Synthesis, Interionic Structure, and Reactivity toward CO and *p*-Methylstyrene of Palladacyclic Compounds Bearing α-Diimine Ligands

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

Palladacyclic compounds $[Pd(C_6H_4(C_6H_5C{=}O)C{=}N{-}R)(N{-}N)][X]$ (R = Et, ^{i}Pr, 2,6-^{i}Pr$_2$C$_6$H$_3$; N–N = bpy = 2,2′-bipyridine, or 1,4-(*o,o′*-dialkylaryl)-1,4-diazabuta-1,3-dienes; $[X]^- = [BF_4]^-$ or $[PF_6]^-$) were synthesized from the dimers $[\{Pd(C_6H_4(C_6H_5C{=}O)C{=}N{-}R)(\mu\text{-}Cl)\}_2]$ and N–N ligands. Their interionic structure in CD_2Cl_2 was determined by means of ^{19}F,^{1}H-HOESY experiments and compared with that in the solid state derived from X-ray single-crystal studies. $[Pd(C_6H_4(C_6H_5C{=}O)C{=}N{-}R)(N{-}N)][X]$ complexes were found to copolymerize CO and *p*-methylstyrene affording syndiotactic or isotactic copolymers when bpy or 1,4-(*o,o′*-dimethylaryl)-1,4-diazabuta-1,3-dienes were used, respectively. The reactions with CO and *p*-methylstyrene of the bpy derivatives were investigated. Two intermediates derived from a single and a double insertion of CO into the Pd–C bonds were isolated and completely characterized in solution.

Introduction. – There is increasing evidence that the solution structure and reactivity of organometallic compounds can be altered by noncovalent interactions. For instance, when ionic compounds are considered, ion pairing may substantially affect the chemical pathway of organic reactions mediated by transition-metal organometallics in terms of chemo-, regio-, and stereoselectivity [1].

It has been demonstrated that NMR spectroscopy is the technique of choice for investigating noncovalent adducts in solution, especially by NOE (nuclear *Overhauser* effect) and PGSE (pulsed-field gradient spin echo) experiments (for recent reviews, see [2]).

For several years, our group has been involved in the application of NOE [3a–c] and PGSE [3d] NMR methodologies to determine the interionic structure in solution (namely, the relative cation–anion orientation and aggregation level) of transition-metal complex ionic adducts. Several combinations of anions (ranging from inorganic, such as $[BF_4]^-$ and $[PF_6]^-$, to more organic ones, like $[BPh_4]^-$, $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$, or $[B(C_6F_5)_4]^-$) and metal geometries (octahedral, square-planar, and 'piano-stool') have been considered. Generally speaking, the results have indicated that the counterion, regardless of its nature, is very often located close to a specific position of the organometallic cation. Quantum-mechanical and mechanical calculations have shown that this is principally due to an accumulation of positive charge in a particular location of the cationic fragment [4].

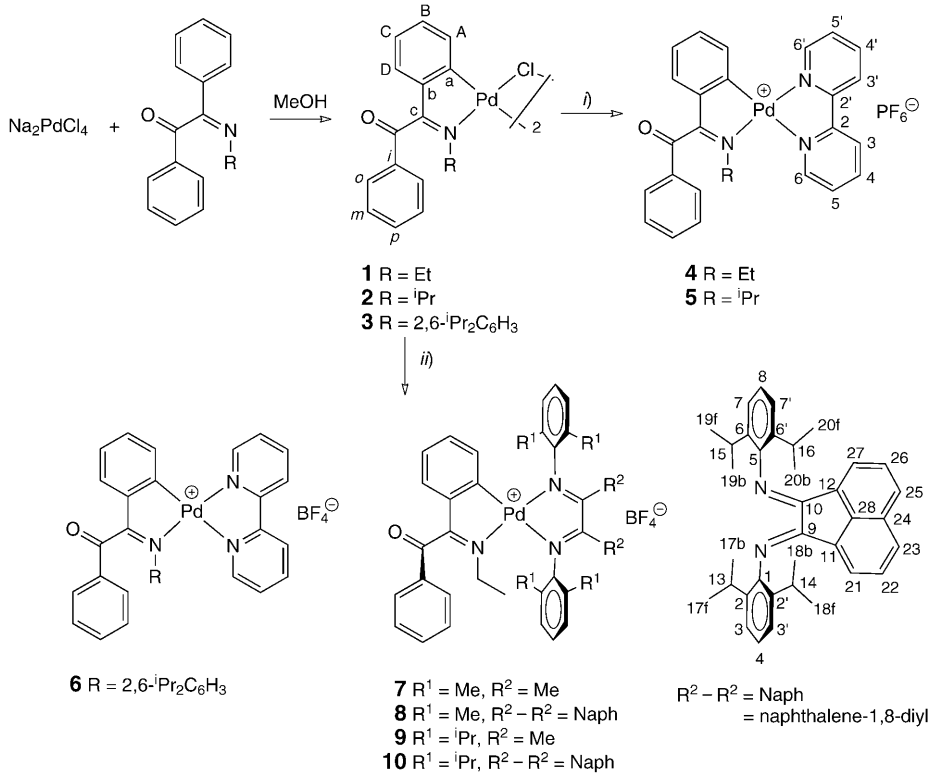
Several square-planar ion pairs of the general formula [M(alkyl)(olefin)(N–N)]X (M = Pd or Pt, and N–N = 2,2′-bipyridine (bpy) or 1,4-diazabuta-1,3-diene derivatives) have been investigated [5] with the two-fold objective of *1*) correlating ion pairing with catalytic activity toward CO/olefin copolymerization and *2*) evaluating the accessibility of a nucleophile to the metal center as a function of the steric hindrance in the apical position by using the anion as a probe [6].

To check the effect of varying the ligands on the cation-charge distribution and, consequently, on the interionic structure of the complexes, we here report on the interionic structure of *ortho*-palladated imines of the general formula [Pd(C_6H_4(C_6H_5C=O)C=N–R)(N–N)][X] derived from the metallation of α-(alkylimino) or α-(arylimino) ketones [7]. Palladacyclic compounds have been known for a long time (for a recent review, see [8]), and applications have been found in organic synthesis [9], bioorganometallic chemistry, material sciences, as well as homogeneous catalysis [10]. While it is well-known that a variety of unsaturated molecules can be inserted into the metal–aryl or metal–alkyl bonds of palladacycles [11], including alkenes and CO [12] (for styrene, see [12a], for CO, see [12f–k]), they have rarely been used as single-component catalysts (precatalysts) in the alternating CO–alkene copolymerization reaction [13]. Here, we also report on the reactivity toward CO and olefins and on preliminary catalytic tests of selected *ortho*-palladated cationic complexes.

Results and Discussion. – *Synthesis.* Cyclopalladated dimers [{Pd(C_6H_4(C_6H_5C=O)C=N–R)(μ-Cl)}$_2$] with R = Et (**1**), ^{i}Pr (**2**), or 2,6-$^i Pr_2C_6H_3$ (**3**) were synthesized by the reaction [14] of $Na_2[PdCl_4]$ with a small excess of the proper α-imino ketone [15] in MeOH (*Scheme 1*). Cationic complexes **4** and **5** were obtained by the reaction of complexes **1** and **2** with bpy in MeOH, respectively, in the presence of a large excess of $NH_4[PF_6]$. Complexes **6**–**10** were synthesized by adding $Ag[BF_4]$ to a solution containing the dimer **1** and a suitable N–N ligand in CH_2Cl_2, followed by filtration of AgCl and precipitation of the final product with hexane (*Scheme 1*). Both the dimers and cationic complexes were stable in the solid state. The cationic compounds showed little sign of decomposition in CH_2Cl_2 solution after several days at room temperature under an inert atmosphere.

Intramolecular Characterization in Solution. All complexes were characterized at room or low temperature by ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy and ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY, ^{19}F,^{1}H-HOESY (= heteronuclear *Overhauser* enhancement spectroscopy), ^{1}H,^{13}C-HMQC, and ^{1}H,^{13}C-HMBC experiments. *ortho*-Metalation at the phenyl substituent bonded to the C=N group can be inferred from the chemical shifts of the C_a resonance (see *Scheme 1* for numbering), which were in the range from δ(C) 153.7 to 159.8, while κN-coordination to Pd is supported by the chemical shifts of the C_c resonance (δ(C) 181.2–185.6), in agreement with literature results with similar compounds [7]. In the cationic complexes **4**–**6**, a dynamic process that averages the two pyridine rings is present [6b]. In the case of **4** and **5**, broad peaks were observed for the bpy protons H–C(6)/H–C(6′), H–C(5)/H–C(5′), H–C(4)/H–C(4′), and H–C(3)/H–C(3′) (see *Scheme 1* for numbering) at room temperature. In contrast, sharper resonances were observed in the ^{1}H-NMR spectrum of **6** at room temperature. This was due to the marked differentiation of the H-atoms of the two pyridine rings of bpy due to the strong shielding effect exerted by the almost perpendicular orientation of the

Scheme 1



i) MeOH, 2,2′-bipyridine, $NH_4[PF_6]$. *ii*) CH_2Cl_2, N,N-ligand, $Ag[BF_4]$.

ortho-disubstituted aryl ring on the pyridine ring of bpy in *cis* position to the imine N-atom (*e.g.*, H–C(6′) and H–C(6) resonate at δ(H) 9.07 and 5.7, resp.). Since similar dynamic processes [5b] are also present for complexes **7**–**10**, NMR investigations were undertaken at low temperature, where the dynamic motion that interconverts the two halves of the N–N ligand is slow on both the chemical-shift and T_1 time scales. The Me resonances of the alkylimino group (or those of the ^{i}Pr groups in the case of complex **6**) are the starting point for assigning all the ^{1}H and ^{13}C resonances. In the case of bpy complexes, starting from the selective NOE interaction of the Me groups with H–C(6), all the other bpy resonances can be easily assigned, following either the scalar or dipolar connectivities. The H_A resonance can then be recognized due to the strong NOE interaction with H–C(6′) and, finally, the remaining H_B, H_C, and H_D of the metalated phenyl ring are assigned by means of the ^{1}H,^{1}H-COSY plot.

