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Formation of P–C Bond through Reductive Coupling between Bridging Phosphido and Benzoquinolinate Groups. Isolation of Complexes of the Pt(II)/Pt(IV)/Pt(II) Sequence[‡]

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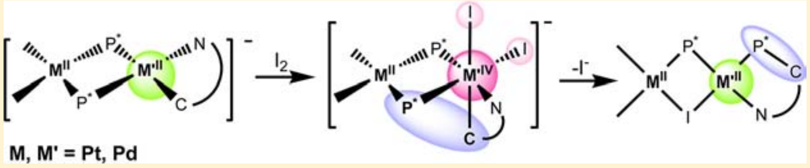
Ⓢ *Supporting Information*



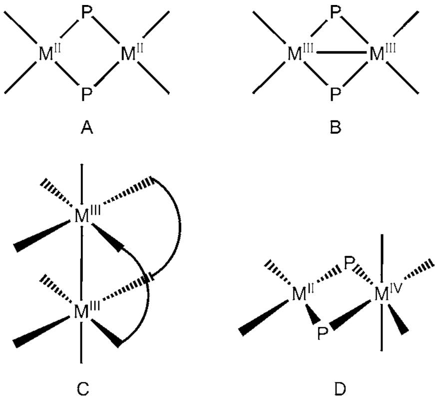
ABSTRACT: The rational synthesis of dinuclear asymmetric phosphanido derivatives of palladium and platinum(II), $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)_2M'(\kappa^2\text{,}N\text{,}C\text{-}C_{13}H_8N)]$ ($R_F = C_6F_5$; M = M′ = Pt, **1**; M = Pt, M′ = Pd, **2**; M = Pd, M′ = Pt, **3**; M = M′ = Pd, **4**), is described. Addition of I_2 to **1**−**4** gives complexes $[(R_F)_2M^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pd^{II}\{PPh_2(C_{13}H_8N)\}]$ (M = M′ = Pt, **6**; M = Pt, M′ = Pd, **7**; M = M′ = Pd, **8**; M = Pd, M′ = Pt **10**) which contain the aminophosphane $PPh_2(C_{13}H_8N)$ ligand formed through a Ph_2P/C^N reductive coupling on the mixed valence M(II)−M′(IV) $[NBu_4][(R_F)_2M^{II}(\mu\text{-}PPh_2)_2M'^{IV}(\kappa^2\text{,}N\text{,}C\text{-} C_{13}H_8N)I_2]$ complexes, which were identified for M^{II} = Pd, M'^{IV} = Pt (**9**), and isolated for M^{II} = Pt, M'^{IV} = Pt (**5**). Complex **5** showed an unusual dynamic behavior consisting in the exchange of two phenyl groups bonded to different P atoms, as well as a "through space" spin−spin coupling between *ortho*-F atoms of the pentafluorophenyl rings.

■ INTRODUCTION

Besides the well-established Pd(0)/Pd(II) redox-processes involved in a variety of palladium-catalyzed transformations and organic synthesis, Pd(II)/Pd(IV) cycles have been playing a complementary role in the past years.[2−19] Moreover, in addition to oxidation of Pd(II) precursors to Pd(IV) complexes, the formation of bimetallic Pd(III) complexes has been also reported.[2,20−24] The formal oxidation state +3 is not dominant either in platinum and in palladium chemistry, and although a quite large number of dinuclear derivatives of Pt(III) are known today,[25−34] only few bimetallic Pd(III) complexes have been reported.[35−38] In some cases the presence of a true bimetallic M(III)−M(III) complex or a M(II)−M(IV) one (B and D, respectively, in Chart 1) is still an open question.[39,40]

In the course of our current research on palladium or platinum phosphanido derivatives, we have reported the synthesis of type A (Chart 1) dinuclear complexes $[NBu_4]_2[(R_F)_2M(\mu\text{-}PPh_2)_2M'(R_F)_2]$ $R_F = C_6F_5$, M = M′ = Pd, Pt; M = Pt, M′ = Pd and their reactions with I_2 (1:1 molar ratio) which result in the formation of different types of complexes depending on the M′ (Pt or Pd) and on the reaction conditions. The B type diplatinum complex $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(R_F)_2]$[41,42] displaying a Pt(III)−Pt(III) bond is obtained through this reaction. Presumably, the bridging phosphanido ligands prevent the formation of a lantern type Pt(III)−Pt(III) compound (Chart 1C), which are by far more common in the context of Pt^{3+} dimers.[25−34] In no case we have previously observed that the oxidation of a Pt(II)−Pt(II) phosphanido complex with I_2 (1:1 molar ratio) occurs only for

Chart 1



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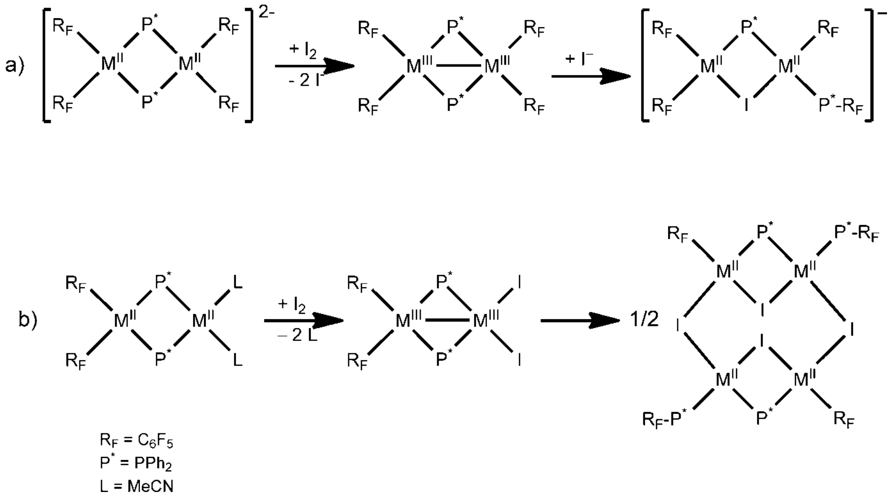
Scheme 1



Scheme 2

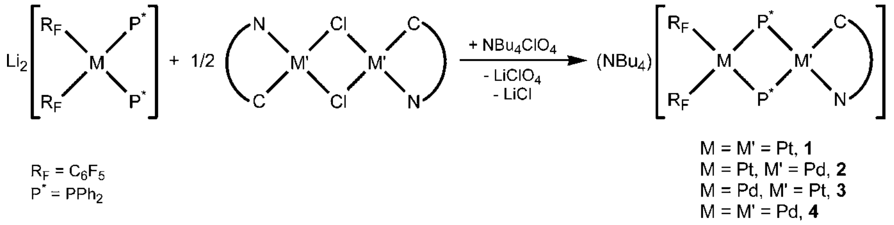
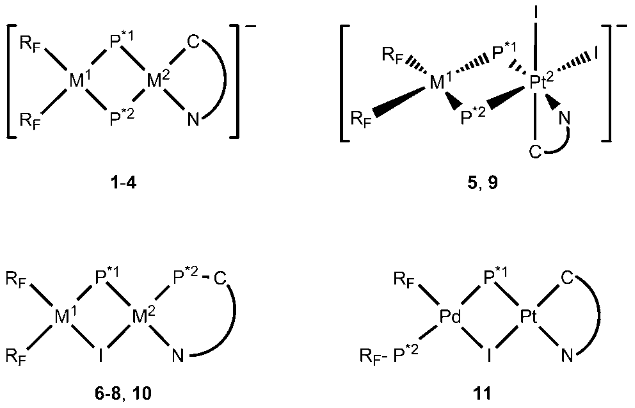


Table 1. $^{31}P\{^{1}H\}$ NMR Data of 1−10 in Deuteroacetone with δ in ppm, J in Hz



1-4

5, 9

6-8, 10

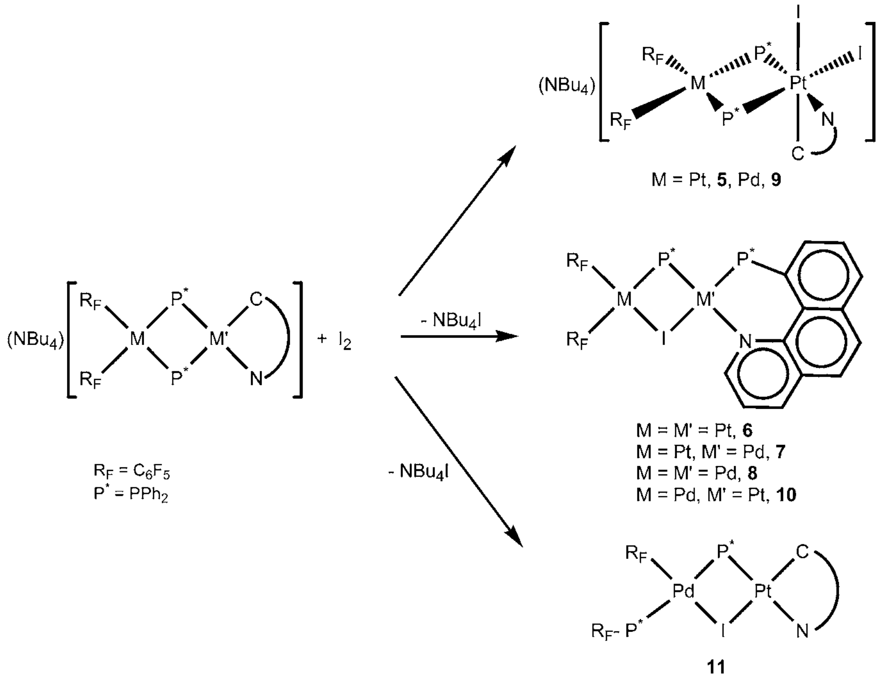
11

complex	δP^1	δP^2	$^2JP^1,P^2$	$^1JPt^1,P^1$	$^1JPt^2,P^1$	$^1JPt^1,P^2$	$^1JPt^2,P^2$	δPt^1	δPt^2
1	−107.9	−118.9	116	1937	2810	1646	1320	−3889[a]	−3717[a]
2	−78.8	−116.6	160	1806		1530		−3909	
3	−95.9	−111.7	160		2658		1213		−3738
4	−58.0	−107.0	204						
5	−115.5	−107.5	126	2032	1807	2189	1270	−3806[b]	−2917[b]
9	−97.7	−89.1	161		1680		1121		−2966
6	−11.4	14.2	2	1846	2513	37	4435	−4238	−4397
7	55.2	37.5	40	1864		97		−4315	
8	66.0	42.3	36						
10	7.9	18.6	2		2542		4307		−4416
11	−5.4	8.7	381		3317				n.d.

[a] ^2JPt−Pt = 541 Hz. [b] ^2JPt−Pt = ca. 100 Hz.

one of the metal centers forming a mixed valence Pt(II)−Pt(IV) compound (Chart 1D). The heterobinuclear complex M = Pt, M′ = Pd or the homobinuclear palladium derivative react with I_2 (1:1 molar ratio) forming $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)(\mu\text{-}I)M'(R_F)(PPh_2R_F)]$[42] which can be considered as the result of the oxidation of the binuclear M(II) to the unstable

Scheme 3



M(III)−M(III) which evolves rapidly, through a PPh_2/C_6F_5 reductive coupling, to the formation of the M(II)−M(II) compound. In fact the Pt(III)−Pt(III) derivative evolves, in the presence of I^-, to the corresponding Pt(II)−Pt(II) compound $[NBu_4][(R_F)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}I)Pt(R_F)(PPh_2R_F)]$[42] (Scheme 1a).

A similar behavior has been observed in the reaction of the dinuclear neutral complexes $[(R_F)_2M(\mu\text{-}PPh_2)_2M'(CH_3CN)_2]$ with I_2 (Scheme 1b).[43,44] Addition of I_2 to these complexes produces the dinuclear Pt(III)−M(III) complexes $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2M^{III}I_2]$ (M = Pt, Pd) which evolve to the tetranuclear platinum and/or palladium(II) complexes $[M_4(\mu\text{-}PPh_2)_2(\mu\text{-}I)_4(R_F)_2(PPh_2R_F)_2]$, through a reductive coupling between a PPh_2 and a R_F groups and formation of the PPh_2R_F ligand (Scheme 1b).[44]

In this Article we report on the synthesis of the new asymmetric dinuclear phosphanido complexes of general formula $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)_2M'(\kappa^2\text{,}N\text{,}C\text{-}C_{13}H_8N)]$ (R_F = C_6F_5; $C_{13}H_8N$ = benzoquinolinate; M and M′ = Pd or Pt) and on the reactivity of these cyclometalated complexes with I_2.

