due to low quality of the crystals. However, the connectivity of the atoms of the anion was established unambiguously and is shown in Scheme 3.

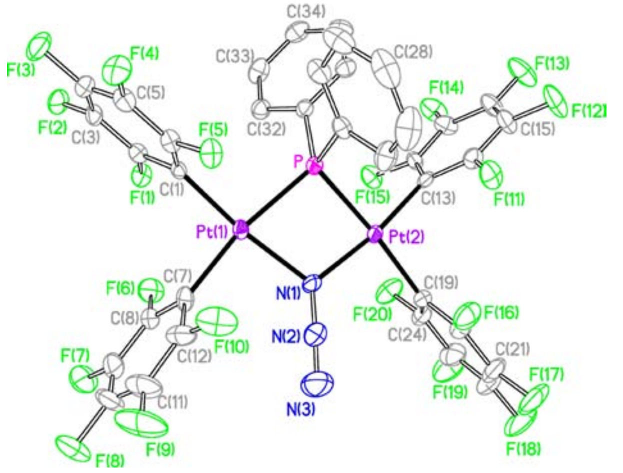


Figure 1. View of the molecular structure of the anion of the complex $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**4a**).

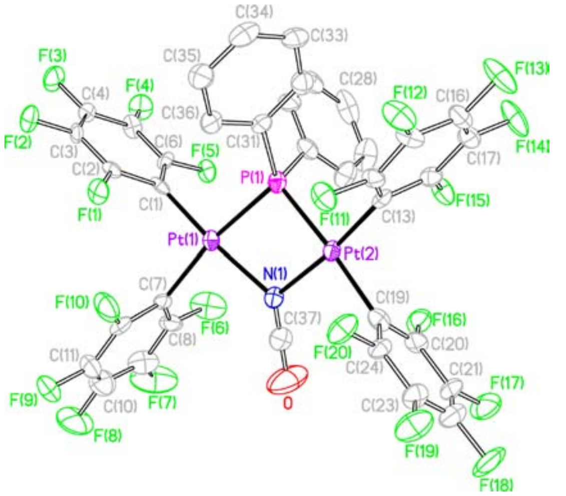


Figure 2. View of the molecular structure of the anion of the complex $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**5a**).

The addition of NaN_3 to a yellow solution of **1** in acetone at room temperature, followed by addition of $[NBu_4]ClO_4$, afforded a mixture of $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**4a**) and $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$ (**4b**) (Scheme 3). It is notable that the four R_F ligands of the Pt(III),Pt(III) starting material are maintained in the Pt(II),Pt(II) complex **4a**, but the two metal centers are joined by a phosphanido and an azide bridging group, indicating that in all likelihood a PPh_2/N_3 reductive elimination took place (Scheme 3) with decomposition of the very unstable PPh_2N_3 formed,[31−33] along with the coordination of an azide group as end-on ($\mu_{1,1}$-N_3) mode. In **4b** the two Pt(II) centers are also joined by a phosphanido and an azide bridging groups, but three R_F and a new $PPh_2(C_6F_5)$ ligand are bonded to the platinum centers, indicating the occurrence of a PPh_2/C_6F_5 reductive coupling (Scheme 3). Complex **4a** was isolated as a pure sample (see Experimental Section), but we were not able to obtain a pure sample of complex **4b**. Nevertheless, the structure of **4b** could be inferred by comparing the characteristic spectroscopic features with those observed for the previously reported $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}I)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$.[19]

Finally, we have carried out the reaction of acetone solutions of **1** with KOCN, followed by addition of $[NBu_4]ClO_4$, with a method similar to the previous reaction with NaN_3. When the reaction was carried out in a 1:2 molar ratio, a mixture of products was once again obtained. In this mixture, complexes $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]$ (**5a**) (Scheme 3) and $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$ (**5b**) analogous to **4a** and **4b**, respectively, were identified by ^{31}P and ^{19}F NMR spectroscopy. All attempts to isolate samples of pure **5a** as well as to separate complex **5a** from **5b**, even using different counterions in the processes, were unsuccessful. The addition of an excess of KOCN to acetone solutions of **1** allowed the isolation of **5b** as a pure sample (although signals of other unidentified species were observed in the ^{31}P NMR spectrum of the crude reaction product, no signals due to complex **5a** were observed). However, crystals of **5a** suitable for X-ray purposes were collected from a concentrated solution of one of the mixtures of **5a** and **5b** (see Experimental Section).

The structures of complexes **4a** and **5a** were established by X-ray diffraction studies. Figures 1 and 2 show views of the corresponding complexes, and Tables 1 and 2 list a selection of relevant bond distances and angles. Complexes **4a** and **5a** display similar structures, with the only difference being one of the bridging ligands, that is N_3^- for **4a** and NCO^- for **5a**. They are dinuclear complexes in which the "$Pt(R_F)_2$" fragments are held together by a PPh_2 and a N_3^- or NCO^- bridges. The Pt atoms lie in the center of conventional square planar environments. The complexes are not planar, with the dihedral angle between the two best Pt square planes 164.1(1)° for **4a** and 163.7(1)° for **5a**. The intermetallic distance is 3.400(1) Å for **4a** and 3.372(1) Å for **5a**, excluding any type of intermetallic interaction, as expected for a dinuclear derivative with a 32 valence electron count (VEC). For both complexes, the environment of the N bridging atom is planar (see Tables 1 and 2), and the geometry of the N−N−N and N−C−O fragments are linear. The Pt−N distances in **4a**, 2.105(4) and 2.101(4) Å, are shorter than those found in the complex with the "$Pt_3(\mu\text{-}1,1,1\text{-}N_3)$" fragment,[34] slightly larger than the Pt−N distances of terminal azido platinum derivatives,[35−37] and similar to the Pt−N distances found in complexes with the "$Pt(\mu\text{-}1,1\text{-}N_3)Pt$" skeleton.[38] In the case of the cyanate derivative no complexes with the skeleton "$M(\mu\text{-}1,1\text{-}NCO)M$" have been characterized by X-ray diffraction (CSD search). It is to note that in both cases the two bridging ligands are bonded to the platinum centers through both a soft and a hard donor atom (P and N) of the PPh_2 and N_3^- or NCO^-, respectively.

The HRMS(−) spectrograms of complexes **3**, **4a**, and **5b** showed intense signals ascribable to the anions of the complexes with an isotope pattern superimposable to that calculated on the basis of the proposed formula.

The ^{19}F NMR spectrum of **3** (deuteroacetone solution) shows 12 signals: four signals of the same intensity (2 F each) in the *o*-F region with platinum satellites, four signal of the same intensity (2 F each) due to *m*-F atoms, and four signals assignable to the four *p*-F atoms. This pattern indicates that the four C_6F_5 groups are inequivalent, and within each ring the two *o*-F atoms (and *m*-F atoms) are equivalent. The spectra of **4a** and **5a** (deuteroacetone solution) show six signals in 2:2:2:1:2:1 intensity ratio, as expected for a complex with two types of inequivalent pentafluorophenyl rings: two rings in position *trans* to the Pt−N bonds and two rings in position

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}N_3)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$ (**4a**·$CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$)

Pt(1)−C(1)	2.001(4)	Pt(1)−C(7)	2.056(4)	Pt(1)−N(1)	2.105(4)
Pt(1)−P	2.3140(11)	Pt(2)−C(13)	2.007(4)	Pt(2)−C(19)	2.062(4)
Pt(2)−N(1)	2.101(4)	Pt(2)−P	2.3067(11)	N(1)−N(2)	1.206(5)
N(2)−N(3)	1.155(6)				