It is known that aromatic α-diimine ligands tend to orient the aryl rings almost perpendicularly to the square-planar coordination plane when they coordinate to a metal center [16]. Analogous to previously studied compounds [5b][17], for complexes **7**–**10**, it is possible to discriminate between the two halves of the N–N ligand lying 'up' or 'down' with respect to the square-planar coordination plane. For example, among

the four resonances of the aryl Me groups of complex **7**, only the one at δ 2.46 (Me(14)) selectively interacts with the H_o of the benzoyl group, while that at δ 2.35 (Me(13)) interacts with the Me group of the Et substituent[1]). Unambiguous discrimination of Me(15) and Me(16) for complexes **7** and **8** were derived from the observation of a very weak NOE between the H_o resonance and the Me resonance at δ 2.31, consequently assigned to Me(16). However, Me(11) and Me(12) of **7** cannot be differentiated because all six Me resonances fall within the range between δ 2.46 and 2.31, making it difficult to observe cross-peaks between them in the ^{1}H,^{1}H-NOESY plot.

For complexes **9** and **10**, H–C(14) and H–C(13) can be recognized due to their selective NOEs with the H_o-atoms of the benzoyl group, and the Me group of the Et substituent, respectively. In addition, the presence of ^{i}Pr substituents makes it possible to differentiate Me(11) from Me(12). Finally, NOE interactions are present between either H_o or Me(20f), which allows H–C(16), H–C(13), and H–C(15) to be assigned as shown in *Fig. 1*.

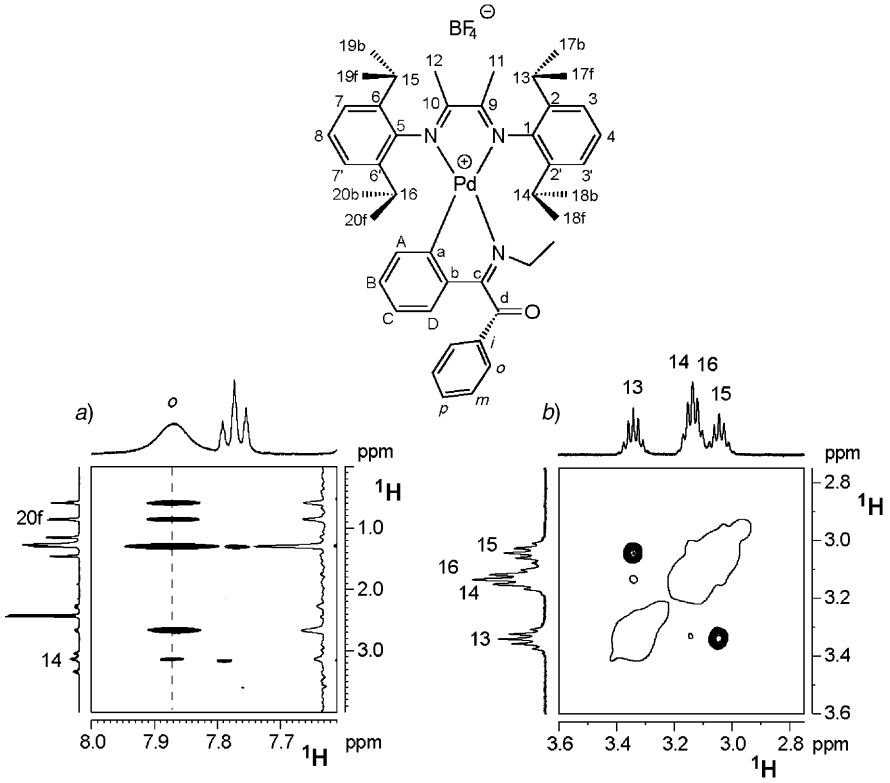


Fig. 1. *Two sections of the ^{1}H,^{1}H-NOESY plot* (CD_2Cl_2, 230 K, mixing time 800 ms) *of complex* **9**

[1]) Supporting information is available upon request from *C. Z.* or *A. M.*

Solid-State Structure of Complexes **4** *and* **6**. Single crystals of compound **4** were obtained from CH_2Cl_2/hexane, while crystals of **6** suitable for an X-ray analysis were grown by layering MeOH and then hexane on top of a concentrated CH_2Cl_2 solution. Both crystals belong to the $P2_1/c$ space group. The unit cell contains four molecules in the case of complex **4**, while there are four molecules of the organometallic fragment and four molecules of MeOH in the case of complex **6**. Selected bond distances and angles are reported in *Table 1*, and ORTEP drawings of the cationic moieties are shown in *Fig. 2*. The Pd-atom presents a distorted square-planar coordination geometry that can be described in terms of five interplanar angles, namely α (between the Pd–N(1)–N(2) and Pd–C(1)–N(3) plane), β (between the Pd–N(1)–N(2) and the mean N(1)–C(32)–C(31)–N(2) plane), β' (between the Pd–C(1)–N(3) and the mean C(1)–C(6)–C(7)–N(3) plane), γ (between the two pyridine rings of bpy), and γ' (between the metalated-ring and the C(15)–N(3)–C(7)–C(8) planes) [18]. In **4**, $\alpha = 15.1(8)^\circ$, $\beta = 19.4(6)^\circ$, $\beta' = 3.6(5)^\circ$, $\gamma = 16.9(7)^\circ$, and $\gamma' = 4.7(6)^\circ$, while in **6**, $\alpha = 13.2(4)^\circ$, $\beta = 16.5(3)^\circ$, $\beta' = 7.1(0)^\circ$, $\gamma = 18.3(0)^\circ$, and $\gamma' = 14.5(9)^\circ$. Since a bow-step conformation requires $\alpha \approx 0^\circ$, and a twist conformation matches with a pretty large value of α (≈ 20–25°) but small values of β and γ ($< 5^\circ$) [18a] the values observed for **4** and **6** indicate that these two limit conformations do not actually describe the overall observed geometry. The distortion at the bpy ligand is, however, more similar to that observed in bis-metalated [Pd(1,1′-biphenyl-2,2′-yl)(bpy)] in which $\gamma = 17.6(6)^\circ$ [19]. The angle between the C(1)–C(6)–C(7)–N(3) mean plane and the *ortho*-substituted phenyl ring (C(15) to C(20)) is $88.6(9)^\circ$ in **6**, in agreement with the solution-NMR results (see above). The Pd–N(2) bond distances (2.172(2) Å in **4** and 2.158(4) Å in **6**) are *ca.* 0.12 Å longer than the Pd–N(1) ones (2.056(3) Å in **4** and 2.037(4) Å in **6**), reflecting the influence exerted by the σ-bonded C(1) atom in *trans* position. The Pd–C(1) bond distances (1.989(3) Å in **4** and 2.003(5) Å in **6**) are comparable to those found for other sp^2 C-atoms, which are either *trans* to a bpy N-atom or involved in cyclometalation (2.000 Å [19], 2.009 Å [19], 1.986 Å [20]).