■ RESULTS AND DISCUSSION

Synthesis of $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)_2M'(C\hat{}N)]$ (R_F = C_6F_5, C^N = Benzoquinolinate, M = M′ = Pt, 1; M = Pt, M′ = Pd, 2; M = Pd, M′ = Pt, 3; M = M′ = Pd, 4). The synthesis of the asymmetric dinuclear derivatives **1**−**4** was carried out by reacting *cis*-$Li_2[M(R_F)_2(PPh_2)_2]$[45] with the binuclear complex $[\{M'(\mu\text{-}Cl)(C\hat{}N)\}_2]$ (1:0.5 molar ratio) in THF (Scheme 2). From the corresponding mixtures, complexes **1**−**4** were isolated as yellow solids. The mononuclear phosphanido complexes behave as bidentate ligands causing the splitting of the $(\mu\text{-}Cl)_2$ bridging system and the displacement of the halide ligand in the binuclear C^N containing complex with formation of the asymmetric complexes **1**−**4**. The complexes were characterized by elemental analysis, HRMS, and multinuclear NMR spectroscopy. The IR spectra of complexes **1**−**4** in the solid state confirmed in all cases the presence of the relevant ligands and do not deserve insights. The HRMS(−) spectrograms of **1**−**4** showed in all cases intense peaks corresponding to $[M]^-$, with an isotope pattern superimposable to that calculated on the basis of the proposed formula.

The $^{31}P\{^1H\}$ NMR spectra of **1**−**4** showed two mutually coupled doublets (AX spin system) with ^{195}Pt satellites for complexes **1**−**3** (Table 1). The δP values in **1**−**4** range from −58.0 to −118.9 ppm. It has been established that usually the chemical shift decreases as the atomic number increases from top to bottom in a triad,[42,46] and in agreement with this, the chemical shifts increases passing from **1** (Pt_2) to **2**, **3** (PtPd), and **4** (Pd_2). The chemical shifts of P atoms in $M(\mu\text{-}PPh_2)_xM'$ frameworks without metal−metal bond appear at high field, and we have observed that δP in $M(\mu\text{-}PPh_2)M'$ usually appears at lower field than those of the doubly bridged $M(\mu\text{-}PPh_2)_2M'$ fragments.[47] The value of δ −58.0 is the highest one found for $M(\mu\text{-}PPh_2)_2M'$ systems and is close to those found in complexes containing single bridging $M(\mu\text{-}PPh_2)M'$ fragments without metal−metal bond.[48] The attributions of the coupling constants between P and Pt were unequivocally made by comparison of $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ spectra. As expected on the basis of the ligand *trans* to P, the lowest values of the ^1JPt,P (1320 Hz for **1** and 1213 Hz for **3**) were found for the coupling constants between P^2 and Pt^2 (P *trans* to benzoquinolinate C) while the highest ones (2810 Hz for **1** and 2658 Hz for **3**) were found for the $^1J$$Pt^2$,$P^1$ (P *trans* to N).[43,49] The coupling constants between the P atoms and Pt^1 in complexes **1**−**2** range from 1530 to 1937 Hz.

The $^{195}Pt\{^1H\}$ NMR spectra of complexes **1**−**3** showed sharp signals for the Pt atoms bonded to benzoquinolinate (Pt^2) and broad multiplets, due to several couplings with unequivalent ^{19}F nuclei, for the Pt atoms bonded to pentafluorophenyl rings (Pt^1). The chemical shift of the Pt^1 was δ −3889 for **1** and δ −3909 for **2**, while those of the Pt^2 were δ −3717 for **1** and δ −3738 for **3** (Table 1). The geminal coupling constant between the two Pt atoms in **1** was 541 Hz.

The ^{19}F NMR spectra of complexes **1**−**4** recorded in deuteroacetone at 298 K showed in all cases different (often partially overlapped) signals for the *o*-F atoms (δ range −110 to −115 ppm), *m*-F atoms (δ range −166 to −167 ppm), and *p*-F atoms (δ range −168 to −169 ppm) of each ring, in agreement with the inequivalence of the two rings.

The partial overlapping of most homologous signals reflects the similarity of the environments of the two rings, while the equivalence of the *ortho* (and *meta*) fluorine atoms within each ring can be explained either by a free rotation about the Pt−C axis at 298 K or by an adopted conformation in solution having a mirror plane containing the skeleton of the molecule with the C_6F_5 rings perpendicular to this plane.

1D and 2D ^1H NMR spectra of **1**−**4** permitted the full assignment of all ^1H NMR signals. The four ^1H NMR spectra are almost superimposable, the main difference being the resonance of the M′−N−C*H*C proton (H2 in the numbering used in the Experimental Section) which falls at about 8.6 ppm when M′ was Pt and at about 8.4 ppm when the benzoquinolinate ligand was bound to Pd. The $^{13}C\{^1H\}$ NMR spectra of **1**−**4** showed clearly all signals due to tertiary carbons and are reported in the Supporting Information.

Reaction of 1−4 with I_2. Complexes **1**−**4** react with I_2 (1:1 molar ratio), and the resulting products depended on the respective starting materials and on the solvent in which the reactions were carried out (Scheme 3).

In a general procedure, a CH_2Cl_2 solution of I_2 was added dropwise to a CH_2Cl_2 solution of the dinuclear complexes $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)_2M'(C\text{^}N)]$ in 1:1 molar ratio at room temperature. For complex **1** the solution was stirred, at room temperature, for 20 h and by addition of *i*-PrOH, a mixture of the Pt(II)−Pt(IV) complexes $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]$ (**5**) and $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (**6**) was isolated. Complex **5** contains a Pt(II) and a Pt(IV) center with a *OC*-6−42 configuration (only one isomer of the pair is depicted in Scheme 3), and **6** is a dinuclear Pt(II)−Pt(II) derivative containing an aminophosphane group. The two metal centers are joined by two different bridging ligands, PPh_2^- and I^-. When the addition of I_2 to **1** was carried out in acetone, only the Pt(II),Pt(IV) complex **5** was obtained, suggesting that **5** might be a precursor of **6** and that the reductive coupling process is not favored in acetone. In fact, deuteroacetone solutions of **5** were stable (^{31}P NMR spectroscopy) for two weeks at room temperature whereas CD_2Cl_2 solutions of **5** evolved in the same period of time into a mixture of **5** and **6** (ca. 70% in **6**).

Complexes **2** (M = Pt, M′ = Pd) and **4** (M = M′ = Pd) react with I_2 under similar reaction conditions producing only the aminophosphane complexes $[(R_F)_2M^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pd^{II}\{PPh_2(C_{13}H_8N)\}]$ (M = Pt **7**, Pd **8**, Scheme 3). In an attempt to detect a Pt(II),Pd(IV) intermediate we carried out the addition of I_2 to complex **2** (1:1 molar ratio) in acetone solution at low temperature (213 K) obtaining, after evaporating the solution to dryness, an orange solid. The $^{31}P\{^1H\}$ NMR spectra in acetone at 213 K and at room temperature indicated this solid to be a mixture of mainly **7** and the tetranuclear species $[NBu_4]_2[\{(R_F)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}I)\}_2]$, described previously,[44] but signals assignable to a Pt(II)−Pd(IV) intermediate complex were not detected.

Finally, when a CH_2Cl_2 solution of I_2 was added to a CH_2Cl_2 solution of $[NBu_4][(R_F)_2Pd(\mu\text{-}PPh_2)_2Pt(C\text{^}N)]$ (**3**) (1:1 molar ratio) and stirred at room temperature for 20 h, and the resulting solution was evaporated to dryness, a yellow solid was isolated. Its $^{31}P\{^1H\}$ NMR spectrum in acetone indicated that this solid is a complex mixture of products in which $[NBu_4][(R_F)_2Pd^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]$ (**9**), $[(R_F)_2Pd^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (**10**), and $[(R_F)(PPh_2R_F)\text{-}Pd^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}(C\text{^}N)]$ (**11**) could be identified (NMR spectroscopy) but not isolated as pure samples. All attempts to separate the mixture were unsuccessful.

Crystal Structures of 5′−8. Crystals of **5** suitable for X-ray studies could not be obtained. For this reason, $[N(PPh_3)_2]\text{-}[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]$ (**5′**) was prepared through two steps: (a) synthesis of $[N(PPh_3)_2][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(C\text{^}N)]$, **1′**, in an analogous procedure than for **1** using $[N(PPh_3)_2]Cl$ instead of NBu_4ClO_4, and (b) the subsequent addition of I_2 to **1′**. The structures of compounds **5′**−**8** have been established by X-ray diffraction studies. Figures 1, 2, S1, and S2 show views of the corresponding complexes and Tables 2, 3, S1, and S2 list their most relevant bond distances and angles. The crystal structure of **5′** confirms its dinuclear nature, with two platinum atoms bridged by two diphenylphosphanido ligands. The long intermetallic separation of 3.572(1) Å and the broad values of the Pt−P−Pt angles

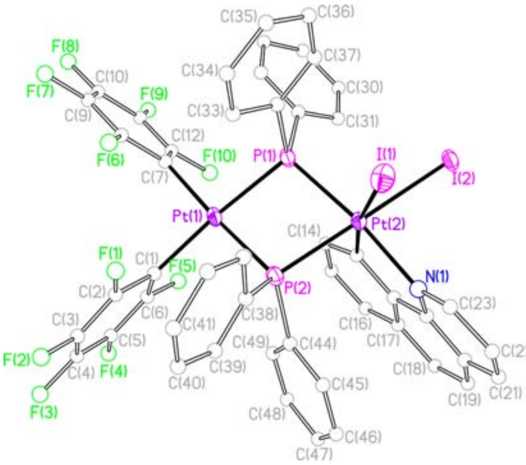


Figure 1. View of the molecular structure of the complex anion of $[N(PPh_3)_2][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]$ (**5′**).

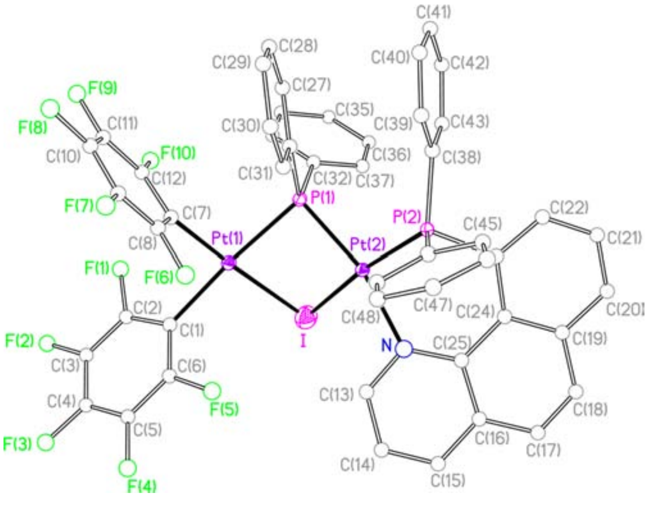


Figure 2. View of the molecular structure of the complex $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (**6**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[N(PPh_3)_2][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$ ($5'\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$)

Pt(1)−C(1)	2.044(7)	Pt(1)−C(7)	2.064(6)	Pt(1)−P(2)	2.2990(18)
Pt(1)−P(1)	2.3033(17)	Pt(2)−C(13)	2.058(6)	Pt(2)−N(1)	2.138(5)
Pt(2)−P(1)	2.3407(17)	Pt(2)−P(2)	2.3837(18)	Pt(2)−I(1)	2.6913(5)
Pt(2)−I(2)	2.7556(5)				
C(1)−Pt(1)−C(7)	87.8(3)	C(1)−Pt(1)−P(2)	96.1(2)		
C(7)−Pt(1)−P(2)	175.66(17)	C(1)−Pt(1)−P(1)	175.42(19)		
C(7)−Pt(1)−P(1)	96.76(18)	P(2)−Pt(1)−P(1)	79.38(6)		
C(13)−Pt(2)−N(1)	80.6(2)	C(13)−Pt(2)−P(1)	94.56(19)		
N(1)−Pt(2)−P(1)	172.56(15)	C(13)−Pt(2)−P(2)	83.10(18)		
N(1)−Pt(2)−P(2)	96.76(15)	P(1)−Pt(2)−P(2)	76.93(6)		
C(13)−Pt(2)−I(1)	169.66(18)	N(1)−Pt(2)−I(1)	90.44(14)		
P(1)−Pt(2)−I(1)	94.82(4)	P(2)−Pt(2)−I(1)	103.27(4)		
C(13)−Pt(2)−I(2)	89.25(18)	N(1)−Pt(2)−I(2)	85.17(15)		
P(1)−Pt(2)−I(2)	100.52(4)	P(2)−Pt(2)−I(2)	171.68(4)		
I(1)−Pt(2)−I(2)	84.775(16)	Pt(1)−P(1)−Pt(2)	100.53(7)		
Pt(1)−P(2)−Pt(2)	99.38(7)				

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (6)

Pt(1)−C(7)	2.008(7)	Pt(1)−C(1)	2.069(7)	Pt(1)−P(1)	2.2924(16)
Pt(1)−I	2.6762(6)	Pt(2)−N	2.138(5)	Pt(2)−P(2)	2.1938(16)
Pt(2)−P(1)	2.2730(16)	Pt(2)−I	2.6779(6)		
C(7)−Pt(1)−C(1)	88.8(3)	C(7)−Pt(1)−P(1)	94.56(18)		
C(1)−Pt(1)−P(1)	175.35(19)	C(7)−Pt(1)−I	176.08(18)		
C(1)−Pt(1)−I	94.31(18)	P(1)−Pt(1)−I	82.25(4)		
N−Pt(2)−P(2)	85.20(16)	N−Pt(2)−P(1)	165.52(17)		
P(2)−Pt(2)−P(1)	103.45(6)	N−Pt(2)−I	90.88(15)		
P(2)−Pt(2)−I	169.07(5)	P(1)−Pt(2)−I	82.57(4)		
Pt(1)−I−Pt(2)	74.880(16)	Pt(2)−P(1)−Pt(1)	90.95(6)		

(100.53(7)° and 99.38(7)°) discard any Pt···Pt interaction. The environment of Pt(1) is fairly typical for this metal in a formal oxidation state +2; that is, it lays in the center of a square planar environment formed by two mutually *cis* pentafluorophenyl ligands and the bridging phosphanido groups. On the other hand, the Pt(2) coordination sphere is octahedral as expected for a Pt^{IV} center. The two iodo ligands are mutually *cis*, with a *OC*-6−42 configuration for Pt(2) (see Figure 1).