C(1)−Pt(1)−C(7)	93.46(16)	C(1)−Pt(1)−N(1)	173.03(15)
C(7)−Pt(1)−N(1)	92.62(15)	C(1)−Pt(1)−P	96.86(11)
C(7)−Pt(1)−P	169.67(12)	N(1)−Pt(1)−P	77.05(10)
C(13)−Pt(2)−C(19)	91.05(16)	C(13)−Pt(2)−N(1)	171.97(14)
C(19)−Pt(2)−N(1)	96.82(15)	C(13)−Pt(2)−P	94.87(11)
C(19)−Pt(2)−P	173.98(12)	N(1)−Pt(2)−P	77.30(10)
Pt(2)−P−Pt(1)	94.74(4)	N(2)−N(1)−Pt(2)	126.2(3)
N(2)−N(1)−Pt(1)	125.8(3)	Pt(2)−N(1)−Pt(1)	107.89(15)
N(3)−N(2)−N(1)	178.5(6)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}NCO)(\mu\text{-}PPh_2)Pt^{II}(R_F)_2]CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$ (**5a**·$CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$)

Pt(1)−C(1)	1.964(7)	Pt(1)−C(7)	2.076(7)	Pt(1)−N(1)	2.155(6)
Pt(1)−P(1)	2.313(2)	Pt(2)−C(13)	1.963(7)	Pt(2)−C(19)	2.062(8)
Pt(2)−N(1)	2.139(6)	Pt(2)−P(1)	2.293(2)	N(1)−C(37)	1.177(9)
O−C(37)	1.188(9)				

C(1)−Pt(1)−C(7)	93.3(3)	C(1)−Pt(1)−N(1)	174.6(2)
C(7)−Pt(1)−N(1)	91.0(2)	C(1)−Pt(1)−P(1)	96.42(19)
C(7)−Pt(1)−P(1)	170.31(19)	N(1)−Pt(1)−P(1)	79.35(16)
C(13)−Pt(2)−C(19)	90.8(3)	C(13)−Pt(2)−N(1)	173.8(2)
C(19)−Pt(2)−N(1)	95.2(2)	C(13)−Pt(2)−P(1)	94.0(2)
C(19)−Pt(2)−P(1)	175.27(19)	N(1)−Pt(2)−P(1)	80.11(16)
Pt(2)−P(1)−Pt(1)	94.13(8)	C(37)−N(1)−Pt(2)	127.7(6)
C(37)−N(1)−Pt(1)	127.3(6)	Pt(2)−N(1)−Pt(1)	103.5(2)
N(1)−C(37)−O	179.7(11)		

trans to the Pt−P bonds. Signals due to complexes **4b** and **5b** are unambiguously identified in the ^{19}F NMR spectra, and the data compare well with those obtained for the previously reported $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}I)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F))]$.[19] The ^{19}F signals due to the new ligand $PPh_2C_6F_5$ appear well separated from those due to the three R_F groups bonded to Pt,[20,24−26,39] and they can be easily assigned in our spectra. The $^{31}P\{^1H\}$ NMR spectra of **3**−**5** in deuteroacetone solution are very informative. The chemical shift of P atom of phosphanido bridging ligands in **1**, δ 281.7, decreases significantly in **3**−**5** as is to be expected due to the change of a "$M(\mu\text{-}PPh_2)_2M$" fragment with metal−metal bond into a saturated "$M(\mu\text{-}X)(\mu\text{-}PPh_2)M$" fragment without Pt−Pt bond.[25,40−42] The transformation of a phosphanido ligand into a *P*,*O*-bridging phosphinito (complex **3**) or a terminal $PPh_2C_6F_5$ phosphane group (complexes **4b** and **5b**) results in signals at δ 127.1, δ 13.4, and δ 12.6, respectively. All data obtained from the spectra are collected in the Experimental Section.

The detection of ^{195}Pt resonances for Pt complexes with C_6F_5 ligands is usually tricky, because of multiple ^{195}Pt−^{19}F couplings along with all other couplings (i.e., with ^{31}P) giving rise to very broad signals. In order to get spectra of good quality, and given that no proton is strongly scalar coupled to each platinum, we decided to carry out $^{195}Pt\{^{19}F\}$ experiments for complexes **3**, **4a**, and **5b**. Figure 5 shows the $^{195}Pt\{^{19}F\}$ spectrum of **3**, showing a doublet for Pt^2 at δ −3719 ($^1J_{Pt-P}$ = 2185 Hz) and a doublet of doublets for Pt^1 at δ −4498 ($^1J_{Pt-P}$ = 3020 and 1840 Hz). For complexes **4a** and **5b** the ^{195}Pt signals were found at δ −3381 (**4a**) and at δ −3522 and δ −3953 (**5b**). ^{195}Pt satellites originated from the geminal ^{195}Pt−^{195}Pt coupling were observable in the $^{195}Pt\{^{19}F\}$ spectrum of **5b**, from which a $^2J_{Pt-Pt}$ = 1310 Hz could be extracted. The chemical shifts found for **3**, **4a**, and **5b** lie in the range expected for phosphanido bridged diplatinum complexes.

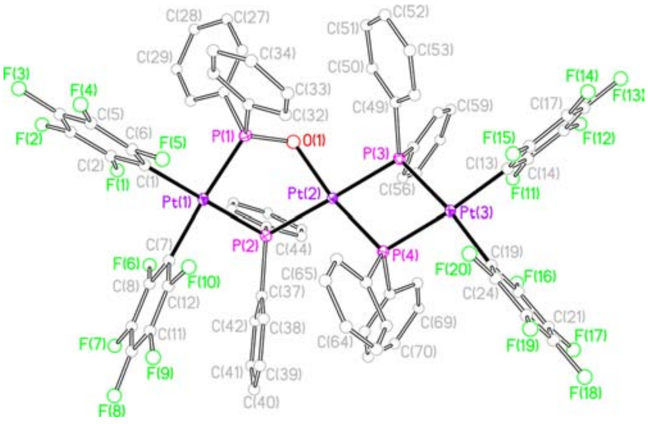


Figure 3. View of the molecular structure of the anion of the complex $[NBzMe_3]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]\cdot$(**6′**).

The IR spectra in the solid state of pure samples of **3**, **4a**, and **5b** were recorded. The absorption in the 950 cm^{-1} region in the pentafluorophenyl derivatives is related with the oxidation state of the metal center bonded to the C_6F_5 group. This absorption appears at 947, 951, and 953 cm^{-1} in the Pt(II) complexes **3**, **4a**, and **5b**, respectively, while it appears at 964 cm^{-1} in the Pt(III) starting material **1**.[23] This red shift of the frequencies is in agreement with the change of the formal

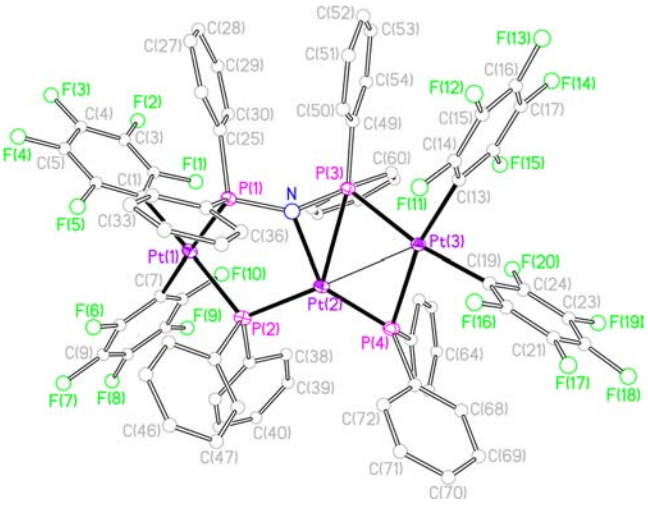


Figure 4. View of the molecular structure of the anion of the complex $[PPh_3Me][Pt_3^{II}(\mu_3\text{-}Ph_2PNPPh_2)(\mu\text{-}PPh_2)_2(R_F)_4]\cdot(7')$.