Table 1. *Coordination Bond Lengths* [Å] *and Angles* [deg] *for Complexes* **4** *and* **6**

	4	**6**		**4**	**6**
Pd–C(1)	1.989(3)	2.003(5)	C(1)–Pd–N(3)	79.90(12)	79.45(18)
Pd–N(1)	2.056(3)	2.037(4)	C(1)–Pd–N(1)	98.00(12)	99.65(19)
Pd–N(2)	2.172(2)	2.158(4)	N(3)–Pd–N(1)	172.62(9)	173.14(16)
Pd–N(3)	2.055(2)	2.034(4)	C(1)–Pd–N(2)	166.87(11)	169.51(18)
			N(3)–Pd–N(2)	106.08(9)	103.91(15)
			N(1)–Pd–N(2)	77.48(9)	78.19(17)

Interionic Structure by HOESY-NMR Experiments. The interionic structure was investigated in CD_2Cl_2 at low temperature by $^{19}F,^1H$-HOESY-NMR experiments. The $^{19}F,^1H$-HOESY plot of **4** recorded at 200 K is reported in *Fig. 3*, *a*. After having scaled the NOE intensity for the number of equivalent nuclei [21], the $^{19}F,^1H$ interactions followed the order: $H-C(6) \approx H-C(5) > H_A \approx CH_2 > H-C(4)$, $H-C(3) > H_B > H-C(6') \approx H-C(3') >$ Me. At 200 K, H_os appear as broad resonances and are not suitable to obtain information on the anion position. A $^{19}F,^1H$-HOESY experiment was also

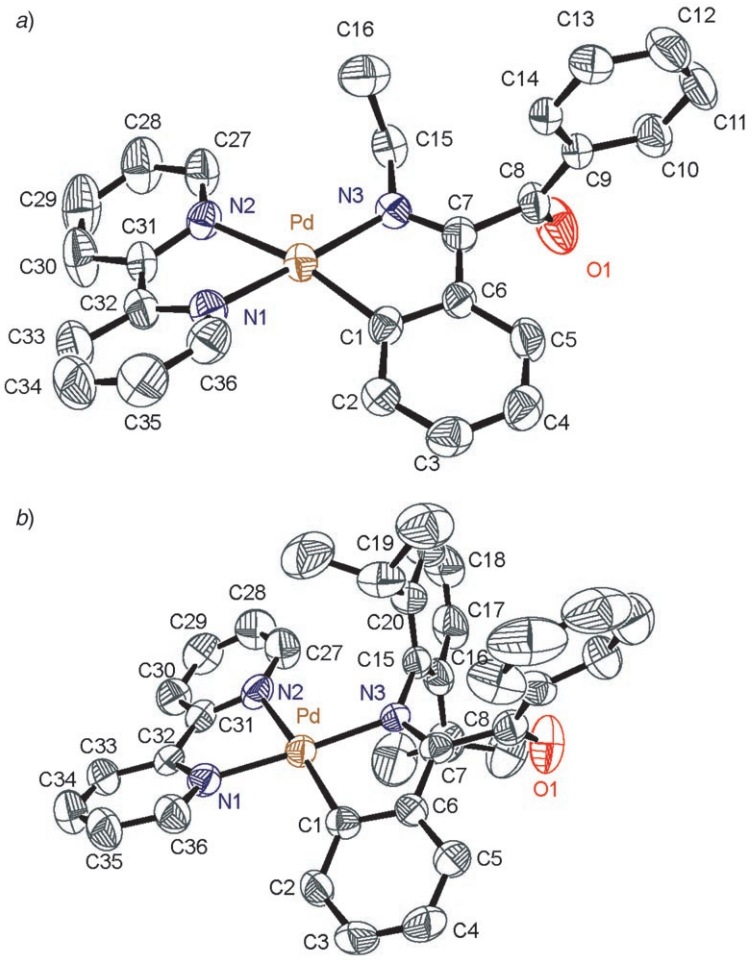


Fig. 2. *ORTEP Representations* (50% ellipsoid probability) *showing the cationic moieties of* a) **4** *and* b) **6**. H-Atoms have been omitted for clarity.

recorded at 230 K where these resonances are relatively sharp; interionic interactions of an intensity comparable to that with H_A were observed for the H_os atoms. All these findings indicate that the anion is mainly located in proximity to the EtN=C and the pyridine moiety of bpy that is in *trans* position relative to the Pd–C σ-bond. A similar anion location was previously found in the [Pd(η^1,η^2-C_8H_{12}OMe)bpy][PF_6] complex [4b][6b]; in that case, however, the anion was located further behind the bpy ligand (the strongest contacts were observed with H–C(3)). This anion shift was probably due to the presence of an additional positively polarized imine C-atom in **4**.

In the solid state, cation couples of **4** are surrounded by several anions. The closest $[PF_6]^-$ anion with respect to the Pd-atom (Pd$\cdots P_A$ distance = 5.431(9) Å, *Fig. 4*,*a*) lies above the square-planar coordination plane, partially shifted toward the imine moiety,

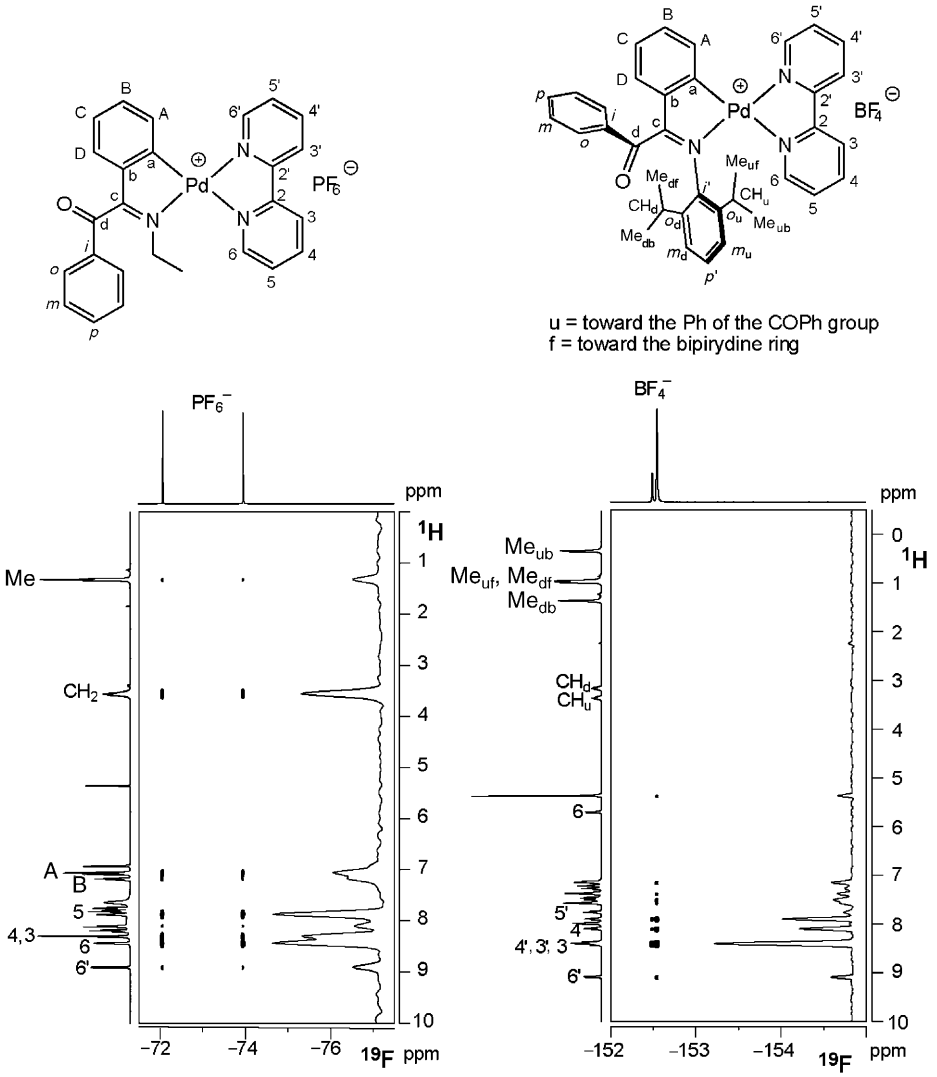


Figure 3. a) *$^{19}F,^{1}H$-HOESY Spectrum* (CD_2Cl_2, 230 K, mixing time 800 ms) *of complex* **4**, *and* b) *$^{19}F,^{1}H$-HOESY spectrum* (CD_2Cl_2, 217 K, mixing time 800 ms) *of complex* **6**.

on the same side as the phenyl of the benzoyl group. The HOESY Data in solution cannot be rationalized by this anion–cation orientation alone. For example, the $P_A\cdots H-C(36)$, and $P_A\cdots H-C(27)$ distances are 5.521(8) and 6.371(9) Å, respectively, while a stronger HOESY contact is observed between the anion and H–C(27) (=H–C(6) in the NMR numbering, *Scheme 1*). The remaining anions are positioned on the periphery, relatively distant from the metal center. Only two of them show a relatively short Pd···P distance. In particular, in orientation 'B' ($Pd\cdots P_B$ distance = 6.814(10) Å, *Fig. 4,a*), the P-atom of the anion is positioned only 0.271 Å away from the mean