Complexes **6**−**8** are isostructural, with a "*cis*-M$(C_6F_5)_2$" fragment (M = Pt in **6** and **7**, and M = Pd in **8**) and a "M$\{PPh_2(C_{13}H_8N)\}$" fragment (M = Pt in **6**, and M = Pd in **7** and **8**) held together through a double bridge formed by one iodo and one diphenylphosphanido ligands. Structural parameters are very similar in the three complexes (see Tables 3, S1, and S2) regardless of the nature of the metal. The metal center of the "*cis*-M$(C_6F_5)_2$" fragment lies in an essentially square planar environment, while the coordination sphere of the metal bonded to the aminophosphane group deviates significantly from planarity. This distortion is probably due to the strain imposed by the chelating coordination of the $PPh_2(C_{13}H_8N)$ ligand. The three structures confirm the coupling of the original diphenylphosphanido and benzoquinolinate ligands, with the formation of a P−C bond. The length of this new bond shows no appreciable differences with the other P−C(Ph) bonds formed by this phosphorus atom, P(2). The new chelate ligand and the metal atom form a non planar six-membered metallacycle. This is reflected in a distortion in the otherwise planar benzoquinolinate skeleton, which is warped, with N−C(25)−C(24)−C(23) torsion angles of 13.7(1)° for **6**, 13.5(1)° for **7**, and 12.7(1)° for **8**. The main difference resides in the intermetallic distance, which is longer for **6** (Pt(1)···Pt(2) = 3.255(1) Å) and very similar for the other two complexes (Pt−Pd = 3.081(1) Å in **7** and Pd(1)−Pd(2) = 3.078(1) Å in **8**). As a related effect, this difference is also found in the dihedral angle formed by the two planes defined by the metal centers and the bridging atoms bonded to them (plane P(1) M(1) I and plane P(1) M(2) I), which is broader in **6** (123.6(1)°) than in **7** or **8** (112.2(1)° in both cases).

Spectroscopic Properties. The NMR features of **5** were addressed in detail, as they were valuable for the study of the dynamic behavior in solution and for the mechanism of transformation into **6**.

The $^{31}P\{^{1}H\}$ NMR of **5** showed two doublets centered at δ −107.5 and δ −115.5, each flanked by three sets of ^{195}Pt satellites arising from isotopomers containing one or two ^{195}Pt atoms. Dipolar couplings (^{1}H NOESY) between protons of the benzoquinolinate ligand and protons of the phenyl ring A (i.e., one of the phenyls bonded to P2, as indicated by $^{1}H-^{31}P$ HMQC spectrum, Figure 3) permitted to assign the ^{31}P NMR signal at δ −107.5 to P2 and, therefore, the ^{31}P NMR signal at δ −115.5 to P1. Comparison with the $^{195}Pt\{^{1}H\}$ NMR spectrum permitted us to assign the direct Pt−P coupling constants. The values of $^{1}J\text{Pt}^{1}-\text{P}^{2}$ and $^{1}J\text{Pt}^{1}-\text{P}^{1}$ in **5** are 2189 and 2032 Hz, while those of the two ^{1}JPt(IV)−P were 1270 Hz ($^{1}J\text{Pt}^{2}-\text{P}^{2}$) and 1807 Hz ($^{1}J\text{Pt}^{2}-\text{P}^{1}$) (Table 1).

Our findings are in accord with literature data: in phosphane derivatives the Pt−P coupling constants in Pt(IV) derivatives are about two-thirds of that of the Pt(II) precursors,[50,51] and a value of 1801 Hz has been published for a ^{1}JPt(IV)−P coupling of a P atom *trans* to an I ligand in a phosphane derivative of platinum(IV).[50] Although values of 830 and 791 Hz for ^{1}JPt−P were reported in 1977 for two derivatives which were claimed

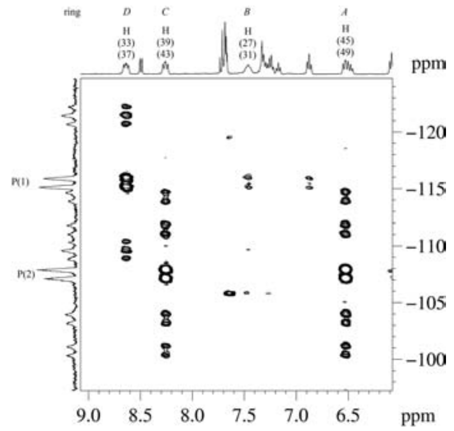
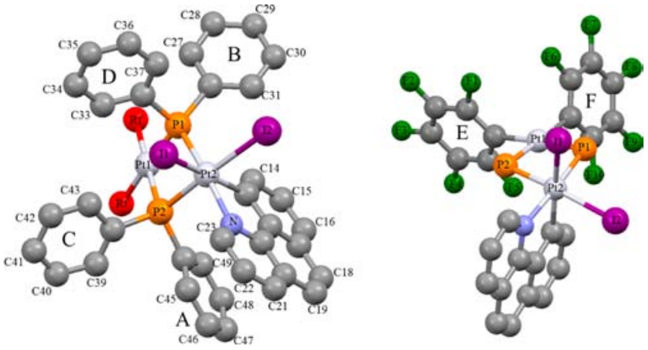


Figure 3. Low-field portion of the $^{1}H-^{31}P$ HMQC spectrum of **5** (400 MHz, C_3D_6O, 298 K).

to be Pt(IV) μ-PH_2 complexes,[52] a complete structural characterization of these complexes or subsequent data have not been reported later. As far as we know, complex **5** is the first platinum(IV) phosphanido derivative characterized unambiguously.

The ^{1}H NMR features of **5** were obtained by combining data extracted from $^{1}H-^{31}P$ HMQC, $^{1}H-^{195}Pt$ HMQC, ^{1}H NOESY, and ^{1}H COSY spectra. The attribution of all signals is reported in Figure S3 (the numbering of the hydrogen atoms coincides with that of the carbon atom to which they are bonded, taken from the solid state structure of **5′**, Chart 2).

Chart 2. Two Views of Complex 5 Showing the Labels for the Rings



In particular, the attribution of the *ortho* protons of the phenyl rings was made on the basis of the $^{1}H-^{31}P$ HMQC spectrum (Figure 3) showing correlations (due to scalar coupling) between P1 and signals at δ_H 8.61 (H33/37) and δ_H 7.44 (H27/31) (*ortho* protons of phenyl rings D and B, respectively) as well as between P2 and signals at δ_H 8.23 (H39/43) and δ_H 6.50 (H45/49) (*ortho* protons of phenyl ring C and A, respectively). ^{1}H NOESY and ^{1}H COSY spectra permitted us to complete the assignment of all protons of the four phenyl rings. The attribution of the protons of the coordinated benzoquinolinate ligand was made on the basis of the $^{1}H-^{195}Pt$ HMQC spectrum (Figure 4) from which the protons scalar coupled to Pt2 could be identified. The analysis of ^{1}H NOESY and ^{1}H COSY spectra permitted us then to complete the assignment of all protons of the benzoquinolinate ligand. Signals due to H23 (δ 10.73), H14 (δ 9.63), and H21(δ 8.46) are well separated from each other, while the remaining five signals (H15, H16, H18, H19, and H22) are partially overlapped in the region ranging from δ 7.70 to δ 7.63. On passing from **1** to **5**, the ^{1}H NMR signals of the benzoquinolinate ring *trans* to I appear significantly shifted to low fields.

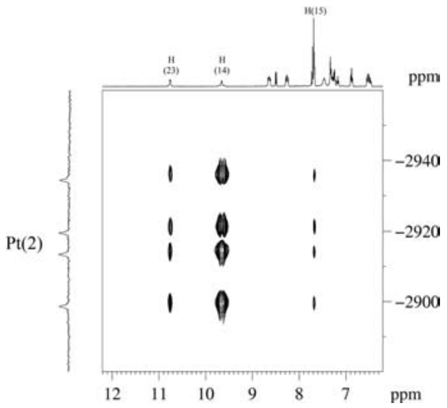


Figure 4. Low-field portion of the $^{1}H-^{195}Pt$ HMQC spectrum of **5** (400 MHz, C_3D_6O, 298 K).

The ^{19}F NMR of **5** at 200 K showed 10 signals, one for each of the ^{19}F atoms of the two rings. The inequivalence of the two rings and of the two halves in each ring indicates that at low *T* the rotation of the pentafluorophenyl groups about the Pt−C bond is slow in the NMR time-scale and the structure in solution resembles that in the solid state. Combining the results of ^{19}F COSY, $^{19}F-^{1}H$ HOESY, and ^{19}F NOESY at various *T*'s permitted us to assign all ^{19}F atoms of **5** as shown in Figure 5 (the numbering is that of the solid state structure of **5′**).

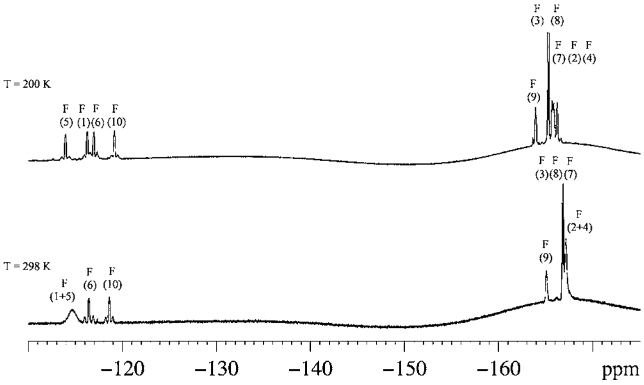


Figure 5. ^{19}F spectra of **5** (376 MHz, C_3D_6O).

At 298 K the signals of the *ortho* (F1 and F5) and of the *meta* (F2 and F4) fluorine atoms of ring E collapse into two very broad signals centered at δ −114.6 and δ −167.2, respectively, with the five signals of ring F (F6−10) remaining separated from each other.[53] This behavior indicates that, upon increasing the temperature from 200 to 298 K, ring E rotates (about the Pt1−C1 axis) with a frequency that averages the resonances of the two halves of the ring. On the other hand, even at 298 K, ring F rotates very slowly about the Pt1−C7 axis, so that the *o*-F and *m*-F still appear inequivalent. In accord to this view, the ^{19}F EXSY spectrum of **5** recorded at 298 K (Figure 6) showed intense cross peaks between the F6 and F10 (the *ortho*-F of ring F) as well as between the F7 and F9 (the *meta*-F of ring F), as a result of the exchange between the fluorine atoms upon

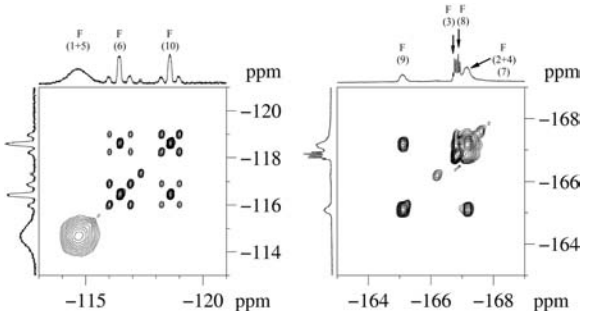


Figure 6. Two portions of the ^{19}F EXSY spectrum of **5** (376 MHz, C_3D_6O, 298 K).

rotation. VT ^{19}F NMR spectra for **5** allowed us to calculate the value of 57 kJ/mol for the activation free energy $\Delta G^{\ddagger}$ of rotation of the E ring of **5**.