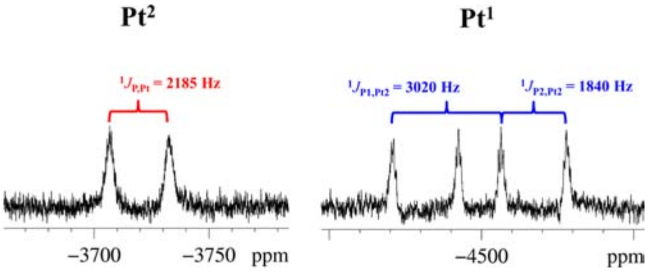


Figure 5. $^{195}Pt\{^{19}F\}$ spectrum of **3** (acetone-d_6, 293 K).

oxidation state of the platinum centers.[23] The spectra of **4a** and **5b** exhibit an strong absorption at 2067 and 2171 cm^{-1}, respectively, corresponding to the stretching vibrations of the azide and cyanate ligand.[43,44]

The reactivity exhibited by **1** toward OH^-, N_3^-, and OCN^- can be easily explained (Scheme 3) assuming that the nucleophile coordinates to one of the platinum(III) centers of **1** through the oxygen atom for the OH^- or the nitrogen atom for the N_3^- and NCO^- groups, giving rise to an anionic, unsaturated Pt(II),Pt(IV) intermediate. Taking into account that five-coordinated Pt(IV) intermediates are usually proposed in reductive elimination processes and some of them crystallographically characterized,[45−54] the unsaturated Pt(II),Pt(IV) species proposed in Scheme 3 could evolve in two different ways: (a) reductive coupling between the phosphanido bridging ligand and the added nucleophile (affording **3** and **4a**/**5a** with $PPh_2(NXY)$ elimination) or (b) coupling between the phosphanido bridging ligand and the C_6F_5 ligand initially present in the starting material (yielding **4b** and **5b**). In both cases, the intermediacy of a five-coordinated P atom, a well established fact for both phosphane and phosphanide derivatives,[40,55−61] has to be invoked.

The addition of OH^- can take place with formation of a coordinated PPh_2OH (PPh_2/OH coupling) which affords the *P*,*O*-bridging phosphinito complex **3** upon deprotonation by a second hydroxide (Scheme 3). Some phosphinito bridged complexes showing the Pt−P−O−Pt sequence have been structurally characterized,[62−67] and examples with both μ-phosphanido and μ-phosphinito Pt(I) derivatives have been synthesized and studied.[68−73] On the other hand, we have recently reported the synthesis of $[(PPh_2R_F)(R_F)Pt^{II}(\mu\text{-}OH)(\mu\text{-}PPh_2)Pt^{II}(dppe)][ClO_4]$[27] which seems to be formed from an undetected Pt(III),Pt(III) cationic intermediate $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(dppe)][ClO_4]_2$ through a PPh_2/C_6F_5 coupling and the coordination of a bridging OH, but we did not observe the PPh_2/OH coupling as in **3**. If the proposed azide or cyanate Pt(II),Pt(IV) intermediates evolve according to pathway a, a P−N bond can be formed by reductive coupling between phosphanido and azide (or cyanate) giving a coordinate PPh_2N_3 (or PPh_2NCO) which eliminates and easily decomposes.[32,33] Finally, the coordination environment of the metal centers can be completed with a $\mu_{1,1}$-N_3 ligand (or NCO), and **4a** (or **5a**) could be formed. Should pathway b be operative, the nucleophile would behave initially as a spectator, and the evolution of the proposed unsaturated intermediate of Pt(II),Pt(IV) could produce the reductive coupling between a phosphanido ligand and a pentafluorophenyl group. The coordination of the metal centers would be completed by bridging coordination of the nucleophile added affording **4b** and **5b**, i.e., a process similar to the one which produces $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}I)(\mu\text{-}PPh_2)Pt^{II}(R_F)(PPh_2R_F)]$.[19] The formation of **3**, **4a,b**, and **5a,b** mixtures indicates that the formation of a P−O bond is favored with respect the P−C coupling but the P−N bond formation competes with the P−C coupling in these intermediates.

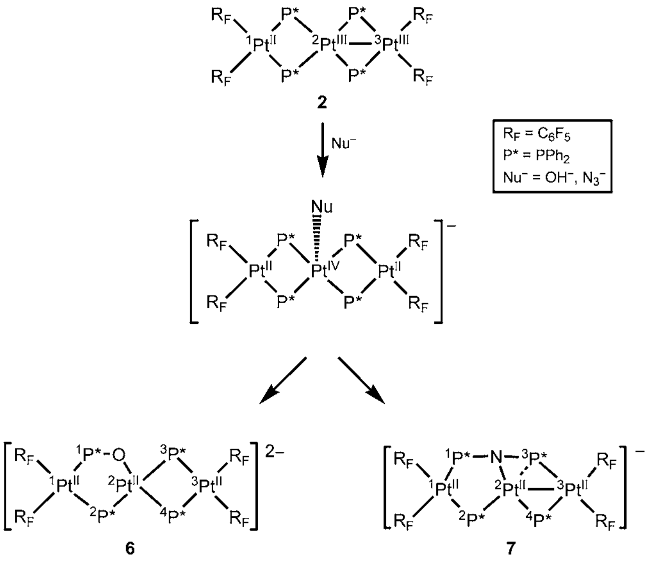
Reaction of $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*(Pt−Pt)* (2) with $OH^-$and N_3^-. The preparation of the trinuclear Pt(III),Pt(III),Pt(II) complex $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*(Pt−Pt)* (**2**) was reported some years ago.[74] Complex **2** is also an unsaturated compound which contains two Pt(III) centers suitable to react with nucleophiles as in **1**. However, **2** displays the Pt(III) centers in two different chemical environments: the terminal Pt(III) bonded to two C_6F_5 and two PPh_2, and the central Pt(III), bonded to four phosphanido ligands. This situation could differentiate the reactivity of the two Pt(III) centers toward the nucleophiles. We have studied the reaction of **2** toward OH^- and N_3^-.

The addition of N^nBu_4OH or NaN_3 (as methanol solutions) to a CH_2Cl_2 or acetone suspension of the trinuclear Pt(III),Pt(III),Pt(II) complex **2** gives, after work-up, the trinuclear platinum(II) derivatives $[NBu_4]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$ (**6**) and $[NBu_4][Pt_3^{II}(\mu_3\text{-}Ph_2PNPPh_2)(\mu\text{-}PPh_2)_2(R_F)_4]$ (**7**), respectively (Scheme 4).

Complexes **6** and **7** show the three platinum centers in formal +2 oxidation state and one PPh_2O^- group bridging two platinum centers in **6** or one $PPh_2NPPh_2^-$ group coordinated as bridging ligand to three platinum atoms in **7**. In both cases the pentafluorophenyl groups remain bonded in mutual *cis*-position to the two terminal platinum centers. Unfortunately, only low quality crystals of **6** and **7** for X-ray studies were obtained. The complete X-ray studies could be performed for the complexes $[NBzMe_3]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$ (**6′**) and $[PPh_3Me][Pt_3^{II}(\mu_3\text{-}Ph_2PNPPh_2)(\mu\text{-}PPh_2)_2)(R_F)_4]$ (**7′**) (see Experimental Section). Figures 3 and 4 show views of the corresponding anions of the complexes, and Tables 3 and 4 list a selection of relevant bond distances and angles.

In the anion of **6′** (see Figure 3) the three metal atoms are disposed in an almost linear arrangement [Pt(1)−Pt(2)−Pt(3) = 156.2(1)°]. Pt(1) and Pt(2) are supported by a phosphanido, $P(2)Ph_2$, and a phosphinito, $Ph_2P(1)−O$, bridging ligands whereas Pt(2) and Pt(3) are supported by two PPh_2 groups,

Scheme 4



P(3) and P(4). Each terminal metal center, Pt(1) and Pt(3), is coordinated to two pentafluorophenyl groups. The three platinum atoms lie in the center of square planar environments in such a way that the core of the anion is not planar. The five membered ring formed by phosphinite P(1)–O, P(2) phosphanide, Pt(1) and Pt(2) atoms is not planar; the dihedral angle between the best C(1), C(7), Pt(1), P(1), P(2) plane and the best O, P(2), Pt(2), P(3), and P(4) plane is 39.6(1)°, and that between the best O, P(2), Pt(2), P(3), and P(4) plane and the best C(13), C(19), Pt(3), P(3), and P(4) plane is 8.6(1)°. The long intermetallic distances [Pt(1)···Pt(2) = 3.846(1) Å, Pt(2)···Pt(3) = 3.599(1) Å] discard any kind of bonding interaction between the metal centers, as expected for a saturated trinuclear platinum complex with 48 valence electron count.