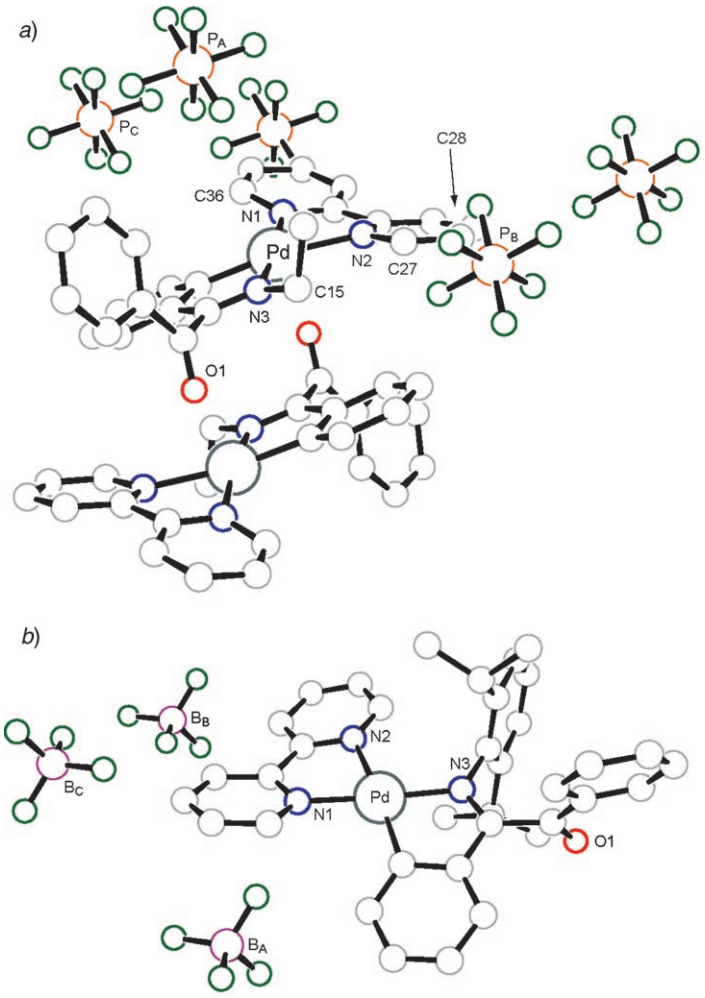


Figure 4. a) *Ball-and-stick representation of compound* **4** *showing the location of the anions around the organometallic cations.* b) *Ball-and-stick representation of the three anions that are closest to a cation of* **6** *in the solid state*

Pd–C(1)–N(1)–N(2)–N(3) plane, strongly shifted toward the pyridine ring in *trans* position with respect to the Pd–C σ-bond. Partial occupation of such an orientation, in which the anion is very close to H–C(27) and H–C(28) (*i.e.* H–C(6) and H–C(5) in the NMR numbering, *Scheme 1*), could account for the strongest HOESY interionic contacts observed in solution ($[PF_6]^-$ with H–C(6) and H–C(5)). In orientation 'C' (Pd$\cdots$P$_C$ distance = 7.508(11) Å, *Fig. 4*, *a*) the anion is closer to the metallated phenyl ring, 2.470(12) Å away from the mean Pd–C(1)–N(1)–N(2)–N(3) plane, on the same side as the phenyl ring of the benzoyl group. Partial occupation of this orientation could explain the observed interionic interaction in solution between the anion and H–C(6′), H_A, and H_B.

The introduction of the bulkier 2,6-$^{i}Pr_2C_6H_3$ substituent at the imine N-atom significantly influences the interionic structure in solution. The low-temperature (217 K) $^{19}F,^{1}H$-HOESY plot of **6** is reported in *Fig. 3,b*. $^{19}F,^{1}H$-Cross-peak intensities follow the order: H–C(3), H–C(3′), H–C(4′) > H–C(5′) > H–C(4) >> H–C(6′) ≈ H_A ≈ H–C(5) > H_B ≈ H_C. It is worth noting that the anion does not show any contact with H–C(6) or the ^{i}Pr H-atoms. This means that it is now located close to the pyridine ring of bpy in a *cis* position relative to the Pd–C σ-bond, and it approaches the cation from a lateral trajectory. While it is not surprising that the steric protection provided by the bulky aryl moiety pushes the anion far away from the imine ligand [22], it is remarkable that the anion occupies a peripheral position instead of staying above and below the square-planar coordination plane, as it usually occurs.

In the solid state, each cation of **6** is surrounded by several $[BF_4]^-$ anions, none of which has a particularly short Pd···B distance. The three closest anions (Pd···B distances of 6.344(5) Å (B_A), 7.735(9) Å (B_B), and 8.135(8) Å (B_C), *Fig. 4,b*) are located on the periphery of the bpy ligand, shifted toward the pyridine ring *cis* to the Pd–C σ-bond (B_A and B_C) or at an intermediate position between the two pyridine rings (B_B). The interionic structure observed in solution is quite well-described by a partial occupation of all three orientations.

The replacement of the 'flat' bpy ligand of **6** with 1,4-(*o,o*′-dialkylaryl)-1,4-diaza-buta-1,3-diene ligands such as in **7**–**10** proved to be very useful for gaining more information about cation–anion interactions. As stated above, the advantage of these ligands is that they have 'reporters' spatially distributed above and below the square-planar coordination plane. Previous investigations carried out with Pd [5b] and Pt [6a][17] complexes showed that the perpendicular orientation of the aryl moieties forms a barrier that blocks the anion approach to the metal center. In complex **7**, as expected, the anion interacted with the six Me groups of the α-diimine ligand. The interactions with Me(11) and Me(12) were the strongest, but it is worth noting that the anion/Me(16) and anion/Me(14) cross-peaks were twice as strong as the corresponding anion/Me(13) and anion/Me(15) cross-peaks[1]). This provides clear evidence that the anion prefers to approach the cation from the same side as the square-planar coordination plane, where the phenyl ring of the benzoyl group lies. This preference is probably dictated by the electronic effect of the benzoyl group. In fact, the anion tends to avoid the two lone pairs present at the O-atom, while it prefers to interact with the partial positive charge that could be delocalized into the phenyl ring [6a].

Essentially the same results were obtained for complexes **8**–**10**. Unfortunately, in the ^{1}H-NMR spectrum of complex **9**, the resonances of the Me groups belonging to the ^{i}Pr substituents are not well separated; therefore, a more detailed anion–cation structural relationship could not be determined. In the case of complexes **8** and **10**, which bear the acenaphthylene backbone, the strongest interionic interactions were observed between the anion and H-atoms on the backside of the ligand, but there was an overall decrease in specificity. This is in agreement with previous observations, and it can be attributed to a reduced tendency to form ion pairs. This may be due to the difficulty that the counteranion has in approaching the imine C-atoms of the coordinated ligand, because it is sterically protected by the acenaphthylene moiety [5b]. In complex **10**, the interaction of Me(18f) with the anion is stronger than that of Me(17f), confirming that $[BF_4]^-$ prefers the side *cis* to the phenyl ring of the benzoyl

group. On the other hand, the anion/Me(18f) cross-peak is larger than that between the anion and Me(20f), as in complex **4**, thus confirming the preference for the side *cis* to the imine of the metalated ligand.

Copolymerization of CO and p-*Methylstyrene.* Complexes **4** and **6**–**8** were tested as catalysts for the CO/*p*-methylstyrene copolymerization. The catalytic reactions were carried out in CH_2Cl_2 at room temperature and 1 atm pressure of CO. The results are summarized in *Table 2*. Complexes **4** and **6** show comparable activities in producing syndiotactic polyketones having similar molecular weights and polydispersivity, and with the usual degree of stereoregularity (*ca.* 85% of *uu* triad). In particular, productivities of 33 and 27 $gCP \cdot gPd^{-1} \cdot h^{-1}$ and molecular weights of 31,200 and 25,200 were observed for complexes **4** and **6**, respectively. Different behaviors were observed for the CO uptake for **4** and **6**. The former did not show any induction period, while the latter showed an induction period of *ca.* 15 min[1]).

Table 2. *Copolymerization Results*

Complex	Reaction time [h]	Productivity [g CP/g Pd]	Stereoregularity	M_w (M_w/M_n)
4	3.5	114	syndiotactic	31200 (2.0)
6	3.5	94	syndiotactic	25200 (2.0)
7	51	18	isotactic	9100 (1.3)

Interestingly, complex **7** produced prevalently isotactic polyketones (*ca.* 79% of *ll* triad), while showing a much lower productivity (0.4 $gCP \cdot gPd^{-1} \cdot h^{-1}$). Thus, an increase of the steric hindrance on the apical positions dramatically changed the catalyst stereospecificity[2]) [23]. The use of even more sterically demanding ligands, as in **8**, completely suppressed the catalytic activity.

Reactivity toward CO and p-*Methylstyrene.* To obtain some insights into the initial steps of the copolymerization reaction, the reactivity of complexes **4** and **5** toward the monomers was investigated by NMR. As expected, the reactivity of complexes **4** and **5** was identical; the reactions that occurred in the case of **5** are illustrated in detail.

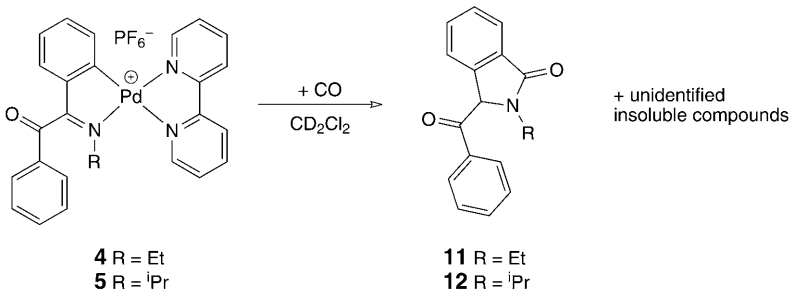
a) *Reactivity toward CO.* When CO was bubbled into a CH_2Cl_2 solution of **5** at room temperature, the initially yellow solution became dark yellow and then colorless, while an amorphous dark precipitate separated from the solution. NMR Analysis of the residual solution showed that 3-benzoyl-2-isopropylisoindolin-1-one (**12**) was quantitatively formed (*Scheme 2*)[3]) [24]. Similarly, **11** was obtained from **4**.