The attribution of the ^{19}F signals to ring E or F was made on the basis of the correlations in the $^{19}F-^{1}H$ HOESY spectrum of **5** at 298 K (Figure 7, τ_m = 0.200 s). The $^{19}F-^{1}H$ HOESY experiment displays correlations deriving from the dinuclear coupling between fluorine atoms and protons in close spatial proximity, and in the case of **5** showed cross peaks between signals at δ_F −118.6 and δ_H 9.63 (H14) as well as between signals at δ_F −116.4 and δ_H 8.61 (*ortho* hydrogens of phenyl ring D, H33/37, Chart 3). Given that the fluorine atom closest to H14 is F10, one of the *ortho* fluorines of ring F (the distance in the crystal structure of **5**′ is 2.79 Å) and the fluorine atom closest to H33/37 is F6 (d = 2.73 Å), we interpret these results admitting that the pentafluorophenyl ring displaying inequivalent *ortho*- and *meta*-fluorine atoms even at 298 K (*F* in Chart 2) is close to the phenyl ring D. These attributions are corroborated by a weak cross peak also present in the $^{19}F-^{1}H$ HOESY spectrum of **5** at 298 K between signals at δ_F −114.6 (F1/5) and δ_H 6.50 (*ortho* hydrogens of phenyl ring A, H45/49).

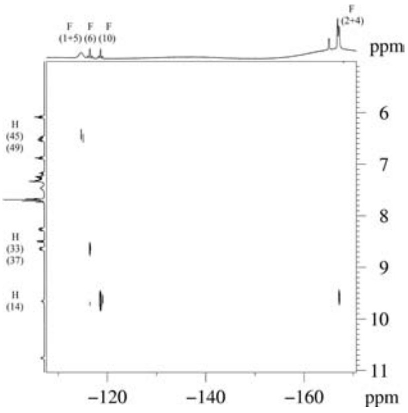
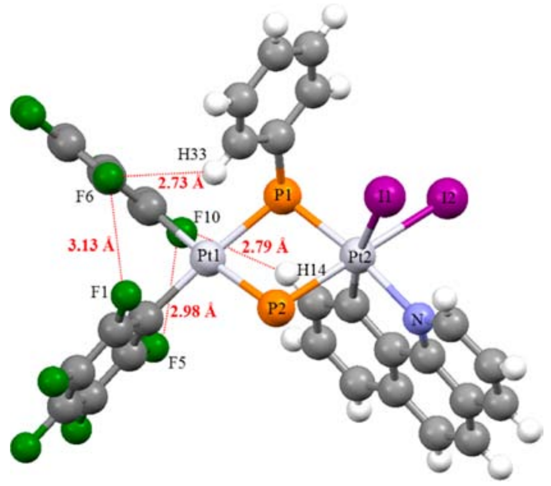


Figure 7. $^{19}F-^{1}H$ HOESY spectrum of **5** (376 MHz, C_3D_6O, 298 K).

Chart 3



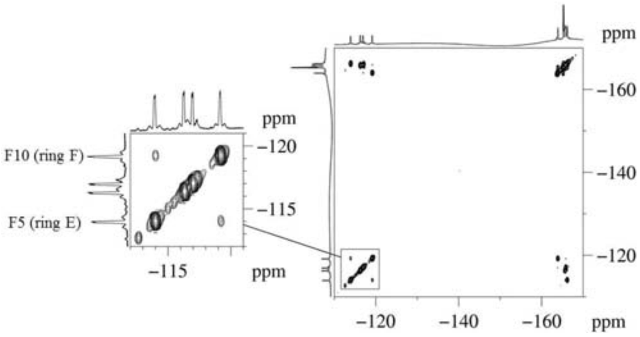


Figure 8. ^{19}F COSY spectrum of **5** (376 MHz, C_3D_6O, 200 K).

An interesting feature deduced from the ^{19}F COSY spectrum of **5** at 200 K (or at 273 K) is an intense cross peak between F5 (one of the *o*-F atoms of ring E) and F10, (one of the *o*-F atoms of ring F) (Figure 8). The scalar correlation between these six bonds away ^{19}F atoms belonging to different pentafluorophenyl rings in mutually *cis* position can be explained in terms of "through space" spin−spin couplings. In fact, the favorable spatial disposition of F5 and F10 (the F5−F10 distance in the solid state structure of **5**′ is 2.98 Å) may facilitate overlap interactions between filled orbitals of the F atoms, resulting in a no net bonding providing, nevertheless, a suitable pathway for transmitting spin information between the coupled nuclei.[54,55] An analogous "through space" coupling was observed also for the F1−F6 couple, whose distance in the solid state structure of **5**′ is 3.13 Å. The existence of the "through space" coupling between F5 and F10 (as well as between F1 and F6) is corroborated by the presence, in the ^{19}F EXSY spectrum of **5** recorded at 200 K, of weak cross peaks between F5 and F10 (as well as between F1 and F6) confirming the spatial proximity of such pairs of ^{19}F atoms in solution at low *T*. Noteworthy, a weak "through space" coupling between *o*-F atoms belonging to different C_6F_5 rings was also observed by recording the ^{19}F COSY spectrum of **7** in deuteroacetone at 298 K (Figure S4).

The $^{195}Pt\{^{1}H\}$ NMR spectrum of **5** showed two signals, one at δ −3806, and the other at δ −2917. Of these, that at δ −3806 gives peaks broadened by multiple couplings with ^{19}F and is ascribed to Pt^1, bonded to pentafluorophenyl rings. The signal at δ −2917 is a sharp doublet of doublets ($^{1}JPt^2-P$ 1270 and 1807 Hz) and is ascribed to the octahedral Pt^2(IV) atom. No geminal Pt−Pt coupling was visible (the half-height width of the signals was $\Delta\nu_{1/2}$ = 50 Hz). The deshielding of the Pt^2 (+800 ppm) observed on passing from formal oxidation state +2 to +4 is in accord to the majority of literature data[56] but contrasts with what is found for the polysilylated compounds described by Tanaka, for which a strong shielding is observed upon Pt(II)→Pt(IV) oxidation.[57]

Multinuclear NMR spectra of complexes **6**−**10** are conclusive to establish their structure and are in accordance with the solid state study. All data extracted from the analysis of the spectra are collected in Table 1. For the aminophosphane complexes **6**−**8** and **10**, P^2 atoms appear at lower-field than those in the starting materials **1**−**4**, as a consequence of the transformation of the diphenylphosphanido ligand involved in a four-membered ring into an aminophosphane ligand, PPh_2(C^N). Expectedly, the ^1JPt−P^2 values of **6** and **10** are larger, 4435 and 4307 Hz. It is well established that the P signals of "M(μ-PPh_2)(μ-X)M" (X = Cl, Br, I, OH) fragment in a saturated phosphanido bridged complex (without M−M bond) appear low-field shifted respect to the fragment M(μ-PPh_2)$_2$M in a saturated platinum or palladium derivative.[58−61] This is true for P^1 in **6**−**8** and **10** (see Table 1) compared with **1**−**4**. In the literature +50 ppm is considered roughly as the lowest limit of δP for the phosphanido group involved in four-membered rings in complexes without metal−metal bonds.[62] The values of δP^1 found for **7** and **8** (55.2 and 66.0 ppm) lie at the lower limit of this range, and $^2J P^1$−P^2 values are much smaller in **6** and **10** (2 Hz) than in **7** and **8** (40 and 36 Hz, respectively). It is also to note that the coupling of the P atom of the phosphane ligand with the Pt^1 center bonded to the C_6F_5 groups, $^3J Pt^1$−P^2, is observed, and this value is larger in the Pt−Pd complex **7** (97 Hz) than in the Pt−Pt one **6** (37 Hz). These three facts suggest some differences between **7**, **8** and **6**, **10** which may be related to the slightly smaller intermetallic distance in **7** and **8** with respect to **6**, as mentioned before.

The ^{19}F NMR spectra of **6**−**8** show three signals (2:2:1 intensity ratio) for each pentafluorophenyl ring, in agreement with the inequivalence of the two C_6F_5 groups, and indicate that in solution the two halves of each ring are equivalent, due to free rotation about the C−M bond. For **6**−**8**, one C_6F_5 ring rotates faster than the other, as evidenced by the difference in sharpness of the corresponding ^{19}F NMR signals. It is conceivable that the C_6F_5 ring *cis* to the bridging iodide suffers from less sterical hindrance than the C_6F_5 ring *cis* to the bridging diphenylphosphanide, thus rotating relatively faster and giving sharper ^{19}F NMR signals.

For the Pd(II)−Pt(IV) complex **9** analogous to **5** the bridging phosphanide ^{31}P resonances were found at δ −97.7 (P^1) and δ −89.1 (P^2) while the direct P−Pt coupling contants were 1121 Hz (^1JPt−P^2) and 1680 Hz (^1JPt−P^1) (Table 1). The ^{195}Pt NMR signal of **9**, obtained from the ^1H−^{195}Pt HMQC spectrum recorded on the mixture of **9**, **10**, and **11**, was found at δ −2966.

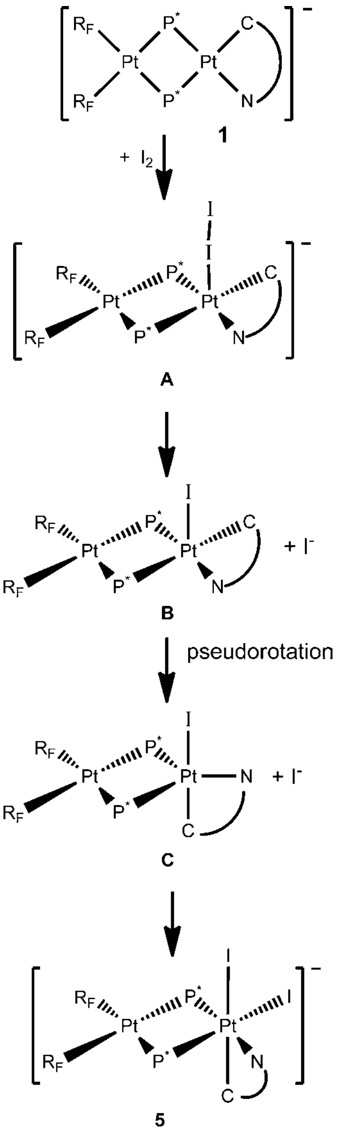
The identification of **11** from the NMR data as [(R_F)(PPh_2R_F)Pd^{II}(μ-PPh_2)(μ-I)Pt^{II}(C^N)] was easily achieved by comparing its spectra with the corresponding ones of the analogous [NBu_4][(R_F)(PPh_2R_F)Pd^{II}(μ-PPh_2)(μ-I)Pt^{II}(R_F)$_2$], prepared earlier in our laboratories.[42] The assignment of the Pt−N bond in *trans* position to the phosphanido group and not to the I ligand was made on the basis of the large value of ^1JPt−P^1 (3317 Hz) extracted from the spectrum. In this case, the ^{19}F NMR is also conclusive because signals due to the $PPh_2C_6F_5$ group appear in the spectrum well separate from those of Pd−C_6F_5.[42,43,49,63−65] ^{19}F NMR data are given in the Experimental Section. The ^{195}Pt NMR signal for complex **10** was found at δ −4416, by ^1H−^{195}Pt HMQC experiments recorded on the mixture of **9**, **10**, and **11**.

Mono- and bidimensional ^1H NMR spectra of **6**−**8** permitted the full assignment of all ^1H NMR signals. In these three cases the spectra display a similar pattern, and eight well separated signals are observed for the C^N part of the aminophosphane ligand. As a consequence of the formation of the P−C bond, the couplings between the P^2 atom and the hydrogen atom are observed in four of the eight signals. To distinguish the homonuclear from the heteronuclear scalar coupling $^1H\{^{31}P\}$ NMR experiments for complexes **6**−**8** were recorded. The data so obtained are reported in the Experimental Section.