The structure of the anion of 7′ is shown in Figure 4. The most remarkable feature is that it contains the bis(diphenylphosphanyl)amide ligand $(Ph_2P)_2N^-$ which has to be formed as a result of the coupling of two PPh_2^- groups and the N_3^- ligand. Below we will comment on the structural characteristics of this ligand in the anion of 7′ and its formation. The whole anion, which is trinuclear, displays two pentafluorophenyl groups coordinated to each terminal platinum center, Pt(1) and Pt(3). The phosphanido group, $P(2)Ph_2$, is bridging Pt(1) and Pt(2) centers while $P(4)Ph_2$ bridges Pt(2) and Pt(3). In addition, the metal mediated formed bis(diphenylphosphanyl)amide ligand bonds the metal centers in an unprecedented way: P(1) is bonded to Pt(1) and P(3) is bonded to Pt(3) while N and P(3) are bonded to Pt(2). The Pt(1)–P(1) and Pt(3)–P(3) distances (2.2885(9) Å and 2.3712(10) Å) are the expected for conventional Pt–P bonds. The fragment N–P(3) can be considered interacting with Pt(2) through a Pt(2)–N covalent bond and Pt(2)–P(3) weak interaction with a Pt(2)–P(3) distance of 2.6207(9) Å. Notwithstanding, considering that the N center is nearly planar (the angles around N atom equals 354.3°) and the two P(1,3)–N (distances are 1.662(3) and 1.636(3) Å, respectively) are shorter than the single-bond P–N, a π-bonding contribution to these P–N bonds should be considered and a η^2 coordination mode of the P(3)–N fragment, to Pt(2) could be invoked.[75−80] Such a type of interaction is well represented usually in lanthanoid bis(diphenylphosphanyl)amido complexes.[33,75,81−85] In 7′ the bis(diphenylphosphanyl)amide behaves as a six electron donor ligand and coordinates to the three platinum centers in an unprecedented μ_3-bridge mode.[86] This type of coordination implies that the P(3) atom is five-coordinated.[55−60] The total valence electron count of the skeleton is 46, and a Pt–Pt bond should be expected. The very different intermetallic distances (Pt(1)–Pt(2) 3.761(1) Å, Pt(2)–Pt(3) 2.7374(2) Å) are in agreement with the existence of an intermetallic bond between Pt(2) and Pt(3) centers.[87]

The two platinum(III) centers of the Pt(III),Pt(III),Pt(II) starting material **2** are different: the terminal Pt(III), which is analogous to the platinum atoms of the Pt(III),Pt(III) dinuclear complex **1**, and the central platinum(III) which is bonded to four P atoms. If it is assumed that the reaction starts with the coordination of the OH^- or N_3^- groups to a platinum(III) center, the formation of **6** and **7** seems to indicate that the coordination of the nucleophile to the central platinum(III) is preferred to the coordination on the terminal Pt(III) center. In this way trinuclear Pt(II),Pt(IV),Pt(II) intermediates could be formed. The reductive coupling between the two groups bonded to the central platinum(IV), phosphanido and hydroxide or azide, forms P–O or P–N bonds and leave the metal center in formal oxidation state (II). Thus, the formation of **6** takes place in a similar way to the formation of the dinuclear complex **3**. However, the formation of complex **7** implies a more complicated process. It could be assumed that a

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[NBzMe_3]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]\cdot 3Me_2CO$ ($6'\cdot 3Me_2CO$)

Pt(1)–C(1)	2.062(4)	Pt(1)–C(7)	2.062(4)	Pt(1)–P(1)	2.2835(10)
Pt(1)–P(2)	2.3137(10)	Pt(2)–O(1)	2.116(2)	Pt(2)–P(4)	2.2590(10)
Pt(2)–P(3)	2.3184(10)	Pt(2)–P(2)	2.3536(10)	Pt(3)–C(13)	2.064(4)
Pt(3)–C(19)	2.065(4)	Pt(3)–P(3)	2.3015(10)	Pt(3)–P(4)	2.3040(10)
P(1)–O(1)	1.553(3)				
C(1)–Pt(1)–C(7)	88.81(14)		C(1)–Pt(1)–P(1)	93.75(10)	
C(7)–Pt(1)–P(1)	174.84(10)		C(1)–Pt(1)–P(2)	177.61(10)	
C(7)–Pt(1)–P(2)	92.07(10)		P(1)–Pt(1)–P(2)	85.54(4)	
O(1)–Pt(2)–P(4)	169.69(6)		O(1)–Pt(2)–P(3)	94.42(7)	
P(4)–Pt(2)–P(3)	76.75(4)		O(1)–Pt(2)–P(2)	82.12(7)	
P(4)–Pt(2)–P(2)	107.46(3)		P(3)–Pt(2)–P(2)	169.99(3)	
C(13)–Pt(3)–C(19)	89.62(14)		C(13)–Pt(3)–P(3)	97.14(10)	
C(19)–Pt(3)–P(3)	173.22(10)		C(13)–Pt(3)–P(4)	172.65(9)	
C(19)–Pt(3)–P(4)	97.08(10)		P(3)–Pt(3)–P(4)	76.21(3)	

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [PPh$_3$Me][Pt$_3$^{II}(μ_3-Ph$_2$PNPPh$_2$)(μ-PPh$_2$)$_2$(R$_F$)$_4$]·Me$_2$CO·*n*-C$_6$H$_{14}$ (7′·Me$_2$CO·*n*-C$_6$H$_{14}$)

Pt(1)−C(7)	2.070(4)	Pt(1)−C(1)	2.075(4)	Pt(1)−P(1)	2.2885(9)
Pt(1)−P(2)	2.3266(10)	Pt(2)−N	2.096(3)	Pt(2)−P(4)	2.1646(10)
Pt(2)−P(2)	2.2780(10)	Pt(2)−P(3)	2.6207(9)	Pt(2)−Pt(3)	2.7374(2)
Pt(3)−C(19)	2.065(4)	Pt(3)−C(13)	2.068(3)	Pt(3)−P(3)	2.3712(10)
Pt(3)−P(4)	2.3989(9)	P(1)−N	1.662(3)		
C(7)−Pt(1)−C(1)	86.18(14)		C(7)−Pt(1)−P(1)	176.54(11)	
C(1)−Pt(1)−P(1)	95.06(10)		C(7)−Pt(1)−P(2)	89.82(10)	
C(1)−Pt(1)−P(2)	175.93(10)		P(1)−Pt(1)−P(2)	88.90(3)	
N−Pt(2)−P(4)	143.29(9)		N−Pt(2)−P(2)	92.68(8)	
P(4)−Pt(2)−P(2)	123.06(4)		N−Pt(2)−P(3)	38.62(8)	
P(4)−Pt(2)−P(3)	105.52(3)		P(2)−Pt(2)−P(3)	125.82(3)	
C(19)−Pt(3)−C(13)	84.22(14)		C(19)−Pt(3)−P(3)	169.65(10)	
C(13)−Pt(3)−P(3)	87.55(10)		C(19)−Pt(3)−P(4)	81.99(10)	
C(13)−Pt(3)−P(4)	166.03(10)		P(3)−Pt(3)−P(4)	106.41(3)	
P(3)−N−P(1)	143.20(19)		P(3)−N−Pt(2)	88.29(13)	
P(1)−N−Pt(2)	122.75(15)				

reductive coupling between a bridging phosphanido ligand and the terminal azide group takes place with formation of a Pt(1)−P(1)−N−Pt(2) system. The formation of the N−P(3) has to take place with concomitant breaking off the Pt(2)−P(3) bond and elimination of N$_2$. The formation of the P−N bonds in some transition metal complexes has been observed,[77−79] and although the synthesis of complexes with the diphosphanylamide (Ph$_2$P)$_2$N$^-$ group is known,[33,75] the synthesis of the bis(diphenylphosphanyl)amide ligand in **7** is unprecedented: it is formally the result of transformation of two phosphanido bridging groups, one terminal azido ligand, and a Pt(IV) center into a new three-dentate ligand, (Ph$_2$P)$_2$N$^-$, a Pt(II) center, and N$_2$. The (Ph$_2$P)$_2$N$^-$ group has been previously used as a polydentate ligand bonded to Pt, but is usually obtained through deprotonation of bis(diphenylphosphanyl)amine (dppa), (Ph$_2$P)$_2$NH, and used in coordination chemistry.[75,81−83,86] In complex **7** the coordination of the bis(diphenylphosphanyl)amide (Ph$_2$P)$_2$N$^-$ is unusual because the six-electron-donor ligand bridges the three platinum centers. Although the formation of the bis(diphenylphosphanyl)amide ligand seems very striking, it is notable that the bridging Ph$_2$P−O$^-$ ligand is isoelectronic with Ph$_2$P−N(X)$^-$, X = PPh$_2$, and the initial processes which afford **6** and **7** are actually analogous.