To trap the intermediates, the reaction of **5** with CO was carried out under strictly anhydrous conditions. The reaction product **14** (*Scheme 3*), which appeared to be stable under CO atmosphere, was completely characterized by multinuclear and multidimensional NMR spectroscopy at room temperature.

Key NMR features that allowed us to propose the formation of complex **14** include the following: *i*) The imine *C*=N resonance at δ 182.6 of **5** disappeared, and the signals of three new quaternary C-atoms

[2]) We have observed this effect before (see [5a]), and it will be the subject of a future report [23].
[3]) Keto amides that are structurally similar to **12** were recently investigated [24].

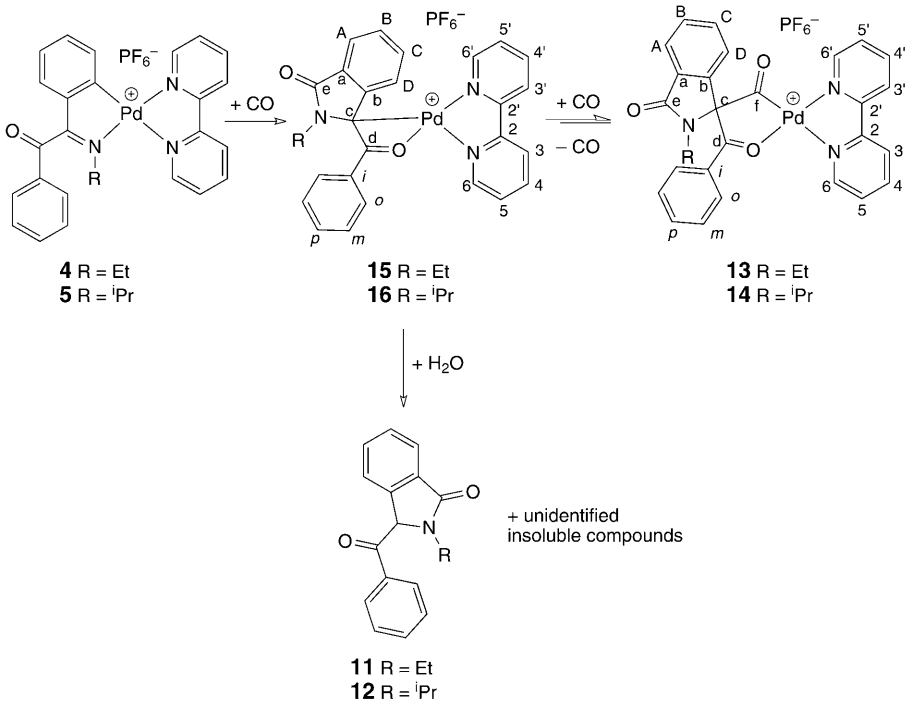
Scheme 2



4 R = Et
5 R = ^{i}Pr

11 R = Et
12 R = ^{i}Pr

Scheme 3



4 R = Et
5 R = ^{i}Pr

15 R = Et
16 R = ^{i}Pr

13 R = Et
14 R = ^{i}Pr

11 R = Et
12 R = ^{i}Pr

appeared at δ 206.0, 168.8, and 100.7. The resonances at δ 168.8 (C_e) and 100.7 ppm (C_c) showed long-range correlation with H_A and H_D, respectively, while the resonance at δ 206.0 (C_f) did not exhibit any long-range correlations. *ii*) The resonance of C_a appeared at δ 131, *i.e.*, at lower frequency by *ca.* 29 ppm than in complex **5**, indicating aryl depalladation. *iii*) The carbonyl resonance of the benzoyl group appeared at δ 209.9, shifted to higher frequency by *ca.* 16 and *ca.* 10 ppm with respect to complex **5** and the free α-imino ketone ligand, respectively, in agreement with the coordination to the Pd-atom through the O-atom [25]. *iv*) The bpy ligand showed eight separated resonances, in agreement with the magnetic inequivalence of the two pyridine moieties of the N–N ligand that were in a slow exchange

regime with respect to the chemical-shift time scale. The proposed structure was also supported by the fact that we were unable to detect any NOEs between H–C(6) and H–C(6′) and any of the H-atoms belonging to the acyl ketone ligand.

The formation of complex **14** is the result of two consecutive insertion reactions of CO into the Pd–aryl and Pd–alkyl bonds. The first CO inserts into the Pd–aryl bond of complex **5**, forming the putative imino-acyl palladacycle intermediate [12j][26], which undergoes a formal insertion of the C=NR moiety into the Pd–acyl bond [12f] (complex **16** in *Scheme 3*), which then inserts a second CO molecule to form **14**. Interestingly, complex **14** is analogous to the intermediate invoked to rationalize the double incorporation of CO or *tert*-butyl isocyanide in cationic complexes similar to **5** bearing a diphosphine ligand [12i]. Complex **16** was, indeed, obtained by decarbonylation of **14** through several freeze-pump-thaw degassing cycles. It was characterized by multinuclear and multidimensional NMR spectroscopy.

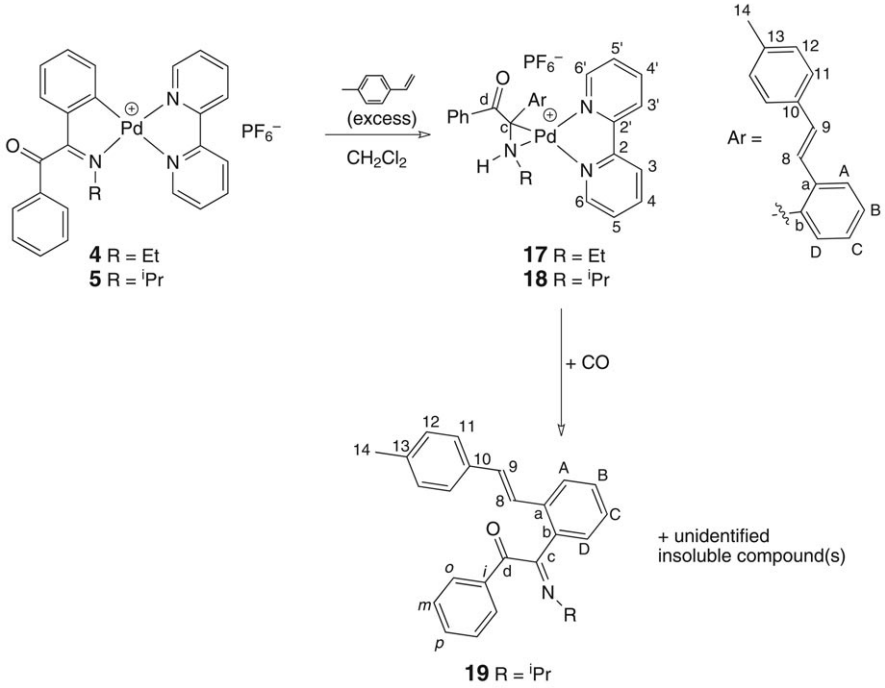
Complex **16** features a quaternary C-atom resonance at δ 45.7 (C_c), consistent with an aliphatic C–Pd bond. In agreement with bpy coordination, H–C(6′) shows a medium-size NOE interaction with one of the Me groups of the ^{i}Pr substituent, and a smaller one with H_A; it is interesting to note that H–C(6′) resonates at relatively low frequency (δ(H) 6.88) suggesting an almost perpendicular orientation of the isoindoline benzo moiety with respect to the square-planar coordination plane. The carbonyl resonance of the benzoyl group appears at δ 217.8. This value is shifted to higher frequency by *ca.* 25, 18.5, and 13 ppm with respect to complex **5**, the free α-imino ketone ligand, and the 'ketonyl' complex *trans*-[Pd(CH_2-COPh)Cl(PPh_3)$_2$], respectively [27]. These data strongly suggest that the carbonyl group is coordinated to the Pd-atom, affording the proposed four-membered palladacycle involving a (carbonyl-κO)alkyl-κC moiety (*Scheme 3*).

Alternatively, complex **16** could be a dimer, in analogy with the complex [{*cis*-($PdPPh_3$)$_2$)}$_2$(μ-CH_2COPh)$_2$](CF_3SO_3)$_2$ [27]. To shed some light on this possibility, we performed PGSE measurements on a mixture containing **13** (*ca.* 2 mM) and **15** (*ca.* 3 mM), obtained from the carbonylation reaction of **4**. The starting complex **4** (*ca.* 6 mM) was used as an external standard. The results indicate that the volumes of **13** and **15** are *ca.* 15–25% greater than that of compound **4**. While these values are a little larger than what was expected for the addition of one or two CO molecules, respectively, they strongly suggest that complexes **13** and **15** are monomeric (in principle, if **15** were a dimer, its volume should be *ca.* 110–120% larger than that of the parent compound **4**). We believe that other possible formulation of complexes **15** and **16** such as η^3-oxoallyl or η^3-benzyl species are unlikely for the following two reasons: *i*) a relevant low-frequency shift of the carbonyl resonance of the benzoyl group would be expected in the case of an η^3-oxoallyl species [28][29]; *ii*) significant low-frequency shifts in both ^{1}H- ($\delta < 7$) and ^{13}C-NMR ($\delta \approx 110-100$) spectra would be expected for the aromatic H- and C-atoms involved in the η^3-benzyl structure [30].