■ DISCUSSION

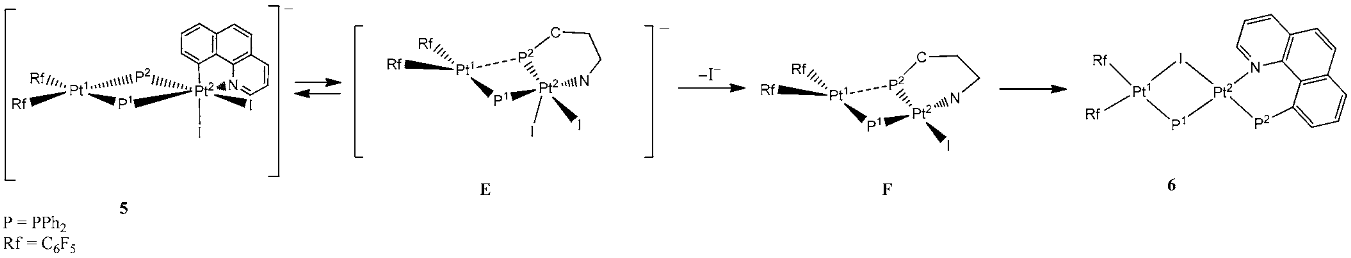
The dinuclear Pt(II),Pt(IV) complex **5** is the result of the oxidative addition of I_2 to one of the platinum centers, the one containing the C^N ligand, in the dinuclear Pt(II),Pt(II) derivative **1**. In the oxidative addition of I_2, it is accepted that I_2 is usually activated heterolytically in an S_N2-like process,[51,66] which in the case of complex **1** could initially consist of the formation of the η^1-I_2 adduct **A**[67] (Scheme 4) followed by iodine dissociation and formation of the square pyramidal Pt(IV) intermediate **B**. The unsaturated intermediate **B** can

Scheme 4

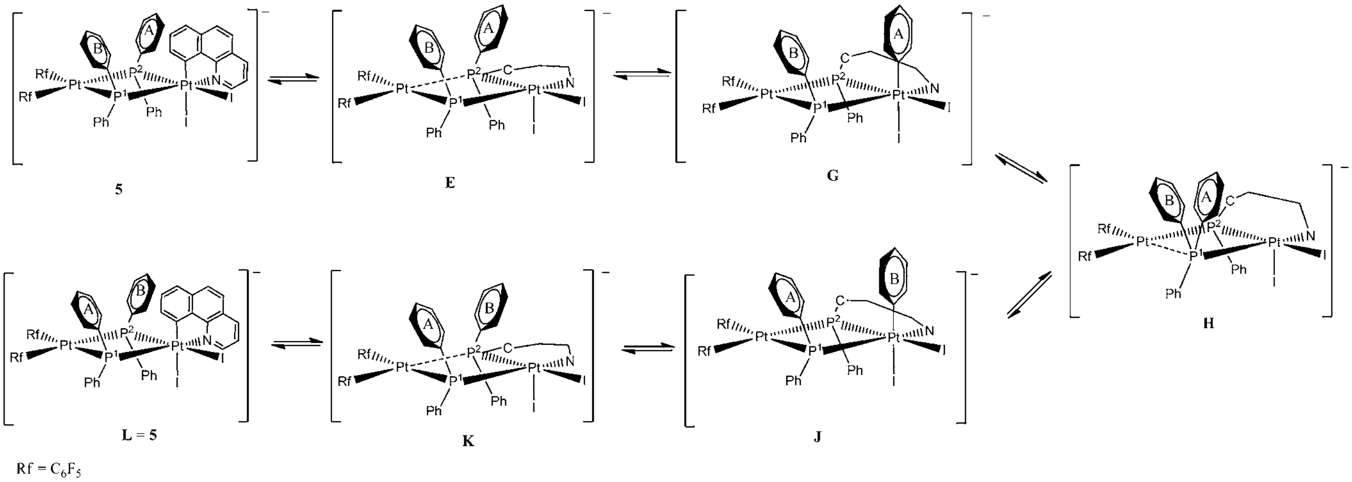


R_F = C_6F_5
P* = PPh_2

Scheme 5



Scheme 6



then rearrange via pseudorotation to the trigonal bipyramid intermediate **C** which, in turn, could uptake the anion I$^-$ giving complex **5** as a result of the formal *cis*-addition (Scheme 4).

Obtaining the aminophosphane species **6** by leaving **5** in dichloromethane (or by carrying out the iodination of **1** in CH_2Cl_2) can be explained by the pathway shown in Scheme 5. Insertion of P^2 onto the Pt−C bond could give intermediate **E**, having a five-coordinate Pt^2. Intermediate **E** may then undergo iodide dissociation to give **F**, which affords **6** upon rupture of the P^2−Pt^1 bond, rotation about the P^1−Pt^2−N axis, and bridging coordination of the iodide bonded to Pt^2. Given that the reaction rate for a dissociative process is inhibited by the addition of an excess of the leaving group, we monitored by ^{31}P NMR the transformation of **5** into **6** in dichloromethane, with and without 5 equiv of $(NBu_4)I$. While the conversion of **5** into **6** was 25% after 64 h in the absence of external iodide, the solution containing **5** and $(NBu_4)I$ showed, after the same time, only signals of **5**.[68] The geometry of the five-coordinate Pt^2 in intermediate **E** could be in principle either trigonal bipyramid or square based pyramid. The analysis of the dynamics in solution of complex **5** revealed indicative in order to discriminate between the two geometries, favoring the square based pyramide one (*vide infra*). The ^{1}H EXSY spectrum of **5** at 298 K in deuteroacetone showed cross peaks between the signals at δ 6.05, 6.45, 6.50 with those at δ 6.85, 7.15, 7.44, respectively (Figure S5), indicating an exchange between the phenyl rings A and B, bonded to two different P atoms (A is bonded to P2 while B is bonded to P1). No evident exchange between protons belonging to C and D rings was observed, thus excluding the exchange of the two entire diphenylphosphanide groups. Such circumstance was confirmed by the absence of cross peaks in the ^{31}P{^{1}H} EXSY spectra of **5** at 298 K, recorded at various mixing times (from 0.100 to 0.800 s). The observed exchange of rings A and B is not immediately rationalizable as it supposedly requires the shift of the phenyl ring A originally bonded to P2, first onto the Pt(IV) atom, and then onto P1, leaving fixed the P atoms. However, given that carbon insertion into μ-PPh$_2$−Pt bonds is not uncommon in diphenylphosphanido bridged Pt or Pd complexes[42,44,49,64,69−73] and that the systems under study do undergo such process in the reactions from **1**−**4** to **6**−**8** and **10**, we propose the mechanism reported in Scheme 6 to rationalize the observed ^{1}H NMR exchange. The fact that only rings A and B are involved in the exchange suggests that the dynamic process concerns only the half of the molecule containing the benzoquinolinate ligand, ring A and ring B (Chart 2).

Thus, as proposed in Scheme 5 for the **5** to **6** conversion, insertion of P^2 onto the Pt^2−C bond in **5** can give species **E** (Scheme 6). In acetone, species **E** may reform **5** by breaking of the P−C^N bond and formation of the Pt−C^N bond, or can give **G** by breaking of the P−Ph$_A$ bond and formation of the Pt−Ph$_A$ bond. The P−Ph$_C$ bond cannot be involved in this process due to its unfavorable position that renders unlikely the shift of Ph$_C$ to the apical coordination site of Pt(IV) (at least in a concerted way). The Ph$_A$ bonded to Pt(IV) in **G** may migrate onto P^1 to give species **H** in which the pentacoordinated P^1 is bonded to three phenyl groups and the free coordination site on Pt is occupied by acetone. At this point, **H** may undergo breaking of the P−Ph$_A$ bond or of the P−Ph$_B$ bond (but not of the P−Ph$_D$ bond) and formation of the Pt−Ph bond to give **G** or **J**, respectively. The path opposite to that which led from **5** to **H** can thus give first **K** and then **L** (identical to **E** and **5**, respectively, but with exchanged phenyl rings A and B). In the light of this finding, the square based pyramid geometry of the five-coordinate Pt^2 in complex **E** is the only one allowing the exchange process involving phenyl rings A and B (with C and D rings not being exchanged).[71,72,74−76]

The mechanisms outlined in Schemes 5 and 6, besides explaining the **5** to **6** conversion and the observed exchange of phenyl rings A and B, may also account for the role of the solvent in the reactivity of **1** toward I_2. In fact, admitting that the stability of the intermediate **E** (which is anionic) increases with the polarity of the solvent, we can envision that species **E** slowly transforms into **F** (giving eventually **6**, Scheme 5) when the reaction is carried out in dichloromethane, whereas **E** isomerizes into **G** to start the exchange process depicted in Scheme 6 when dissolved in acetone.

The exchange between phenyl rings bonded to two different P atoms was observed (^{1}H EXSY in deuteroacetone at 298 K of the mixture containing a great amount of **9**) also for complex **9**, the Pd−Pt analogue of **5**.

Examples of polynuclear complexes in which the phosphane ligand adopts a μ^2-PR_3 coordination mode are well-known.[77−80] These complexes that show a pentacoordinated P atom provide a structural model as reaction intermediates in the oxidative addition processes of the P−C bond to a metal center to form phosphanido derivatives. In this work, species **E**, **H**, and **K** (Scheme 6) are proposed as intermediates in the inverse process: from phosphanido to a phosphane derivative.

The reaction products between equimolar amounts of **2** and I_2 in acetone at 213 K afforded, as mentioned before, **7** and $[NBu_4]_2[\{(R_F)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}I)\}_2]$. The presence of the tetranuclear derivative of platinum and palladium(II) showing the "Pt(μ-PPh_2)$_2$Pd" fragment is explainable with a C−I reductive elimination from the Pd(IV) system in an intermediate similar to **5**. In addition, the reactions of **1** or **4** with I_2 did not produce in any case complexes containing the $PPh_2C_6F_5$ ligand, which could be the result of a P−C_6F_5 reductive coupling, but only compounds with the P−C^N ligand. This fact suggests that the initial oxidative addition takes place in the metal fragment which is bonded to the benzoquinolinate ligand, in accord to the mechanism shown in Scheme 4. Considering that the reaction of **1** (Pt−Pt) with I_2 in CH_2Cl_2 permitted us to isolate the oxidized complex **5**, and the aminophosphane derivative **6**, while only the aminophosphane derivative is obtained in the reaction of the homologous Pd−Pd derivative **4** with I_2 in the same conditions, it seems clear that the reductive coupling is faster on palladium derivatives. This result is not unexpected and parallels what was found for the addition of I_2 to complexes $[NBu_4]_2[(R_F)_2Pt(\mu\text{-}PPh_2)_2M(R_F)_2]$ (M = Pt, Pd). In these cases the isolated complexes $[NBu_4][(R_F)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}I)M(R_F)(PPh_2R_F)]$ contained the ligand PPh_2R_F, as a consequence of a PPh_2 and C_6F_5 reductive coupling, but only for M = Pt the intermediate dinuclear Pt(III)−Pt(III) was observed and isolated. In complex **2** the C^N chelate ligand is bonded to a palladium center, the platinum atom is bonded to the C_6F_5 groups, and the oxidative addition occurs only on the palladium center. Finally, complex **3** shows the C^N chelate ligand bonded to a platinum center and the palladium atom bonded to the C_6F_5 groups and the identification of the complexes **9**, **10**, and **11** after reacting **3** with I_2 indicates that the oxidative addition of I_2 takes place in all likelihood on both metal centers. The oxidative addition to the Pt(II) center could produce **9** and **10** while the oxidative addition to Pd(II), and the subsequent reductive coupling of the PPh_2 and C_6F_5 groups on the intermediate and unstable Pd(IV) complex, could produce complex **11** with the $PPh_2C_6F_5$ ligand coordinated to the Pd(II) center.

Interestingly, although formation of C−C and C−X (X = halogen) bonds from M(IV) derivatives (M = Pt, Pd) is now well documented,[5,81−85] in our case the reductive coupling between a phosphanido bridge and the cyclometaled C,N ligand, with P−C bond formation, is observed.

It is worth commenting that the phosphanido ligands have been widely used as building blocks for the synthesis of a great variety of polynuclear palladium and platinum complexes due to their flexibility and to the stability of the M−P bonds, both facts being the main reasons of the retention of the polynuclear fragment $M(\mu\text{-}PR_2)_xM'$ (M, M′ = Pd, Pt) during the chemical reactions of phosphanido complexes.[86,87] However, nowadays, examples in which the polynuclear fragment $M(\mu\text{-}PR_2)_xM'$ evolves,[48,59,69,88−92] and the phosphanido ligand is transformed into another ligand[42,44,49,64,69−73,93−95] or is coordinated in a nonclassical bonding mode,[69,96−99] have already been reported. The process that produces **6** from **1** is the transformation of a phosphanido bridging ligand and a C^N chelate ligand into an aminophosphane group through a reductive coupling induced by oxidation. The formation of aminophosphane ligands had already been reported through a reductive elimination process on palladium(II) complexes leaving Pd(0) substrates.[100,101]

■ CONCLUDING REMARKS

The asymmetric homo- or heteronuclear complexes **1**−**4**, $[NBu_4][(R_F)_2M(\mu\text{-}PPh_2)_2M'(C_{13}H_8N)]$, were prepared by the adequate reactions of $Li_2[M(R_F)_2(PPh_2)_2]$ with $[\{M'(\mu\text{-}Cl)(C\text{^}N)\}_2]$. The addition of I_2 to these complexes resulted in the formation of a different type of complexes, the nature of which is mainly dependent on the type of binuclear compound used. In the case of the homodinuclear derivative **1**, M = M′ = Pt, it was possible to isolate the dinuclear Pt(II),Pt(IV) complex $[NBu_4][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C\text{^}N)I_2]$ carrying out the reaction in acetone. For the other starting materials (**2**−**4**) and also for **1** when the reaction is carried out in CH_2Cl_2, the resulting compounds are M(II),M′(II) complexes which contain PPh_2−$C_{13}H_8N$ ligand as a result of the reductive coupling between a PPh_2 group and the benzoquinolinate ligand with formation of a P−C bond. The new resulting ligand remains coordinate chelated to one of the metal centers.

It seems also clear that the reductive coupling induced after addition of I_2 is faster on the palladium than on the platinum complexes and that it is also preferred on the metal center bonded to the C^N ligand than on the metal center bonded to the two C_6F_5 groups.