The HRMS(−) spectrograms of complexes **6** and **7** showed intense signals ascribable to the anions of the complexes with an isotope pattern superimposable to that calculated on the basis of the proposed formula.

The ^{31}P{^{1}H} NMR spectra of **6** and **7** in deuteroacetone solution shows four signals. The signals are broad as a consequence of unresolved coupling with the ^{19}F nuclei and are in full agreement with the solid state structure. Complex **6** shows at the low field of spectrum a signal at δ 123.6 due to the P atom of the new phosphinito group (P^1 see Figure 3 for atom numbering) and a doublet (290 Hz) at δ 13.9 assignable to P atom of the phosphanido group in the "Pt(μ-P^{2}Ph$_2$)Pt" fragment. Signals due to P^3 and P^4 appear at high field, as is expected for a four-membered "Pt(μ-PPh$_2$)$_2$Pt" ring without metal−metal bond.[88] In the spectrum of **7**, the signals due to P atoms of phosphanido groups appear at δ 140.6 and at δ 30.7 as broad singlets and are assigned to P^4 and P^2, respectively (see Figure 4 for atom numbering). These chemical shifts are those expected for single diphenylphosphanido "Pt(μ-PPh$_2$)Pt" system with and without metal−metal bond, respectively. The signals due to P atoms of the new bis(diphenylphosphanyl)amide ligand appear centered at δ 128.4 and at δ 31.7 as broad doublets ($^2J_{P1,P3} \approx 70$ Hz). The signal at δ 128.4 shows only a pair of platinum satellites and is assigned to P^1. The signal due to P^3 and centered at δ 31.7 shows, besides platinum satellites due to the coupling with Pt^3 ($^1J_{Pt^3,P^3} \approx 1700$ Hz), satellites due to the coupling with Pt^2 in agreement with the Pt(2)···P(3) distance in solid state (2.7374(2) Å). The value of this coupling between Pt^2 and P^3 (ca. 510 Hz) is in the range of that observed in other complex in which a pentacoordinated P atom of a phosphanido group bridges three platinum centers.[59]

^{31}P EXSY experiments carried out in acetone-d_6 solution revealed that complex **7** is fluxional. In fact, the ^{31}P EXSY spectrum at 323 K (Figure 6) shows exchange cross peaks between the signals at δ 128.4 and at δ 31.7 (P^1/P^3 exchange) and between the signals at δ 140.6 and at δ 30.7 (P^4/P^2 exchange). This outcome can be explained in terms of an equilibrium in which the Pt−Pt bond migrates from one side of the molecule to the other (Scheme 5). A Pt−Pt bond migration was already observed for **2** in acetone-d_6.[74] However, while in the case of **2** the fast exchange regime is attained already at room temperature, for **7** the fast exchange regime is not yet attained at 323 K.

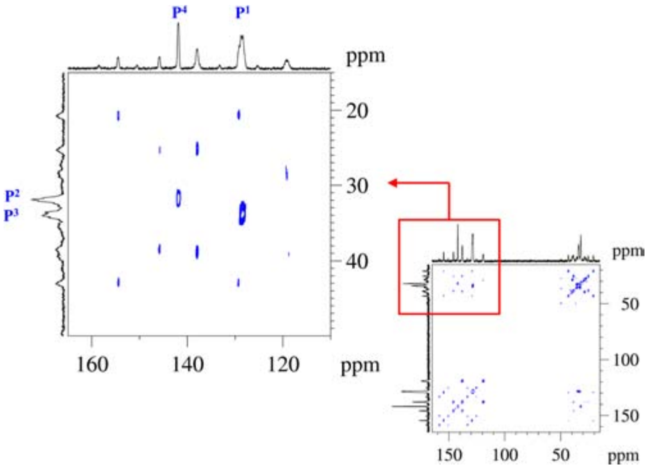


Figure 6. ^{31}P EXSY spectrum of **7** (acetone-d_6, 323 K).

Scheme 5. Dynamic Behavior of 7 at 323 K

The ^{195}Pt NMR data for **6** and **7** were obtained carrying out, as in the cases of **3**, **4a**, and **5b**, ^{195}Pt{^{19}F} experiments. The signals of **6** were found at δ −4497 (Pt^{1}), δ −3657 (Pt^{2}), δ −3828 (Pt^{3}), while those for **7** were found at δ −4506 (Pt^{1}), δ −4868 (Pt^{2}),δ −5439 (Pt^{3}).

■ CONCLUDING REMARKS

Phosphanido groups have shown to be excellent ligands in development of molecular architecture and synthesis of specific transition metal complexes.[88,89] The strong P−M bond was thought to be the reason for the stability and the very low reactivity of polynuclear complexes containing bridging phosphanido ligands. Nevertheless, the oxidation of the metal centers has been shown to be a way to induce an unexpected reactivity on bridging phosphanido ligands.[20−22,25,90] In this work we conclude that, in the oxidized Pt(III) binuclear derivative, the phosphanido group reacts not only with the ligands bonded to the metal center in the starting material (formation of [NBu$_4$][(R$_F$)$_2$Pt^{II}(μ-X)(μ-PPh$_2$)Pt^{II}(R$_F$)-(PPh$_2$R$_F$)] **4b** and **5b**), but also with the suitable groups added to the oxidized intermediates as is demonstrated with the formation of **3**, **4a**, and **5a**. The synthesis of **6** and **7** indicates that the coordination of hydroxide or azide to the central platinum(III) of the trinuclear complex **2**, "Pt^{III}(μ-P)$_4$" fragment, is preferred to the coordination to the terminal platinum(III), "Pt^{III}(R$_F$)$_2$(μ-P)$_2$" fragment. The PPh$_2$/OH$^-$ or PPh$_2$/N$_3{}^-$ reductive couplings form new ligands in the coordination sphere of the platinum.

■ EXPERIMENTAL SECTION

General Procedures and Materials. C, H, and N analyses were performed with a Perkin-Elmer 2400 CHNS analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (ATR in the range 250−4000 cm^{-1}). NMR spectra in solution were recorded on a Bruker AV-400 spectrometer with SiMe$_4$, CFCl$_3$, 85% H$_3$PO$_4$, and H$_2$PtCl$_6$ as external references for ^{1}H, ^{19}F, ^{31}P, and ^{195}Pt, respectively. ^{195}Pt{^{19}F} experiments were carried out setting the offset of the decoupler at the chemical shift of the *ortho*-F atoms of each complex. High resolution mass spectrometry (HRMS) was performed using a time-of-flight mass spectrometer equipped with an electrospray ion source (Bruker micrOTOF-Q II). The analyses were carried out in negative ion mode. The samples were introduced as acetonitrile solutions by continuous infusion with the aid of a syringe pump at a flow rate of 180 μL/h. The instrument was operated at end plate offset −500 V and capillary −4500 V. Nebulizer pressure was 0.3 bar (N$_2$) and the drying gas (N$_2$) flow 4 L/min. Drying gas temperature was set at 453 K. The software used for the simulations is Bruker Daltonics Data Analysis (version 4.0). Literature method was used to prepare the starting materials [(R$_F$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{III}(R$_F$)$_2$][23] and [(R$_F$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{II}(R$_F$)$_2$].[74]

Caution! *Azido complexes are potentially explosive, especially in the presence of organic ligands. Therefore, these compounds must be handled with care and prepared only in small amounts.*

Reaction of [(R$_F$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{III}(R$_F$)$_2$](*Pt^{III}−Pt^{III}*) with N^{n}Bu$_4$OH. To a yellow solution of **1** (0.156 g, 0.110 mmol) in CH$_2$Cl$_2$ (25 mL) was added 0.220 mol of N^{n}Bu$_4$OH (0.22 mL of 1 M methanol solution). The solution was stirred at room temperature for 10 min, and the resulting pale yellow solution was evaporated to dryness. The residue was washed three times with ^{i}PrOH/hexane (1 mL/5 mL) and recrystallized from CH$_2$Cl$_2$/^{i}PrOH. Complex **3** (white solid) was filtered and washed with ^{i}PrOH (2 × 0.5 mL). Yield: 0.114 g, 54%. Anal. Found (Calcd for C$_{80}$F$_{20}$H$_{92}$N$_2$OP$_2$Pt$_2$): C, 49.67 (49.79); H, 4.80 (4.81); N 1.31 (1.45).