Addition of H_2O to both solutions of **14** or **16** resulted in the quantitative formation of 3-benzoyl-2-isopropylisoindolin-1-one (**12**), and precipitation of an amorphous dark solid. Interestingly, the formation of **12** was accompanied by the disappearance of both the bpy and anion resonances in the ^{1}H- and ^{19}F-NMR spectra, respectively.

Neither complex **14** nor **16** inserted *p*-methylstyrene after 12 h at room temperature, even when the latter was present in a 5- to 50-fold excess. In addition, compounds

Scheme 4



14 and **16** were the main products when the carbonylation of **5** was carried out in the presence of an excess of *p*-methylstyrene (Pd/*p*-methylstyrene molar ratio 1:3).

b) *Reactivity toward* p-*Methylstyrene*. The reaction of **5** with *p*-methylstyrene was much slower than that with CO. When complex **5** in CH_2Cl_2 was left at room temperature overnight in the presence of a large excess of *p*-methylstyrene (40- to 150-fold excess), it was clearly transformed into complex **18** (*Scheme 4*). Unfortunately, all attempts to obtain single crystals of **18** suitable for X-ray investigation were unsuccessful. Consequently, complex **18** was characterized in solution by IR and NMR spectroscopy.

The IR spectrum of **18** in CH_2Cl_2 showed two bands at 1625 and 1605 cm^{-1}. The ^{1}H-NMR established that two species are present in solution in a *ca.* 85:15 molar ratio, and the ^{1}H-EXSY spectrum indicated that they interconvert. Due to partial overlapping, only the resonances of the major component could be completely recognized. Key NMR features are: *i*) signals of two quaternary C-atoms at δ 76.6 (C_c) and 188.4 (C_d); they show long-range correlations with H_D and H_o, respectively, while none of them show ^{1}H,^{13}C single-bond correlations. *ii*) A broad resonance is present at δ *ca.* 6.2 (NH). This resonance does not show any ^{1}H,^{13}C single-bond correlation and appears as a br. *d* (or as a br. *t* in case of **17** obtained from **4**). *iii*) ^{1}H,^{13}C-HMBC and ^{1}H,^{1}H-NOESY Experiments demonstrate that the styryl unit is attached at C_a, while the olefinic coupling constant ($J \approx 16$ Hz) indicates a *trans* geometry of the C=C bond. *iv*) Strong dipolar interactions are observed between H–C(6′) and H_D, as well as between the NH and ^{i}Pr moieties and H–C(6) in the ^{1}H,^{1}H-NOESY experiment[1]). All these NMR observations are consistent

with the proposed structure for complex **18**; in particular, the chemical shift of C_c (δ 76.6) is similar to that recently reported by *Lu* and *Peters* [31] for analogous Pd complexes that, in some cases, were structurally characterized in the solid state by X-ray diffraction studies.

In principle, other structural arrangements can be written for compound **18**. A binuclear C_c-bound palladacycle, which could be formed by combining two molecules of **18** either through the carbonyl, the amine, or the alkene functionalities, can be ruled out because PGSE measurements in CD_2Cl_2 indicate that compound **17** (from **4**) has a volume similar to that of complex **7**, and a *ca.* 50% larger volume than **4**. Since a 33% volume increment would be expected on passing from **4** to **17**, these data strongly suggest that dimerization is not occurring. Mononuclear structures involving coordination by the C=C bond do not seem to be supported by NMR data, judging from the H–C(8)/H–C(9) and C(8)/C(9) chemical shift (δ(H) 7.05, δ(C) 133.9 and 123.43, resp.). In addition, an η^3-benzyl structure is not consistent with the δ(C) and δ(H) values of the C_A to C_a aromatic ring [30].

A plausible mechanism for the formation of **18** is an olefin insertion into the Pd–aryl bond, followed by β-hydride elimination to form a putative Pd–H species, which then undergoes internal addition at the C=N bond. In contrast to **16**, compound **18** do not react with H_2O in CH_2Cl_2. At room temperature in CD_2Cl_2, complex **18** did not insert CO; rather, imino ketone **19** was formed quantitatively (*Scheme 4*) together with a large amount of a dark precipitate. With the formation of **19**, both the bpy and anion resonances disappeared in the ^{1}H- and ^{19}F-NMR spectra.

c) *Implications in Catalysis.* The results discussed above suggest that the isolated and characterized intermediates of the carbonylation and of the reaction with *p*-methylstyrene, namely complexes **13**–**18**, do not directly enter the catalytic cycle of the copolymerization reaction; they are probably off-loop species. In fact, complexes **13**–**16** did not insert *p*-methylstyrene even after a period three times longer than the overall polymerization time, while reacting **18** with CO resulted in the formation of the substituted α-imino ketone **19**. A sequential insertion was never observed. Consequently, the cationic complexes tested in the CO/*p*-methylstyrene copolymerization should be considered as pre-catalysts. According to the literature [32], the 'real' active species is supposed to be a hydropalladium complex bearing the N–N ligand. To obtain evidence regarding the formation of [PdH] complexes, we prepared a complex **4′** similar to **4**, with the $[BARF]^-$ ($=[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$) counterion instead of $[PF_6]^-$ in an attempt to avoid the precipitation of Pd and bpy and, thereby give the possibility of detecting hydride species. Carbonylation of **4′** in nonanhydrous CD_2Cl_2 was then followed by NMR. Indeed no precipitate was observed. As expected, compound **11** was formed along with several other species. The resonance at δ –14.8 in the ^{1}H-NMR spectrum indicated the formation of $[Pd_2(\mu\text{-CO})(\mu\text{-H})(N\text{–}N)_2][BARF]$ (N–N = bpy), which had been previously characterized by us [33], and which supports the formation of the hydropalladium intermediate.

Conclusions. – We have established that the novel palladacyclic compounds $[Pd\{C_6H_4(C_6H_5C{=}O)C{=}N\text{–}R\}(N\text{–}N)][X]$ can promote the copolymerization reaction of CO and *p*-methylstyrene, when the N–N ligand is not sterically demanding in the apical position, affording syndiotactic (N–N = bpy) and isotactic (N–N = (2,6-

$Me_2C_6H_3$)–N=C(Me)–C(Me)=N–(2,6-$Me_2C_6H_3$)) copolymers. The reaction of the palladacyclic compounds **4** and **5** with CO were investigated in detail, and two species derived from a single (**15** and **16**) and a double (**13** and **14**) CO insertion into the Pd–C bonds were isolated and characterized in solution by multinuclear and multidimensional NMR spectroscopy. The reaction of **4** and **5** with *p*-methylstyrene was also investigated, and the reaction products **17** and **18**, respectively, were characterized. Finally, the relative anion–cation orientation was determined both in solution and solid state (for **4** and **6**) by means of $^{19}F,^{1}H$-HOESY NMR spectroscopy and X-ray single-crystal diffraction studies, respectively. The anion position in solution is strongly dependent on the steric and electronic properties of the ligand, and it is only vaguely similar to that observed in the solid state.

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Experimental Part

General. Manipulation of all complexes was carried out either in air or by using standard *Schlenk* or high-vacuum techniques. N_2 was deoxygenated and dried by passage through two purification towers charged with activated *R3-11G-BASF* catalysts and 4-Å activated molecular sieves, respectively. Unless otherwise stated, solvents were dried and purified by standard methods and freshly distilled under N_2. *p*-Methylstyrene was dried over calcium hydride and distilled before use. The other CP-grade chemicals were used as received. CD_2Cl_2 (*Cortec*) was either degassed and stored over 3 Å molecular sieves, vacuum-distilled from calcium hydride directly into a 5-mm *J. Yang* NMR tube, or used as received. CO (CP grade 99.99%) was supplied by *Air Liquide*. α-Imino ketones, were synthesized according to [15]. 1D and 2D ^{1}H-, $^{13}C\{^1H\}$-, and ^{19}F-NMR Spectra, $^{13}C\{^1H\}$-ATP, $^1H,^1H$-COSY, $^1H,^1H$-NOESY, $^1H,^{13}C$-HMQC, and $^1H,^{13}C$-HMBC experiments: *Bruker-Avance-DRX-400* spectrometer equipped with a *Great 1/10* gradient unit and a *QNP* probe with a *Z*-gradient coil; δ in ppm with external referencing rel. to $SiMe_4$ (^{1}H and ^{13}C) and CCl_3F (^{19}F), *J* in Hz. Typical 2D $^1H,^1H$-NOESY and $^{19}F,^1H$-HOESY plots were recorded with a mixing time of 500–800 ms. ^{1}H-PGSE Experiments were acquired by using the standard stimulated echo pulse sequence [34] at 296 K without spinning. Samples having concentrations in the range 2–6 mM were prepared in CD_2Cl_2. The shape of the gradients was rectangular, their duration was 4 ms, and their strength was varied during the experiments. All the spectra were acquired by using 32 K points and a spectral width of 5000 Hz, and processed with a line broadening of 1.0 Hz. Gradients were calibrated with a sample of HDO (0.04%) in D_2O (known diffusion coefficient in the range 274–318 K) [35] under exactly the same conditions as with the sample of interest. The residual solvent signal at δ 5.32 was used as internal standard to take into account random changes in the actual temp. inside the probe as well as gradient-strength reproducibility. The data were treated according to a reported methodology [36]. Elemental analyses (C, H, N): *Fisons-Instruments-1108 CHNS-O* elemental analyzer.