The identification of **9**−**11** obtained from **3** indicates that the oxidative addition of I_2 on the Pd center bonded to two pentafluorophenyl groups competes with the addition on the Pt center bonded to the C^N ligand.

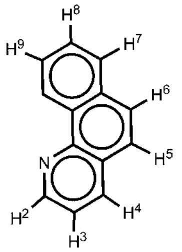
It is also remarkable that while the oxidative addition of I_2 to these unsymmetrical complexes results initially in the formation of mixed-valence M(II),M′(IV) complexes (in some cases very unstable), the reaction of I_2 with the symmetric complexes $[NBu_4]_2[(R_F)_2M(\mu\text{-}PPh_2)_2M'(R_F)_2]$ results in the formation of M(III)−M′(III) derivatives.

Finally, in addition to the two well-known characteristics of phosphanido ligands frequently discussed since the chemistry of phosphanido complexes flourished (their flexibility, which allows them to support a great variety of structural situations, and the stability of M−P bond) a third characteristic has to be added today, the ability of the diphenylphosphanido group as a very versatile ligand capable of stabilizing complexes of palladium or platinum in very different oxidation states: I, II, III, and IV.

■ EXPERIMENTAL SECTION

General Comments. C, H, and N analyses were performed with a Perkin-Elmer 2400 analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra in solution were recorded on a Bruker AV 400 spectrometer with SiMe$_4$, CFCl$_3$, 85% H$_3$PO$_4$, and aqueous [PtCl$_6$]$^{2-}$ as external references for ^{1}H, ^{19}F, ^{31}P, and ^{195}Pt, respectively. The signal attributions and coupling constant assessment was made on the basis of a multinuclear NMR analysis of each compound including, besides 1D spectra, ^{1}H COSY, ^{1}H NOESY, ^{1}H−^{31}P HMQC, ^{1}H−^{195}Pt HMQC, ^{19}F COSY, ^{19}H−^{1}H HOESY, and ^{19}F NOESY experiments. Literature methods were used to prepare the starting materials *cis*-[M(R$_F$)$_2$(PPh$_2$H)$_2$], M = Pd, Pt[45] and [{M(μ-Cl)(C^N)}$_2$], M = Pd,[102] Pt.[103]

Synthesis of [NBu$_4$][(R$_F$)$_2$M(μ-PPh$_2$)$_2$M′(C^N)]. *M = M′ = Pt, 1.* To a colorless solution of *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (0.601 g, 0.667 mmol) in THF (10 mL) at −78 °C was added *n*-butyllitium (2.5 M in hexanes, 0.54 mL, 1.35 mmol) under an argon atmosphere. The resulting yellow solution was stirred for 15 min, and [{Pt(μ-Cl)(C^N)}$_2$] (0.273 g, 0.334 mmol) was added. The suspension was allowed to reach room temperature, stirred for 20 h, and evaporated to dryness. CH$_2$Cl$_2$ (25 mL) was added to the resulting residue, and a solid was filtered through Celite. The CH$_2$Cl$_2$ solution was evaporated to dryness, and the residue was dissolved in ^{i}PrOH (ca. 30 mL). NBu$_4$ClO$_4$ (0.228 g, 0.667 mmol) was added to the solution, and **1** crystallized as a yellow solid, which was filtered, washed with ^{i}PrOH (3 × 1 mL), and dried, 0.873 g, 86% yield. Found: C, 51.35; H, 4.44; N, 1.93. C$_{65}$F$_{10}$H$_{64}$N$_2$P$_2$Pt$_2$ requires C, 51.52; H, 4.26; N, 1.85. HRMS(−), exact mass for the anion [C$_{49}$H$_{28}$F$_{10}$NP$_2$Pt$_2$]$^-$: 1272.0835. Measured *m*/*z*: 1272.0823 (M)$^-$.



^{31}P{^{1}H} NMR (161 MHz, 298 K, (CD$_3$)$_2$CO): δ −107.9 (d, ^{2}JP,P = 116 Hz, ^{1}JP1,Pt2 = 2810 Hz, ^{1}JP1,Pt1 = 1937 Hz, P1), −118.9 (d, ^{2}JP,P = 116 Hz, ^{1}JP2,Pt2 = 1320 Hz, ^{1}JP2,Pt1 = 1646 Hz, P2).

^{19}F NMR (376 MHz, 298 K, (CD$_3$)$_2$CO): δ −113.9 (m, 4 *o*-F, ^{3}JPt,F = ca. 330 Hz), −167.4 (ddd, 2 *m*-F, ^{3}JF,F = 25 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 9 Hz), −166.7 (2 *m*-F, ddd, 2 *m*-F, ^{3}JF,P = 25 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 11 Hz), −169.1 (t, 1 *p*-F, ^{3}JF,F = 20 Hz), −169.2 (t, 1 *p*-F, ^{3}JF,F = 20 Hz) ppm.

^{1}H NMR (400 MHz, 298 K, (CD$_3$)$_2$CO): 8.66 (m,1H, H2), 8.45 (dd, 1H, ^{3}JH,H = 8.0, ^{4}JH,H = 1.0 Hz, H4), 7.96 (m, 4H, *o*-Ph bonded to P1*)*, 7.85 (m, 4H, *o*-Ph bonded to P2), 7.82 (d, 1H, ^{3}JH,H = 8.8 Hz, H6), 7.68 (d, 1H, ^{3}JH,H = 8.8 Hz, H5), 7.51 (dd, 1H, ^{3}JHH = 7.8 Hz, ^{4}JHH = 0.6 Hz, H7), 7.30 (d, 1H, ^{3}JH,H = 8.0 Hz, H3), 7.29 (d, 1H, ^{3}JH,H = 7.9 Hz, H9), from 7.20 to 7.03 (m, 13 H, overlapped *m*-Ph + *p*-Ph + H8*)*, 3.49 (m 8H, NBu$_4$$^{+}$), 1.87 (m 8H, NBu$_4$$^{+}$), 1.48 (pseudosextet, 8H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$), 1.02 (t, 12H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$) ppm.

^{195}Pt{^{1}H} NMR (86 MHz, 298 K, (CD$_3$)$_2$CO): δ −3717 (dd, ^{1}JPt2,P2 = 1320 Hz, ^{1}JPt2,P1 = 2810 Hz, ^{2}JPt,Pt = 541 Hz, Pt2), δ −3889 (m, ^{1}JPt1,P2 = 1646 Hz, ^{1}JPt1,P1 = 1937 Hz,Pt1).

M = Pt, M′ = Pd, 2. Complex **2** was prepared similarly from *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (1.000 g, 1.110 mmol), *n*-butyllitium (2.5 M in hexanes, 0.89 mL, 2.22 mmol), [{Pd(μ-Cl)(C^N)}$_2$] (0.355 g, 0.555 mmol), and NBu$_4$ClO$_4$ (0.380 g, 1.110 mmol) as a yellow solid, 1.177 g, 74% yield. Found: C, 54.49; H, 4.41; N, 1.89. C$_{65}$F$_{10}$H$_{64}$N$_2$P$_2$PdPt requires C, 54.72; H, 4.52; N, 1.96. HRMS(−), exact mass for the anion [C$_{49}$H$_{28}$F$_{10}$NP$_2$PdPt]$^-$: 1184.0240. Measured *m*/*z*: 1184.0366 (M)$^-$.

^{31}P{^{1}H} NMR (161 MHz, 298 K, (CD$_3$)$_2$CO): δ −78.8 (d, ^{2}JP,P = 160 Hz, ^{1}JP1,Pt2 = 2648 Hz, P1), −116.6 (d, ^{2}JP,P = 160 Hz, ^{1}JP2,Pt1 = 1530 Hz, P2).

^{19}F NMR (376 MHz, 298 K, (CD$_3$)$_2$CO): δ −113.8 (m, 4 *o*-F, ^{3}JPt,F = ca. 330 Hz), −167.4 (ddd, 2 *m*-F, ^{3}JF,F = 25 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 9 Hz), −167.7 (2 *m*-F, ddd, 2 *m*-F, ^{3}JF,P = 25 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 10 Hz), −169.17 (t, 1 *p*-F, ^{3}JF,F = 20 Hz), −169.24 (t, 1 *p*-F, ^{3}JF,F = 20 Hz) ppm.

^{1}H NMR (400 MHz, 298 K, (CD$_3$)$_2$CO): 8.41 (dd, 1H, ^{3}JH,H = 8.0, ^{4}JH,H = 1.0 Hz, H4), 8.36 (m,1H, H2), 7.93 (m, 4H, *o*-Ph bonded to P1*)*, 7.82 (d, 1H, ^{3}JH,H = 8.6 Hz, H6), 7.79 (m, 4H, *o*-Ph bonded to P2), 7.70 (d, 1H, ^{3}JH,H = 8.6 Hz, H5), 7.50 (d, 1H, ^{3}JHH = 7.3 Hz, H7), 7.27 (d, 1H, ^{3}JH,H = 7.9 Hz, H3), 7.26 (d, 1H, ^{3}JH,H = 7.9 Hz, H9), from 7.17 to 7.00 (m, 13 H, overlapped *m*-Ph + *p*-Ph + H8*)*, 3.49 (m 8H, NBu$_4$$^{+}$), 1.87 (m 8H, NBu$_4$$^{+}$), 1.48 (pseudosextet, 8H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$), 1.02 (t, 12H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$) ppm.

^{195}Pt{^{1}H} NMR (86 MHz, 298 K, (CD$_3$)$_2$CO): δ −3909 (m, ^{1}JPt1,P2 = 1530 Hz, ^{1}JPt1,P1 = 1806 Hz, Pt1).

M = Pd, M′ = Pt, 3. Complex **3** was prepared similarly from *cis*-[Pd(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (0.400 g, 0.492 mmol), *n*-butyllitium (2.5 M in hexanes, 0.39 mL, 0.98 mmol), [{Pt(μ-Cl)(C^N)}$_2$] (0.201 g, 0.246 mmol), and NBu$_4$ClO$_4$ (0.168 g, 0.492 mmol) as a yellow solid, 0.463 g, 66% yield. Found: C, 54.52; H, 4.63; N, 1.90. C$_{65}$F$_{10}$H$_{64}$N$_2$P$_2$PdPt requires C, 54.72; H, 4.52; N, 1.96. HRMS(−), exact mass for the anion [C$_{49}$H$_{28}$F$_{10}$NP$_2$PdPt]$^-$: 1184.0240. Measured *m*/*z*: 1184.0334 (M)$^-$.

^{31}P{^{1}H} NMR (161 MHz, 298 K, (CD$_3$)$_2$CO): δ −95.9 (d, ^{2}JP,P = 160 Hz, ^{1}JP1,Pt2 = 2658 Hz, P1), −111.7 (d, ^{2}JP,P = 160 Hz, ^{1}JP2,Pt1 = 1213 Hz, P2).

^{19}F NMR (376 MHz, 298 K, (CD$_3$)$_2$CO): δ −110.7 (m, 4 *o*-F), −166.3 (ddd, 2 *m*-F, ^{3}JF,F = 27 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 10 Hz), −166.6 (2 *m*-F, ddd, 2 *m*-F, ^{3}JF,P = 27 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 12 Hz), −168.0 (t, ^{3}JF,F = 20 Hz, 2 *p*-F overlapped) ppm.

^{1}H NMR (400 MHz, 298 K, (CD$_3$)$_2$CO): 8.62 (m,1H, H2), 8.45 (dd, 1H, ^{3}JH,H = 7.9, ^{4}JH,H = 1.3 Hz, H4), 7.94 (m, 4H, *o*-Ph bonded to P1*)*, 7.84 (m, 4H, *o*-Ph bonded to P2), 7.83 (d, 1H, ^{3}JH,H = 8.8 Hz, H6), 7.68 (d, 1H, ^{3}JH,H = 8.8 Hz, H5), 7.52 (d, 1H, ^{3}JHH = 7.8 Hz, H7), 7.26 (d, 1H, ^{3}JH,H = 8.0 Hz, H3), 7.25 (d, 1H, ^{3}JH,H = 8.2 Hz, H9), from 7.18 to 7.03 (m, 13 H, overlapped *m*-Ph + *p*-Ph + H8*)*, 3.49 (m 8H, NBu$_4$$^{+}$), 1.87 (m 8H, NBu$_4$$^{+}$), 1.48 (pseudosextet, 8H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$), 1.02 (t, 12H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$) ppm.

^{195}Pt{^{1}H} NMR (86 MHz, 298 K, (CD$_3$)$_2$CO): δ −3738 (dd, ^{1}JPt,P2 = 1213 Hz, ^{1}JPt,P1 = 2658 Hz).