HRMS (−), exact mass for the dianion [C$_{48}$F$_{20}$H$_{20}$OP$_2$Pt$_2$]$^{2-}$: 721.9984 Da. Measured m/z: 721.9980 (M)$^{2-}$. ^{1}H NMR (acetone-d_6, 293 K, 400 MHz), δ: 7.69 (pseudo t, 2 H, ${}^{3}J_{H,H}$ = 8.2 Hz, *o*-H bonded to *P*Ph$_2$), 7.56 (pseudo t, 2 H, ${}^{3}J_{H,H}$ = 8.0 Hz, *o*-H bonded to *P*-O), 7.10 (t, 1 H, ${}^{3}J_{H,H}$ = 6.8 Hz, *p*-H bonded to *P*Ph$_2$), 7.04 (pseudo t, 2 H, ${}^{3}J_{H,H}$ = 7.2 Hz, *m*-H bonded to *P*Ph$_2$), 6.89 (t, 1 H, ${}^{3}J_{H,H}$ = 6.8 Hz, *p*-H bonded to *P*Ph$_2$), 6.82 (pseudo t, 2 H, ${}^{3}J_{H,H}$ = 7.2 Hz, *m*-H bonded to *P*Ph$_2$), 3.49 (m, 16H, NBu$_4{}^+$), 1.87 (m, 16 H, NBu$_4{}^+$), 1.48 (pseudo sextet, 16H, ${}^{3}J_{H,H}$ = 7.4 Hz, NBu$_4{}^+$), 1.02 (t, 24 H, ${}^{3}J_{H,H}$ = 7.4 Hz, NBu$_4{}^+$). ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −114.1 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 308 Hz), −115.2 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 334 Hz), −116.4 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 349 Hz), −116.7 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 526 Hz), −168.7 (2 *m*-F), −169.0 (2 *m*-F), −169.2 (2 *m*-F), −169.7 (1 *p*-F), −170.3 (1 *p*-F), −170.6 (1 *p*-F), −171.7 (2 *m*-F), −173.6 (1 *p*-F). ^{31}P{^{1}H} NMR (acetone-d_6, 293 K, 162.0 MHz), δ: 127.1 (${}^{1}J_{P,Pt1}$ = 3020 Hz, *P*-O), 0.1 (${}^{1}J_{P,Pt2}$ = 2185, ${}^{1}J_{P,Pt1}$ = 1840 Hz, *P*Ph$_2$) ppm. ^{195}Pt{^{19}F} NMR (acetone-d_6, 293 K, 86 MHz), δ: −3719 (d, ${}^{1}J_{Pt2,P}$ = 2185 Hz, Pt^2), −4498 (dd, ${}^{1}J_{Pt1,P}$ = 3020 Hz, ${}^{1}J_{Pt1,P}$ = 1840 Hz, Pt^1).

Reaction of [(R$_F$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{III}(R$_F$)$_2$](*Pt^{III}−Pt^{III}*) with NaN$_3$. To a yellow solution of **1** (0.169 g, 0.118 mmol) in acetone (30 mL) was added NaN$_3$ (0.018 g, 0.277 mmol) in MeOH (10 mL). The colorless solution was stirred, at room temperature, for 20 h and then evaporated to dryness. The residue was treated with CH$_2$Cl$_2$ (20 mL), NBu$_4$ClO$_4$ (0.081 g, 0.236 mmol) was added, and the resulting mixture was filtered through Celite. The solution was evaporated to ca. 2 mL, and ^{i}PrOH (20 mL) was added and then evaporated to ca. 5 mL. Complex **4a** crystallized as a white solid which was stirred for 30 min, filtered, and washed with cold ^{i}PrOH (2 × 0.5 mL). Yield: 0.071 g, 34%. Anal. Found (Calcd for C$_{68}$F$_{20}$H$_{82}$N$_5$PPt$_2$): C, 45.51 (46.13); H, 4.79 (4.67); N 3.63 (3.96).

In another experiment, NaN$_3$ (0.018 g, 0.277 mmol) in acetone (20 mL) was added to a yellow solution of **1** (0.171 g, 0.120 mmol) in acetone (35 mL). The mixture was worked up as in the case of **4a**, and although dark brown solids were obtained to 253 K, these solids turned into oil at room temperature. The NMR study of the oils shows the material to be a mixture in which **4a** and **4b** are identified.

Data for **4a** follow. HRMS (−), exact mass for the dianion [C$_{36}$H$_{10}$F$_{20}$N$_3$PPt$_2$]$^{2-}$: 642.4795 Da. Measured m/z: 642.4790 (M)$^{2-}$. ^{1}H NMR (acetone-d_6, 293 K, 400 MHz), δ: 7.64 (pseudo t, 2 H, ${}^{3}J_{H,H}$ = 8.3 Hz, *o*-H bonded to *P*Ph$_2$), 7.56 (m, 3 H, *m*-H + *p*-H bonded to *P*Ph$_2$), 3.49 (m, 16 H, NBu$_4{}^+$), 1.87 (m, 16H, NBu$_4{}^+$), 1.48 (pseudo sextet, 16 H, ${}^{3}J_{H,H}$ = 7.4 Hz, NBu$_4{}^+$), 1.02 (t, 24 H, ${}^{3}J_{H,H}$ = 7.4 Hz, NBu$_4{}^+$). ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −117.5 (4 *o*-F, ${}^{3}J_{Pt,F}$ = 512 Hz), −118.0 (4 *o*-F, ${}^{3}J_{Pt,F}$ = 331 Hz), −168.1 (4 *m*-F), −168.3 (2 *p*-F), −170.9 (4 *m*-F), −171.6 (2 *p*-F). ^{31}P{^{1}H} NMR (acetone-d_6, 293 K, 162.0 MHz), δ: −75.9 ppm, ${}^{1}J_{P,Pt}$ = 2138 Hz. ^{195}Pt{^{19}F} NMR (acetone-d_6, 293 K, 86 MHz), δ: −3381 (d, ${}^{1}J_{Pt,P}$ = 2138 Hz).

Data for **4b** follow. ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −117.6 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 507 Hz), −118.3 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 421 Hz), −119.0 (2 *o*-F, ${}^{3}J_{Pt,F}$ = 303 Hz), −127.6 (2 *o*-F, PPh$_2C_6F_5$), −153.7 (1 *p*-F, PPh$_2C_6F_5$), −165.0 (2 *m*-F, PPh$_2C_6F_5$), −166.8 (1 *p*-F), −167.6 (2 *m*-F), −167.8 (2 *m*-F), −168.2 (2 *m*-F), −169.7 (1 *p*-F), −170.0 (1 *p*-F). ^{31}P{^{1}H} NMR (acetone-d_6, 293 K, 162.0 MHz), δ: 13.4 (${}^{1}J_{P,Pt}$ = 2216 Hz, ${}^{2}J_{P,P}$ = 320 Hz, PPh$_2$C$_6$F$_5$), −55.3 (${}^{1}J_{P,Pt} \approx {}^{1}J_{P,Pt'} \approx$ 2148 Hz, μ-PPh$_2$) ppm.