Copolymerization Reactions. In a typical copolymerization reaction, the Pd^{II} complex (0.14 mmol) was dissolved at r.t. in CH_2Cl_2 (5 ml) under N_2, then *p*-methylstyrene (*ca.* 5.5 ml, 42 mmol) was added (olefin/Pd molar ratio 300:1). The resulting soln. was transferred into a thermostated *Schlenk* flask equipped with a CO gas line and a tank for the CO. The soln. was allowed to react for 3.5 h at 22°. The resulting gray polymer was precipitated with MeOH and washed with MeOH. To remove metallic Pd, the polymer was redissolved in $CHCl_3$, filtered through *Celite*, precipitated with MeOH, washed with MeOH, and dried under vacuum. For NMR characterization, samples were prepared by dissolving *ca.* 35 mg of the copolymer in $(CF_3)_2CHOH/CDCl_3$ 1:1 (*v/v*). The molecular weights (M_w) of polymers and the mass distributions (M_w/M_n) were determined by gel-permeation chromatography *vs.* polystyrene standards. The analyses were recorded on a *Knauer* HPLC (*K-501* pump; *K-2501-UV* detector) with a

PLgel 5-μm 10^4 Å GPC column; $CHCl_3$ flow rate 0.6 ml/min). Samples were prepared by dissolving the copolymer (2 mg) in $CHCl_3$ (10 ml). The statistical calculations were performed with the *Bruker-Chromstar* software program.

X-Ray Crystallography. Single crystals of complexes **4** and **6**, suitable for X-ray diffraction, were obtained as described above. Data were collected on a *Xcalibur* (*CCD* areal) diffractometer of *Oxford Instr.* by using Mo-*Kα* graphite-monochromated radiation (*λ* 0.71069 Å). The *ω*-phi scans and the frame data were acquired with the CRYSALIS (*CCD 171*) software at r.t. The crystal-to-detector distance was 65.77 mm. The frames were processed with the CRYSALIS (*RED 171*) software to give the *hkl* files corrected for scan speed, background, *Lorentz*, and polarization effects. Standard reflections were measured periodically and showed no apparent variation in intensity during data collection in either of the complexes, so, no correction for crystal decomposition was necessary. The data were corrected for absorption using semiempirical multiscan methods [37].

The structures were solved by the direct methods with the SIR97 [38] program and refined by the full-matrix least-squares method on F^2 with the SHELXL-97 [39] WinGX [40] version. All non-H-atoms were refined anisotropically. The H-atoms were added at the calculated positions and refined by using a riding model.

In the crystal of complex **6**, a molecule of MeOH was present that probably came from the crystallization process. The two atoms (C, O) of MeOH were refined anisotropically, but no H-atom was added.

Selected bond lengths and angles are given in *Table 1*, while the structural parameters and the refinements for the two complexes are given in *Table 3*. Atomic coordinates, anisotropic displacement coefficients, and an extended list of interatomic distances and angles are available as supporting information[1]). CCDC 295788 and CCDC 295789 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif from the *Cambridge Crystallographic Data Centre.*

Di-μ-chlorobis{2-[1-(ethylimino-κN)-2-oxo-2-phenylethyl]phenyl-κC}dipalladium (**1**). $Na_2[PdCl_4]$ (1.0 g, 3.4 mmol) was suspended in freshly dist. MeOH (20 ml) and ligand Et–N=C(Ph)–C(Ph)=O (0.9 g, 3.8 mmol) was added. After 1 d, the yellow precipitate that formed was separated by filtration, rinsed with cold MeOH and dried *i.v.*: 1.14 g (89%) of **1**. ^{1}H-NMR (CD_2Cl_2, 298 K): 8.02 (*d*, $^3J_{o,m}$=7.4, H_o); 7.77 (*t*, $^3J_{p,m}$=7.4, H_p); 7.60 (*t*, $^3J_{m,p}$=$^3J_{m,o}$=7.4, H_m); 7.47 (*t*, $^3J_{B,A}$=$^3J_{B,C}$=7.9, H_B); 7.12 (*d*, $^3J_{A,B}$=7.9, H_A); 6.99 (*dd*, $^3J_{C,B}$=7.9, $^3J_{C,D}$=7.1, H_C); 6.79 (*d*, $^3J_{D,C}$=7.1, H_D); 3.55 (*m*, MeCH_2); 1.44 (*m*, *Me*CH_2).

Di-μ-chlorobis{2-[1-(isopropylimino-κN)-2-oxo-2-phenylethyl]phenyl-κC}dipalladium (**2**). As described for **1**, with $Na_2[PdCl_4]$ (0.5 g, 1.7 mmol), MeOH (20 ml) and ^{i}Pr–N=C(Ph)–C(Ph)=O (0.47

Table 3. *Crystal Data and Details of Refinements for Complexes* **4** *and* **6**

	4	**6**		**4**	**6**
Formula	$C_{26}H_{22}F_6N_3OPPd$	$C_{37}H_{34}BF_4N_3O_2Pd$	μ(Mo-$K\alpha$) [mm^{-1}]	0.840	0.572
M	643.84	745.90	Total data collected	26144	24273
Cryst. system	monoclinic	monoclinic	Unique obs. data	9675	10007
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	Criterion for observation	$F_0 > 4s(F_0)$	$F_0 > 4s(F_0)$
a [Å]	11.229(5)	10.736(5)	Unique data used in the	7630	7205
b [Å]	16.245(5)	27.099(5)	refinement (NO)		
c [Å]	14.355(5)	12.726(5)	No. of params. refined (NV)	351	444
β [deg]	94.123(5)	103.89(5)	R_{int}	0.0353	0.0497
V [Å^3]	2611.8(17)	3594(2)	$wR(F_2)$	0.0619	0.1313
Z	4	4	*G.o.f.*	0.932	1.051
d_{calc} [g m^{-3}]	1.637	1.378	Mean shift/esd, final cycle	0.000	0.001
Cryst. size	0.15×0.10×0.07	0.20×0.15×0.10	Max pos. electron dens.	0.385	0.601
[mm]			Max neg. electron dens.	−0.364	−0.738
			θ range [°]	3.10 to 33.00	5.37 to 29.77

g, 1.8 mmol): 0.55 g (82%) of **2**. ^{1}H-NMR (CD_2Cl_2, 298 K): 8.00 (*dd*, $^3J_{o,m}$ = 7.2, $^4J_{o,p}$ = 1.2, H_o); 7.80 (*t*, $^3J_{p,m}$ = 8.2, H_p); 7.57 (*m*, H_m and H_B); 7.12 (*d*, $^3J_{A,B}$ = 7.2, H_A); 6.94 (*t*, $^3J_{C,B} = {}^3J_{C,D}$ = 7.0, H_C); 6.74 (*d*, $^3J_{D,C}$ = 7.0, H_D); 3.72 (*sept.*, ^3J = 6.3, Me_2CH); 1.47 (*d*, ^3J = 6.3, Me_2CH).

Di-μ-chlorobis{2-{1-[(2,6-diisopropylphenyl)imino-κN]-2-oxo-2-phenylethyl}phenyl-κC}dipalladium (**3**). As described for **1**, with $Na_2[PdCl_4]$ (1 g, 3.4 mmol), MeOH (20 ml), and (2,6-^{i}Pr$_2$C$_6$H$_3$–N=C(Ph)–C(Ph)=O (1.4 g, 3.8 mmol, 2 d): 1.43 g (83%). ^{1}H-NMR (CD_2Cl_2, 298 K): 7.86 (*d*, $^3J_{o,m}$ = 7.6, H_o); 7.65 (*t*, $^3J_{p,m}$ = 7.6, H_p); 7.47 (*t*, $^3J_{m,p} = {}^3J_{m,o}$ = 7.6, H_m); 7.27 (*t*, $^3J_{p',m'} = {}^3J_{p',m'}$ = 7.6, $H_{p'}$); 7.13 (*m*, H_B, H_A, H_C, $H_{m'}$); 6.99 (*dd*, $^3J_{D,C}$ = 6.7, $^4J_{D,B}$ = 1.5, H_D); 6.89 (*m*, $H_{m''}$); 3.29 (*m*, Me_2CH); 1.55 (*d*, ^3J = 6.3, Me_2CH); 1.52 (*d*, ^3J = 6.7, Me_2CH); 0.91 (br. *d*, Me_2CH).