M = M′ = Pd, 4. Complex **4** was prepared similarly from *cis*-[Pd(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (0.432 g, 0.534 mmol), *n*-butyllitium (2.5 M in hexanes, 0.43 mL, 1.07 mmol), [{Pd(μ-Cl)(C^N)}$_2$] (0.170 g, 0.267 mmol), and NBu$_4$ClO$_4$ (0.183 g, 0.534 mmol) as a yellow solid, 0.509 g, 72% yield. Found: C, 58.06; H, 4.80; N, 2.11. C$_{65}$F$_{10}$H$_{64}$N$_2$P$_2$Pd$_2$ requires C, 58.35; H, 4.82; N, 2.09. HRMS(−), exact mass for the anion [C$_{49}$H$_{28}$F$_{10}$NP$_2$Pd$_2$]$^-$: 1095.9637. Measured *m*/*z*: 1095.9626 (M)$^-$.

^{31}P{^{1}H} NMR (161 MHz, 298 K, (CD$_3$)$_2$CO): δ −58.0 (d, ^{2}JP,P = 204 Hz, P1), −107.4 (d, ^{2}JP,P = 204 Hz, P2).

^{19}F NMR (376 MHz, 298 K, (CD$_3$)$_2$CO): δ −110.5 (m, 4 *o*-F), −166.3 (ddd, 2 *m*-F, ^{3}JF,F = 27 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 10 Hz), −166.6 (2 *m*-F, ddd, 2 *m*-F, ^{3}JF,P = 27 Hz, ^{3}JF,F = 20 Hz, ^{5}JF,P = 12 Hz), −168.0 (t, ^{3}JF,F = 20 Hz, 2 *p*-F overlapped) ppm.

^{1}H NMR (400 MHz, 298 K, (CD$_3$)$_2$CO): 8.40 (dd, 1H, ^{3}JH,H = 8.2 Hz, ^{4}JH,H = 0.9 Hz, H4), 8.35 (m, 1H, H2), 7.92 (m, 4H, *o*-Ph bonded to P1*)*, 7.82 (d, 1H, ^{3}JH,H = 8.6 Hz, H6), 7.78 (m, 4H, *o*-Ph bonded to P2), 7.70 (d, 1H, ^{3}JH,H = 8.6 Hz, H5), 7.50 (d, 1H, ^{3}JHH = 7.6 Hz, H7), 7.25 (d, 1H, ^{3}JH,H = 8.0 Hz, H9), 7.24 (d, 1H, ^{3}JH,H = 7.9 Hz, H3), from 7.16 to 6.99 (m, 13 H, overlapped *m*-Ph + *p*-Ph + H8*)*, 3.49 (m 8H, NBu$_4$$^{+}$), 1.87 (m 8H, NBu$_4$$^{+}$), 1.48 (pseudosextet, 8H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$), 1.02 (t, 12H, ^{3}JH,H = 7.4 Hz, NBu$_4$$^{+}$) ppm.

Addition of I_2 to 1. To a yellow solution of **1** (0.180 g, 0.118 mmol) in acetone (20 mL) was added I_2 (0.030 g, 0.118 mmol) in acetone (10 mL) dropwise. The solution was stirred at room temperature for 3.5 h, and the resulting red solution was evaporated to ca. 1 mL. *i*-PrOH (10 mL) was added, and **5** crystallized as a yellow solid which was filtered, washed with *i*-PrOH (2 × 1 mL), and air-dried, 0.175 g, 84% yield. Found: C, 43.73; H, 3.61; N, 1.63. $C_{65}F_{10}H_{64}I_2N_2P_2Pt_2$ requires C, 44.13; H, 3.65; N, 1.58. HRMS(−), exact mass for the anion $[C_{49}H_{28}F_{10}I_2P_2Pt_2]^-$: 1525.8924. Measured *m*/*z*: 1525.8911 $(M)^-$.

[NBu$_4$][(R$_F$)$_2$Pt(*μ*-PPh$_2$)$_2$Pt(C^N)I$_2$] (5). ^{31}P{^{1}H} NMR (161 MHz, 298 K, $(CD_3)_2CO$): δ −107.5 (d, ^2JP,P = 126 Hz, ^1JP2,Pt2 = 1270 Hz, ^1JP2,Pt1 = 2189 Hz, P2), −115.5 (d, ^2JP,P = 126 Hz, ^1JP1,Pt2 = 1807 Hz, ^1JP1,Pt1 = 2032 Hz, P1).

^{19}F NMR (376 MHz, 298 K, $(CD_3)_2CO$): δ −114.6 (very broad, 2F, F1+F5), −116.4 (1F, ^3JPt,F = 335 Hz, F6), −118.6 (1F, ^3JPt,F = 267 Hz, F10), −165.1 (1F, F9), −166.8 (t, 1 F, ^3JF,F = 19 Hz, F3), −166.9 (t, 1 F, ^3JF,F = 20 Hz, F8), from −167.0 to −166.3 (m, 3 F, F7 + F2 + F4) ppm.

^{19}F NMR (376 MHz, 200 K, $(CD_3)_2CO$): δ −113.9 (1F, ^3JPt,F = 302 Hz, F5), −116.2 (1F, ^3JPt,F = 237 Hz, F1), −116.9 (1F, ^3JPt,F = 230 Hz, F6), −119.1 (1F, ^3JPt,F = 252 Hz, F10), −163.9 (1F, F9), −165.2 (t, 1F, ^3JF,F = 20 Hz, F3), −165.3 (t, 1F, ^3JF,F = 20 Hz, F8), −165.7 (1F, F7), −165.9 (1F, F2), −166.2 (1F, F4) ppm.

^{1}H NMR (700 MHz, 298 K, $(CD_3)_2CO$): δ 10.73 (d, 1H, ^3JH,H = 5.2 Hz, H23), δ 9.64 (m, 1H, ^3JH,Pt = 39 Hz, H14), δ 8.61 (dd, 2H, ^3JH,H = 7.2 Hz, ^3JH,P = 11.3 Hz, H33/37), δ 8.46 (dd, 1H, ^4JH,H = 1.3, ^3JH,H = 7.8, H21), δ 8.23 (dd, 2H, ^3JH,H = 7.7 Hz, ^3JH,P = 10.6 Hz, H 39/43), δ 7.69 (d, 1H, ^3JH,H = 8.7 Hz, H18), δ 7.66 (partially overlapped dd, 1H, ^3JH,H = 5.2 Hz, ^3JH,H = 7.8, H 22), δ from 7.66 to 7.64 (m, 3H, H 15 + H16 + H19), δ 7.44 (broad m, 2H, H 27/31), δ 7.31 (d, 1H, ^3JH,H = 7.2, H 35), δ 7.29 (pseudo t, 2H, ^3JH,H = 7.2 Hz, H 34/H36), δ 7.26 (d, 1H, ^3JH,H = 7.2, H41), δ 7.21 (pseudo t, 2H, ^3JH,H = 7.7 Hz, H 40/H42), δ 7.15 (t, 1H, ^3JH,H = 7.1, H 29), δ 6.85 (pseudo t, 2H, ^3JH,H = 7.6 Hz, H 28/H30), δ 6.50 (dd, 2H, ^3JH,H = 8.3 Hz, ^3JH,P = 10.0 Hz, H 45/H49), δ 6.45 (t, 1H, ^3JH,H = 7.2, H47), δ 6.05 (pseudo t, 2H, ^3JH,H = 7.4 Hz, H 46/H48), 3.47 (m, 8H, NBu_4^+), 1.84 (m, 8H, NBu_4^+), 1.45 (pseudosextet, 8H, ^3JH,H = 7.4, NBu_4^+), 0.97 (t, 12H,^3JH,H = 7.4, NBu_4^+) ppm.

^{195}Pt{^{1}H} NMR (86 MHz, 298 K, $(CD_3)_2CO$): δ −2917 (dd, ^1JPt2,P2 = 1270 Hz, ^1JPt2,P1 = 1807 Hz, ^2JPt,Pt = 100 Hz, Pt2), δ −3806 (broad, Pt1).

To a yellow solution of **1** (0.281 g, 0.185 mmol) in CH_2Cl_2 (20 mL) was added dropwise I_2 (0.047 g, 0.185 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 20 h, and the resulting orange solution was evaporated to ca. 1 mL. *i*-PrOH (10 mL) was added, and a yellow solid crystallized which was filtered, washed with *i*-PrOH (2 × 1 mL), and air-dried, 0.231 g. The solid was characterized by NMR spectroscopy as a mixture of **5** and **6**. The analysis of solids obtained from different preparations showed about 20−25% of **6** in the mixtures. A 0.202 g portion of a mixture was dissolved in 1 mL of CH_2Cl_2 and passed through a silica column (3 cm^2 × 15 cm) with CH_2Cl_2 as eluent, and the CH_2Cl_2 solution was evaporated to ca. 1 mL. *n*-Hexane (10 mL) was added, and **6** crystallized as a yellow solid, 0.085 g. Found: C, 41.77; H, 2.01; N, 1.01. $C_{49}F_{10}H_{28}INP_2Pt_2$ requires C, 42.04; H, 2.02; N, 1.00. HRMS(+), exact mass for $[C_{49}H_{28}F_{10}NP_2Pt]$: 1398.9868. Measured *m*/*z*: 1421.9502 $(M + Na)^+$.

[(R$_F$)$_2$Pt(*μ*-PPh$_2$)(*μ*-I)Pt{PPh$_2$(C$_{13}$H$_8$N)}] (6). ^{31}P{^{1}H} NMR (161 MHz, 298 K, $(CD_3)_2CO$): δ −11.4 (d, ^2JP,P = 2 Hz, ^1JP1,Pt2 = 2513 Hz, ^1JP1,Pt1 = 1846 Hz, P1), 14.2 (d, ^2JP,P = 2 Hz, ^1JP2,Pt2 = 4435 Hz, ^3JP2,Pt1 = 37 Hz, P2) ppm.

^{19}F NMR (376 MHz, 298 K, $(CD_3)_2CO$): δ −115.2 (m, 2F, ^3JPt,F = 330 Hz, F1/5), −117.3 (m, 2F, ^3JPt,F = 536 Hz, F6/10), −165.2 (t, 1F, ^3JF,F = 19 Hz, F3), −166.2 (ddd, 2F, ^3JF,F = 22 Hz, ^3JF,F = 20 Hz, ^5JF,P = 9 Hz, F2/4), −167.4 (t, 1F, ^3JF,F = 19 Hz, F8), −167.5 (m, 2F, F7/9) ppm.

^{1}H NMR (400 MHz, 298 K, $(CD_3)_2CO$): 10.58 (broad d, 1H, ^3JH,H = 5.0 Hz, H13), 8.94 (dd, 1H, ^3JH,H = 8.0 Hz, ^4JH,H = 1.5 Hz, H15), 8.52 (d of pseudo t, 1H, ^3JH,H = 8.0 Hz, ^4JH,H = 1.2 Hz, H20), 8.32 (dd, 1H, ^3JH,H = 8.9 Hz, ^4JH,H = 1.6 Hz, H18), 8.18 (d, 1H, ^3JH,H = 8.9 Hz, H17), 8.07 (dd, 1H, ^3JH,H = 8.0 Hz, ^3JH,H = 5.2 Hz, H14), 7.98 (pseudo t of d, 1H, ^3JH,H = 7.8 Hz, ^4JH,P = 1.5 Hz, H21), 7.65 (ddd, 1H, ^3JH,H = 13.5 Hz, ^3JH,H = 7.5 Hz, ^3JH,P = 1.2 Hz, H22), from 7.65 to 7.52 (broad, 4H, H33, H37, H27, H31), from 7.52 to 7.41 (m, 6H, H39, H41, H43, H45, H47, H49), from 7.32 to 7.23 (m, 4H, overlapped H40/42 + H46/48), 7.22 (m, 2H, overlapped H29+H35), 7.07 (m, 4H, overlapped H28/30 + H34/36) ppm.

^{195}Pt{^{1}H} NMR (86 MHz, 298 K, $(CD_3)_2CO$): δ −4238 (m, ^1JPt1,P1 = 1846 Hz, ^3JPt1,F6/10 = 536 Hz, ^3JPt1,F1/5 = 330 Hz, Pt1), δ −4397 (dd, ^1JPt2,P2 = 4435 Hz, ^1JPt2,P1 = 2513 Hz, Pt2) ppm.

Addition of I_2 to 2 and 4. To a yellow solution of **2** (0.204 g, 0.143 mmol) in CH_2Cl_2 (20 mL) was added dropwise I_2 (0.036 g, 0.143 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 20 h, and the red solution was evaporated to ca. 1 mL. *i*-PrOH (10 mL) was added, and **7** crystallized as a yellow solid which was filtered, washed with *i*-PrOH (2 × 1 mL), and air-dried, 0.136 g, 72% yield. Found: C, 44.62; H, 2.00; N, 1.00. $C_{49}F_{10}H_{28}INP_2PdPt$ requires C, 44.89; H, 2.15; N, 1.07. HRMS(+), exact mass for $[C_{49}H_{28}F_{10}INP_2PdPt]$: 1310.9274. Measured *m*/*z*: 1333.9183 $(M + Na)^+$.