Reaction of [(R$_F$)$_2$Pt^{III}(μ-PPh$_2$)$_2$Pt^{III}(R$_F$)$_2$](*Pt^{III}−Pt^{III}*) with KOCN. To a yellow solution of **1** (0.170 g, 0.119 mmol) in acetone (35 mL) was added KOCN (0.040 g, 0.493 mmol), and the mixture was stirred at room temperature for 20 h. The mixture was evaporated to dryness, CH$_2$Cl$_2$ (20 mL) and NBu$_4$ClO$_4$ (0.041 g, 0.120 mmol) were added, and the mixture was filtered through Celite. The solution was evaporated to ca. 2 mL; ^{i}PrOH (10 mL) was added and evaporated to ca. 5 mL. The solution was maintained in the freezer for 10 h. A small amount of a white solid crystallized which was filtered, washed with cold ^{i}PrOH (2 × 0.5 mL), and discarded. The filtrate was evaporated to ca. 3 mL and cooled ca. to 230 K, so that **5b** crystallized as a white solid which was quickly filtered and washed with cold ^iPrOH (2 × 0.5 mL). Yield: 0.047 g, 23%. Anal. Found (Calcd for $C_{65}F_{20}H_{56}N_2OP_2Pt_2$): C, 45.40 (45.57); H, 3.07 (3.29); N 1.73 (1.64).

To a yellow solution of **1** (0.220 g, 0.154 mmol) in acetone (35 mL) was added KOCN (0.025 g, 0.308 mmol), and the mixture was stirred for 20 h. The colorless solution was evaporated to dryness, and CH_2Cl_2 (15 mL) was added. NBu_4ClO_4 (0.053 g, 0.154 mmol) was added, and the mixture was filtered through Celite. The solution was evaporated to ca. 5 mL, and ^iPrOH (15 mL) was added and evaporated to 5 mL. A white solid crystallized and was filtered and washed with ^iPrOH (2 × 0.5 mL), 0.010 g. Three more fractions of white solid were obtained from the mother liquors. All of these four fractions contain mainly **5a** and **5b** in a molar ratio of ca. 3:1, 1:1, 1:4, and 1:6, respectively. All attempts to carry out the reaction process with a greater amount of NBu_4ClO_4 resulted in oily products that we have not been able to crystallize.

Data for **5a** follow. ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −117.5 (4 *o*-F, $^3J_{Pt,F}$ = 538 Hz), −117.7 (4 *o*-F, $^3J_{Pt,F}$ not measured, overlapped signals), −168.0 (4 *m*-F), −168.5 (2 *p*-F), −170.9 (4 *m*-F), −171.7 (2 *p*-F). $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K, 162.0 MHz), δ: −72.9 ppm, $^1J_{P,Pt}$ = 2100 Hz.

Data for **5b** follow. HRMS (−), exact mass for the anion $[C_{49}H_{20}F_{20}NOP_2Pt_2]^-$: 1469.9994 Da. Measured *m*/*z*: 1469.9977 $(M)^-$. ^1H NMR (acetone-d_6, 293 K, 400 MHz), δ: 8.22 (dd, 2 H, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,P}$ = 12.3 Hz, *o*-H bonded to $PPh_2C_6F_5$), 7.73 (dd, 2 H, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,P}$ = 10.2 Hz, *o*-H bonded to PPh_2), from 7.66 to 7.56 (m, 3 H, *p*-H + *m*-H bonded to $PPh_2C_6F_5$), from 7.31 to 7.20 (m, 3 H, *p*-H + *m*-H bonded to PPh_2), 3.49 (m, 8 H, NBu_4^+), 1.87 (m, 8 H, NBu_4^+), 1.48 (pseudo sextet, 8 H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+), 1.02 (t, 12 H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+). ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −117.5 (2 *o*-F, $^3J_{Pt,F}$ = 543 Hz), −118.1 (2 *o*-F, $^3J_{Pt,F}$ = 452 Hz), −118.5 (2 *o*-F, $^3J_{Pt,F}$ = 346 Hz), −127.4 (2 *o*-F, $PPh_2C_6F_5$), −153.8 (1 *p*-F, $PPh_2C_6F_5$), −165.0 (2 *m*-F, $PPh_2C_6F_5$), −166.8 (1 *p*-F), −167.7 (2 *m*-F), −168.0 (2 *m*-F), −168.3 (2 *m*-F), −169.7 (1 *p*-F), −170.0 (1 *p*-F). $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K, 162.0 MHz), δ: 12.6 ($^1J_{P,Pt2}$ = 2210 Hz, $^2J_{P,P}$ = 325 Hz, $PPh_2C_6F_5$), −40.5 ($^1J_{P,Pt1} \approx {}^1J_{P,Pt2} \approx$ 2100 Hz, μ-PPh_2) ppm. $^{195}Pt\{^{19}F\}$ NMR (acetone-d_6, 293 K, 86 MHz), δ: −3522 (d, $^1J_{Pt,\mu\text{-}P}$ = 2100 Hz, $^2J_{Pt,Pt}$ = 1310 Hz, Pt^1), −3953 (dd, $^1J_{Pt2,\mu\text{-}P}$ = 2100 Hz, $^1J_{Pt2,P}$ = 2210 Hz, $^2J_{Pt,Pt}$ = 1310 Hz, Pt^2).

Reaction of $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*($Pt^{III}$−$Pt^{III}$)* with N^nBu_4OH. To a red suspension of **2** (0.162 g, 0.081 mmol) in CH_2Cl_2 (15 mL) was added 0.160 mol of NBu_4OH (0.16 mL of 1.0 M methanol solution). The solution was stirred for 20 h, and the pale yellow solution was evaporated to ca. 1 mL. $CHCl_3$ (10 mL) was added, and **6** crystallized as a white solid which was filtered and washed with cold $CHCl_3$ (2 × 0.5 mL). Yield: 0.142 g, 78%. Anal. Found (Calcd for $C_{104}F_{20}H_{112}N_2OP_4Pt_3$): C, 49.99 (50.02); H, 4.12 (4.48); N 1.09 (1.12).

HRMS (−), exact mass for the anion $[C_{72}H_{40}F_{20}OP_4Pt_3]^{2-}$: 1004.5331 Da. Measured *m*/*z*: 1004.5321 $(M)^{2-}$. ^1H NMR (acetone-d_6, 293 K, 400 MHz), δ: 7.85 (pseudo t, 2 H, *J* = 7.1 Hz, *o*-H bonded to P^3), from 7.36 to 7.25 (m, 4 H, *o*-H bonded to P^4 and *o*-H bonded to P^1), from 7.20 to 6.98 (m, 9 H, *o*-H bonded to P^2, *m*-H + *p*-H bonded to P^3, *m*-H + *p*-H bonded to P^1, *p*-H bonded to P^4), 6.92 (pseudo t, 2 H, *J* = 7.2 Hz, *m*-H bonded to P^4), 6.84 (t, 1 H, *J* = 6.9 Hz, *p*-H bonded to P^2), 6.59 (pseudo t, 2 H, *J* = 6.9 Hz, *m*-H bonded to P^2), 3.49 (m, 16 H, NBu_4^+), 1.87 (m, 16 H, NBu_4^+), 1.48 (pseudo sextet, 16 H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+), 1.02 (t, 24 H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+). ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: from −114 to −116 (8 *o*-F), −168.6 (2 *m*-F), from −168.9 to −169.4 (6 *m*-F), −170.0 (1 *p*-F), −170.4 (1 *p*-F), −170.6 (2 *p*-F). $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K, 162.0 MHz), δ: 123.6 ($^1J_{P1,Pt1}$ = 2969 Hz, P^1), 13.9 ($J_{P2,Pt1}$ = 1840 Hz, $J_{P2,Pt2}$ = 1710 Hz, $^2J_{P2,P3}$ = 293 Hz, P^2), −147.9 (d, $^1J_{P4,Pt2}$ = 2857 Hz, $^1J_{P4,Pt3}$ = 1947 Hz, $^2J_{P3,P4}$ = 153 Hz, P^4), −150.5 (dd, $^1J_{P3,Pt2}$ = 1792 Hz, $^1J_{P3,Pt3}$ = 1874 Hz, $^2J_{P2,P3}$ = 293 Hz, $^2J_{P3,P4}$ = 153 Hz, P^3) ppm. $^{195}Pt\{^{19}F\}$ NMR (acetone-d_6, 293 K, 86 MHz), δ: −3657 (ddd, $^1J_{Pt2,P4}$ = 2857 Hz, $^1J_{Pt2,P3}$ = 1792 Hz, $^1J_{Pt2,P2}$ = 1740 Hz, Pt^2), −3828 (dd, $^1J_{Pt3,P4}$ = 1947 Hz, $^1J_{P3,Pt3}$ = 1874 Hz, Pt^3), −4497 (dd, $^1J_{Pt1,P1}$ = 2969 Hz, $^1J_{Pt1,P2}$ = 1840 Hz, Pt^1).