[(R$_F$)$_2$Pt(*μ*-PPh$_2$)(*μ*-I)Pd{PPh$_2$(C$_{13}$H$_8$N)}] (7). ^{31}P{^{1}H} NMR (298 K, $(CD_3)_2CO$, 161 MHz): δ 55.2 (m, ^2JP,P = 40 Hz, ^1JP1,Pt = 1864 Hz, P1), 37.5 (d, ^2JP,P = 40 Hz, ^3JP2,Pt = 97 Hz, P2) ppm.

^{19}F NMR (376 MHz, 298 K, $(CD_3)_2CO$): δ −115.5 (m, 2F, ^3JPt,F = 319 Hz, F1/5), −116.2 (m, 2F, ^3JPt,F = 526 Hz, F6/10), −165.1 (t, 1F, ^3JF,F = 20 Hz, F3), −166.2 (ddd, 2F, ^3JF,F = 22 Hz, ^3JF,F = 20 Hz, ^5JF,P = 9 Hz, F2/4), −166.8 (t, 1F, ^3JF,F = 19 Hz, F8), −167.2 (m, 2F, F7/9) ppm.

^{1}H NMR (400 MHz, 298 K, $(CD_3)_2CO$): 10.56 (broad d, 1H, ^3JH,H = 4.8 Hz, H13), 8.83 (dd, 1H, ^3JH,H = 8.0 Hz, ^4JH,H = 1.5 Hz, H15), 8.49 (d of pseudo t, 1H, ^3JH,H = 8.0 Hz, ^4JH,H = 1.0 Hz, H20), 8.27 (dd, 1H, ^3JH,H = 8.7 Hz, ^4JH,H = 1.5 Hz, H18), 8.13 (d, 1H, ^3JH,H = 8.7 Hz, H17), 7.99 (dd, 1H, ^3JH,H = 8.0 Hz, ^3JH,H = 5.1 Hz, H14), 7.90 (ddd, 1H, ^3JH,H = 7.7 Hz, ^3JH,H = 7.8 Hz, ^4JH,P = 1.2 Hz, H21), 7.70 (ddd, 1H, ^3JH,H = 12.9 Hz, ^3JH,H = 7.6 Hz, ^3JH,P = 1.1 Hz, H22), from 7.60 to 7.45 (m, 10H, H27, H31, H33, H37, H39, H41, H43, H45, H47, H49), 7.30 (m, 4H, overlapped H40/42 + H46/48), 7.24 (m, 2H, overlapped H29+H35), 7.08 (m, 4H, overlapped H28/30 + H34/36) ppm.

^{195}Pt{^{1}H} NMR (298 K, $(CD_3)_2CO$, 86 MHz): δ −4315 (dd, ^1JPt,P1 = 1864 Hz, ^3JPt,P2 = 97 Hz).

A similar procedure, using **4** (0.170 g, 0.127 mmol) and I_2 (0.032 g, 0.127 mmol), produces complex **8** as a yellow solid, 0.094 g, 60% yield. Solutions of **8** slowly became dark. Minor amounts of black palladium could be present in the samples of **8**. Found: C, 47.60; H, 2.20; N, 1.10. $C_{49}F_{10}H_{28}INP_2Pd_2$ requires C, 48.14; H, 2.31; N, 1.15. HRMS(+), exact mass for $[C_{49}H_{28}F_{10}INP_2Pd_2]$: 1222.8671. Measured: *m*/*z*: 1245.8558 $(M + Na)^+$.

[(R$_F$)$_2$Pd(*μ*-PPh$_2$)(*μ*-I)Pd{PPh$_2$(C$_{13}$H$_8$N)}] (8). ^{31}P{^{1}H} NMR (161 MHz, 298 K, $(CD_3)_2CO$): δ 66.0 (m, ^2JP,P = 36 Hz, P1), 42.3 (d, ^2JP,P = 36 Hz, P2) ppm.

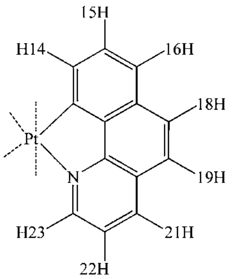
^{19}F NMR (376 MHz, 298 K, $(CD_3)_2CO$): δ −112.5 (very broad, 2F, F1/5), −113.6 (broad, 2F, F6/10), −164.3 (t, 1F, ^3JF,F = 20 Hz, F3), −165.2 (t of d, 1F, ^3JF,F = 20 Hz, ^4JF,F = 2 Hz, F8), −165.4 (ddd, 2F, ^3JF,F = 23 Hz, ^3JF,F = 19 Hz, ^5JF,P = 11 Hz, F2/4), −165.9 (dd, ^3JF,F = 24 Hz, ^3JF,F = 20 Hz, 2F, F7/9) ppm.

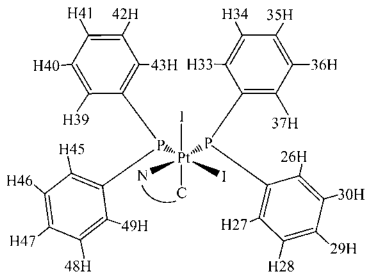
^{1}H NMR (400 MHz, 298 K, $(CD_3)_2CO$): 10.50 (broad d, 1H, ^3JH,H = 4.9 Hz, H13), 8.84 (dd, 1H, ^3JH,H = 8.0 Hz, ^4JH,H = 1.4 Hz, H15), 8.51 (d of pseudo t, 1H, ^3JH,H = 7.9 Hz, ^4JH,H = 1.2 Hz, H20), 8.29 (dd, 1H, ^3JH,H = 8.8 Hz, ^4JH,H = 1.4 Hz, H18), 8.15 (d, 1H, ^3JH,H = 8.8 Hz, H17), 8.00 (dd, 1H, ^3JH,H = 8.0 Hz, ^3JH,H = 5.1 Hz, H14), 7.95 (pseudo t of d, 1H, ^3JH,H = 7.8 Hz, ^4JH,P = 1.0 Hz, H21), 7.70 (ddd, 1H, ^3JH,H = 13.0 Hz, ^3JH,H = 7.5 Hz, ^3JH,P = 1.0 Hz, H22), from 7.64 to 7.39 (m, 10H, H27, H31, H33, H37, H39, H41, H43, H45, H47, H49), from 7.36 to 7.27 (m, 4H, overlapped H40/

42+H46/48), from 7.27 to 7.19 (m, 2H, overlapped H29+H35), from 7.14 to 7.01 (m, 4H, overlapped H28/30+H34/36) ppm.

*Addition of I_2 to **3**.* To a yellow solution of **3** (0.150 g, 0.105 mmol) in CH_2Cl_2 (10 mL) was added dropwise I_2 (0.027 g, 0.106 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 20 h and evaporated to dryness to render a yellow solid. Its $^{31}P\{^1H\}$ NMR spectrum in acetone indicated that this solid is a complex mixture of products in which $[NBu_4][(R_F)_2Pd^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C^\wedge N)I_2]$ (**9**), $[(R_F)_2Pd^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (**10**), and $[(R_F)(PPh_2R_F)Pd^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}(C^\wedge N)]$ (**11**) could be identified (NMR spectroscopy) but not isolated as pure samples. All attempts to separate the mixture were unsuccessful.

Spectroscopic features of $[NBu_4][(R_F)_2Pd(\mu\text{-}PPh_2)_2Pt(C^\wedge N)I_2]$ (9). $^{31}P\{^1H\}$ NMR (161 MHz, 298 K, $(CD_3)_2CO$): δ −89.1 (broad d, ^{2}JP,P = 161 Hz, ^{1}JP2,Pt = 1121 Hz, P2), −97.7 (broad d, ^{2}JP,P = 161 Hz, ^{1}JP1,Pt = 1680 Hz, P1).





^1H NMR (400 MHz, 298 K, $(CD_3)_2CO$): δ 10.76 (m, 1H, H23), δ 9.47 (d, 1H, ^{3}JH,H = 6.5 Hz, ^{3}JH,Pt = 41 Hz, H14), δ 8.56 (dd, 2H, ^{3}JH,H = 7.3 Hz, ^{3}JH,P = 11.8 Hz, H33/37), δ 8.48 (d, 1H, ^{3}JH,H = 8.0, H21), δ 8.24 (dd, 2H, ^{3}JH,H = 8.2 Hz, ^{3}JH,P = 10.8 Hz, H 39/43), δ from 7.76 to 7.63 (overlapped, 5H, H15 + H16 + H18+ H19 + H22), δ 7.50 (pseudo t, 2H, ^{3}JH,H = 9.0 Hz, H 27/H31), δ from 7.33 to 7.14 (overlapped, 7H, H29 + H34 + H35 + H36 + H40 + H41 + H42), δ from 7.56 to 7.465 (partially overlapped, 3H, H 45 + H47 + H49), δ 6.10 (pseudo t, 2H, ^{3}JH,H = 7.8 Hz, H 46/H48), 3.50 (m, 8H, NBu_4^+), 1.86 (m, 8H, NBu_4^+), 1.48 (m, 8H, NBu_4^+), 1.02 (t, 12H, NBu_4^+) ppm.

$^{195}Pt\{^1H\}$ NMR (86 MHz, 298 K, $(CD_3)_2CO$): δ −2966 (dd, ^{1}JPt,P2 = 1121 Hz, ^{1}JPt,P1 = 1680 Hz).

X-ray Structure Determinations. Crystal data and other details of the structure analyses are presented in Table 4. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes in 3 mL of acetone (**5′**) or CH_2Cl_2 (**6**−**8**) at 5 °C. Crystals were mounted at the end of a quartz fiber. 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.[104] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares on F^2 with SHELXL-97.[105] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to

Table 4. Crystal Data and Structure Refinement for Complexes $[N(PPh_3)_2][(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(C^\wedge N)I_2]\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$ ($5'\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$), $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pt^{II}\{PPh_2(C_{13}H_8N)\}]$ (6), $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pd^{II}\{PPh_2(C_{13}H_8N)\}]\cdot n\text{-}C_6H_{14}\cdot 0.75CH_2Cl_2$ ($7\cdot n\text{-}C_6H_{14}\cdot 0.75CH_2Cl_2$), and $[(R_F)_2Pd^{II}(\mu\text{-}PPh_2)(\mu\text{-}I)Pd^{II}\{PPh_2(C_{13}H_8N)\}]\cdot 0.75n\text{-}C_6H_{14}$ ($8\cdot 0.75n\text{-}C_6H_{14}$)

	$5'\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$	**6**	$7\cdot n\text{-}C_6H_{14}\cdot 0.75CH_2Cl_2$	$8\cdot 3CH_2Cl_2$
formula	$C_{85}H_{58}F_{10}I_2N_2OP_4Pt_2\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$	$C_{49}H_{28}F_{10}INP_2Pt_2$	$C_{49}H_{28}F_{10}INP_2PdPt\cdot n\text{-}C_6H_{14}\cdot 0.75CH_2Cl_2$	$C_{49}H_{28}F_{10}INP_2Pd_2\cdot 0.75n\text{-}C_6H_{14}$
M_t [g mol^{-1}]	2144.82	1399.74	1460.92	1286.99
T [K]	100(1)	100(1)	100(1)	100(1)
λ [Å]	0.710 73	0.71073	0.710 73	0.710 73
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$Pbca$	$P2_1/c$	$P2_1/c$
a [Å]	10.3642(2)	11.7997(1)	17.2984(3)	17.1149(7)
b [Å]	19.8014(4)	20.9853(2)	13.6095(2)	13.7727(4)
c [Å]	20.3880(4)	34.6859(3)	22.9239(4)	22.9446(7)
α [deg]	88.4788(15)	90	90	90
β [deg]	81.7974(16)	90	96.7838(14)	97.294(3)
γ [deg]	80.0805(17)	90	90	90
V [Å^3]	4079.44(14)	8588.93(13)	5359.02(15)	5364.7(3)
Z	2	8	4	4
ρ [g cm^{-3}]	1.746	2.165	1.811	1.593
μ [mm^{-1}]	4.332	7.383	3.727	1.375
F(000)	2077	5264	2830	2526
2θ range [deg]	8.36−52.0	7.5−57.9	7.5−57.9	7.6−57.9
no. reflns collected	79857	50175	48264	58471
no. unique reflns	15993	10363	12672	12899
R(int)	0.0821	0.0267	0.0594	0.0569
final R indices [$I > 2\theta(I)$][a]				
R1	0.0482	0.0387	0.0349	0.0795
wR2	0.1254	0.1168	0.0590	0.2136
R indices (all data)				
R1	0.0620	0.0455	0.0683	0.1095
wR2	0.1304	0.1211	0.0621	0.2254
GOF on F^2[b]	1.010	1.061	1.018	1.068

[a] $R1 = \sum(|F_o| - |F_c|)/\sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. [b] $GOF = [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data of **5′**$\cdot Me_2CO\cdot 0.25n\text{-}C_6H_{14}$, **6**, **7**$\cdot n\text{-}C_6H_{14}\cdot 0.75CH_2Cl_2$, and **8**$\cdot 3CH_2Cl_2$ (CIF format). NMR spectra, figures, tables, and HRMS spectrograms. 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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