Synthesis of $[NBzMe_3]_2[(R_F)_2Pt^{II}(\mu\text{-}Ph_2PO)(\mu\text{-}PPh_2)Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$ (6′). To a red solution of **2** (0.100 g, 0.050 mmol) in CH_2Cl_2 (25 mL) was added 0.108 mol of $NBzMe_3OH$ (0.048 mL of 40% methanol solution), and this mixture stirred for 4 h. The solution was evaporated to ca. 3 mL, and $CHCl_3$ (10 mL) was added and evaporated to ca. 3 mL. Compound **6′** crystallized as a very pale yellow solid which was filtered and washed with cold $CHCl_3$ (2 × 0.5 mL). Yield: 0.093 g, 78%.

Reaction of $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}(R_F)_2]$*($Pt^{III}$−$Pt^{III}$)* with NaN_3. NaN_3 (0.008 g, 0.120 mmol) dissolved in methanol (5 mL) was added to a red solution of **2** (0.100 g, 0.050 mmol) in acetone (25 mL) and stirred for 20 h. The yellow solution was evaporated to dryness, and MeOH (8 mL) was added to the residue. NBu_4ClO_4 (0.035 g, 0.100 mmol) was added to the yellow solution, and **7** crystallized as a yellow solid which was filtered and washed with MeOH (2 × 0.5 mL). ^iPrOH (8 mL) was added to the filtrate, and evaporation to ca. 10 mL produces a second crop of **7**. Yield: 0.073 g, 65%. Anal. Found (Calcd for $C_{88}F_{20}H_{76}N_2P_4Pt_3$): C, 47.26 (46.96); H, 3.44 (3.40); N 1.15 (1.24).

HRMS (−), exact mass for the anion $[C_{72}H_{40}F_{20}NP_4Pt_3]^-$: 2007.0739 Da. Measured *m*/*z*: 2007.0680 $(M)^-$. ^1H NMR (acetone-d_6, 293 K, 400 MHz), δ: 7.76 (dd, 4 H, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,P}$ = 10.9 Hz, *o*-H bonded to P^3), 7.63 (dd, 4 H, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,P}$ = 9.7 Hz, *o*-H bonded to P^1), 7.41 (t, 2 H, $^3J_{H,H}$ = 6.5 Hz, *p*-H), 7.31 (t, 2 H, $^3J_{H,H}$ = 7.1 Hz, *p*-H), from 7.22 to 7.02 (m, 22 H), 6.97 (t, 2 H, $^3J_{H,H}$ = 6.5 Hz, *p*-H bonded to P^2), 6.72 (pseudo t, 4 H, *J* = 6.5 Hz, *m*-H bonded to P^2), 3.49 (m, 8 H, NBu_4^+), 1.87 (m, 8 H, NBu_4^+), 1.48 (pseudo sextet, 8H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+), 1.02 (t, 12H, $^3J_{H,H}$ = 7.4 Hz, NBu_4^+). ^{19}F NMR (acetone-d_6, 293 K, 376.5 MHz), δ: −116.3 (4 *o*-F, $^3J_{Pt,F}$ = 328 Hz), −116.7 (2 *o*-F, $^3J_{Pt,F}$ = 312 Hz), −117.5 (2 *o*-F, $^3J_{Pt,F}$ = 295 Hz), −166.1 (1 *p*-F), −166.2 (1 *p*-F), −166.7 (2 *m*-F), −167.2 (2 *m*-F), −167.9 (4 *m*-F), −168.2 (1 *p*-F), −168.8 (1 *p*-F) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K, 162.0 MHz), δ: 140.6 (P^4, $^1J_{P4,Pt3}$ = 1280, $^1J_{P4,Pt2}$ = 4070 Hz), 128.4 (P^1, $^1J_{P1,Pt1}$ = 3045 Hz, $^2J_{P1,P3}$ = 70 Hz), 31.7 (P^3, $^1J_{P3,Pt3}$ = 1690 Hz, $J_{P3,Pt2}$ = 510 Hz, $^2J_{P1,P3}$ = 70 Hz), 30.7 (P^2, $^1J_{P2,Pt1}$ = 2100, $^1J_{P2,Pt2}$ = 3580 Hz) ppm. $^{195}Pt\{^{19}F\}$ NMR (acetone-d_6, 293 K, 86 MHz), δ: −4506 (dd, $^1J_{Pt1,P1}$ = 3045 Hz, $J_{Pt1,P2}$ = 2100 Hz, Pt^1), −4868 (ddd, $^1J_{Pt2,P2}$ = 3580 Hz, $^1J_{Pt2,P4}$ = 4070 Hz, $J_{Pt2,P3}$ = 510 Hz, Pt^2), −5439 (dd, $^1J_{Pt3,P3}$ = 1690 Hz, $^1J_{Pt3,P4}$ = 1280 Hz, Pt^3).

Synthesis of $[PPh_3Me][Pt_3^{II}(\mu_3\text{-}Ph_2PNPPh_2)(\mu\text{-}PPh_2)_2)(R_F)_4]$ (7′). Complex 7′ was prepared similarly to 7 from NaN_3 (0.012 g, 0.185 mmol) dissolved in methanol (7 mL), **2** (0.111 g, 0.056 mmol) in acetone (25 mL), and $[PMePh_3][ClO_4]$ (0.022 g, 0.058 mmol) as a yellow solid. Yield: 0.069 g, 54%.

X-ray Structure Determinations. Crystal data and other details of the structure analyses are presented in Supporting Information Table S1. Suitable crystals of **4a** and **5a** for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of **4a** or a **5a**/**5b** mixture, respectively, in CH_2Cl_2. Crystals of **6′** and **7′** were obtained by slow diffusion of *n*-hexane into concentrated solutions of **6′** and **7′** in acetone. Crystals were mounted at the end of quartz fibres. The radiation used in all cases was graphite monochromated Mo Kα (λ = 0.710 73 Å). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.[91] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares on F^2 with SHELXL-97.[92] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of $4a\cdot CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$, constraints in the geometry and the thermal parameters of the *n*-hexane molecule were applied. In the structure of $5a\cdot CH_2Cl_2\cdot 0.5n\text{-}C_6H_{14}$, the data collected were weak due to the fact that the only suitable crystal was very small. This causes some problems that reflect mainly in the thermal anisotropic parameters of some atoms, for which weak restraints were applied. Moreover, one very diffuse *n*-hexane moiety (one of the solvents used in the crystallization) was found in the electron density maps, and had to be refined with half occupancy and restraints in its geometric parameters. Isotropic displacement parameters were used for all the atoms of this solvent molecule. In the structure of **7′**, one of the methyl groups of the acetone solvent molecules is disordered over two positions which were refined with 0.5 partial occupancy. Also, restraints were used in the anistropic thermal parameters of the *n*-hexane solvent molecule. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 3.

■ ASSOCIATED CONTENT

S Supporting Information

Crystal data and other details of the structure analyses. Crystallographic data of **4a**·CH_2Cl_2·0.5*n*-C_6H_{14}, **5a**·CH_2Cl_2·0.5*n*-C_6H_{14}, **6′**·3Me_2CO, and **7′**·Me_2CO·*n*-C_6H_{14} (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Professor Dr. María P. García.

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