(2,2′-Bipyridine-κN^2,κN$^{2'}$){2-[1-(ethylimino-κN)-2-oxo-2-phenylethyl]phenyl-κC}palladium(1+) Hexafluorophosphate(1−) (**4**). To a suspension of **1** (200 mg, 0.26 mmol) in freshly dist. MeOH (10 ml), 2,2′-bipyridine (89 mg, 0.57 mmol) was added. After a few minutes, the suspension became a soln. to which $NH_4[PF_6]$ (184 mg, 1.14 mmol) was added. A yellow precipitate formed instantaneously. The solid was recovered by filtration, rinsed with cold MeOH, and dried *i.v.*: 245 mg (73%) of **4**. ^{1}H-NMR (CD_2Cl_2, 230 K): 8.99 (*d*, ^3J(6′,5′) = 5.4, H–C(6′)); 8.55 (*d*, ^3J(6,5) = 4.9, H–C(6)); 8.50 (*d*, ^3J(3,4) = 4.7, H–C(3)); 8.32 (*m*, H–C(4), H–C(3′), H–C(4′)); 8.04 (br. *d*, H_o); 7.84 (*m*, H–C(5), H_p, H–C(5′)); 7.62 (*m*, H_m); 7.28 (*t*, $^3J_{B,C} = {}^3J_{B,A}$ = 7.6, H_B); 7.16 (*d*, $^3J_{A,B}$ = 7.6, H_A); 7.12 (*t*, $^3J_{C,B} = {}^3J_{C,D}$ = 7.6, H_C); 6.94 (*d*, $^3J_{D,C}$ = 7.6, H_D); 3.68 (*q*, ^3J = 7.1, $MeCH_2$); 1.40 (*t*, ^3J = 7.1, $MeCH_2$). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 230 K): 193.1 (*s*, C_d); 183.7 (*s*, C_c); 159.8 (*s*, C_a); 156.8 (*s*, C(2) or C(2′)); 155.1 (*s*, C(2) or C(2′)); 153.7 (*s*, C(6′)); 149.9 (*s*, C(6)); 146.1 (*s*, C_b); 141.7 (*s*, C(4)); 141.7 (*s*, C(4′)); 137.1 (*s*, C_p); 134.3 (*s*, C_A); 133.5 (*s*, C_i); 132.9 (*s*, C_B); 130.2 (*s*, C_m, C_o); 128.9 (*s*, C_D); 128.5 (*s*, C(5′)); 128.2 (*s*, C(5)); 126.4 (*s*, C_C); 124.4 (*s*, C(3)); 124.1 (*s*, C(3′)); 50.7 (*s*, $MeCH_2$); 15.4 (*s*, $MeCH_2$). ^{19}F-NMR (CD_2Cl_2, 230 K): −73.17 (*d*, ^1J(F,P) = 712, $[PF_6]^-$). Anal. calc. for $C_{26}H_{22}F_6N_3OPPd$ (643.86): C 48.50, H 3.44, N 6.53; found: C 48.52, H 3.46, N 6.51.

(2,2′-Bipyridine-κN^2,κN$^{2'}$){2-[1-isopropylimino-κN)-2-oxo-2-phenylethyl]phenyl-κC}palladium(1+) Hexafluorophosphate(1−) (**5**). As described for **4**, with **2** (200 mg, 0.25 mmol), MeOH (10 ml), 2,2′-bipyridine (85 mg, 0.54 mmol), and $NH_4[PF_6]$ (176 mg, 1.08 mmol): 192 mg (75%) of **5**. ^{1}H-NMR (CD_2Cl_2, 298 K): 9.04 (*d*, ^3J(6′,5′) = ^3J(6,5) = 5.1, H–C(6′), H–C(6)); 8.41 (*d*, ^3J(3,4) = ^3J(3′,4′) = 7.8, H–C(3), H–C(3′)); 8.35 (*t*, ^3J(4,3) = ^3J(4′,3′) = 7.8, H–C(4), H–C(4′)); 8.09 (*d*, $^3J_{o,m}$ = 7.2, H_o); 7.83 (*m*, H–C(5), H_p, H–C(5′)); 7.67 (*t*, $^3J_{m,p}$ = 7.7, H_m); 7.31 (*dt*, $^3J_{B,A} = {}^3J_{B,C}$ = 7.2, $^4J_{B,D}$ = 1.5, H_B); 7.14 (*m*, H_A, H_C); 6.92 (*dd*, $^3J_{D,C}$ = 7.2, $^4J_{D,B}$ = 1.6, H_D); 4.08 (*sept.*, ^3J = 6.8, Me_2CH); 1.59 (*d*, ^3J = 6.8, Me_2CH); 1.56 (*d*, ^3J = 6.8, Me_2CH). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 298 K): 192.9 (*s*, C_d); 182.6 (*s*, C_c); 159.0 (*s*, C_a); 156.1 (br., C(2), C(2′)); 153.0 (br., C(6), C(6′)); 146.5 (*s*, C_b); 141.5 (*s*, C(4)); 136.6 (*s*, C_p); 134.6 (*s*, C_A); 134.0 (*s*, C_i); 132.6 (*s*, C_B); 130.09 (*s*, C_o); 130.05 (*s*, C_m); 128.9 (*s*, C_D); 127.9 (*s*, C(5), C(5′)); 126.5 (*s*, C_C); 124.3 (*s*, C(3), C(3′)); 58.3 (*s*, Me_2CH); 22.9 (*s*, Me_2CH); 22.0 (*s*, Me_2CH). Anal. calc. for $C_{27}H_{24}F_6N_3OPPd$ (657.88): C 49.29, H 3.68, N 6.39; found: C 49.40, H 3.77, N 6.54.

(2,2′-Bipyridine-κN^2,κN$^{2'}$){2-{1-[(2,6-diisopropylphenyl)imino-κN]-2-oxo-2-phenylethyl}phenyl-κC}palladium(1+) Tetrafluoroborate(1−) (**6**). Complex **3** (300 mg, 0.30 mmol) and 2,2′-bipyridine (109 mg, 0.70 mmol) were dissolved in freshly dist. CH_2Cl_2 (10 ml). After the initial suspension was transformed into a soln., $Ag[BF_4]$ (116 mg, 0.60 mmol) was added, and the soln. was stirred for 30 min. The precipitated AgCl was removed by filtration and the volume of the soln. was reduced to *ca.* 2 ml. Addition of hexane caused the precipitation of the product, which was recovered by filtration, rinsed with cold hexane and dried *i.v.*: 289 mg (67%) of **6**. ^{1}H-NMR (CD_2Cl_2, 217 K; for numbering see *Fig. 3*): 9.07 (*d*, ^3J(6′,5′) = 5.6, H–C(6′)); 8.40 (*m*, H–C(4′), H–C(3′), H–C(3)); 8.10 (*ddd*, ^3J(4,3) = ^3J(4,5) = 7.6, ^4J(4,6) = 1.4, H–C(4)); 7.99 (*d*, $^3J_{o,m}$ = 7.6, H_o); 7.90 (*ddd*, ^3J(5′,4′) = ^3J(5′,6′) = ^3J(6′,5′) = 5.6, ^3J(5′,3′) = 1.4, H–C(5′)); 7.76 (*t*, $^3J_{p,m}$ = 7.2, H_p); 7.57 (*dd*, $^3J_{m,p}$ = 7.2, $^3J_{m,o} = {}^3J_{o,m}$ = 7.6, H_m); 7.51 (*ddd*, $^3J_{B,A} = {}^3J_{B,C}$ = 8.0, $^4J_{B,D}$ = 1.6, H_B); 7.47 (*dd*, $^3J_{p',mu} = {}^3J_{p',md}$ = 7.6, $H_{p'}$); 7.38 (*d*, $^3J_{A,B}$ = 8.0, H_A); 7.35 (*dd*, $^3J_{md,p'}$ = 7.6, $^4J_{md,mu}$ = 0.8, H_{md}); 7.27 (*dd*, $^3J_{C,D} = {}^3J_{C,B}$ = 7.6, H_C); 7.21 (*dd*, $^3J_{D,C}$ = 7.6, $^4J_{D,B}$ = 1.6, H_D); 7.14 (*m*, H–C(5), H_{mu}); 5.7 (*d*, ^3J(6,5) = 5.2, H–C(6)); 3.36 (*sept.*, ^3J = 6.4, CH_u); 3.16 (*sept.*, ^3J = 6.4, CH_d); 1.36 (*d*, ^3J = 6.4, Me_{db}); 0.98 (*d*, ^3J = 6.4, Me_{uf}); 0.95 (*d*, ^3J = 6.4, Me_{df}); 0.34 (*d*, ^3J = 6.4, Me_{ub}). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 217 K; for numbering, see *Fig. 3*): 191.0 (*s*, C_d); 185.6 (*s*, C_c); 161.0 (*s*, C_a); 156.9 (*s*, C(2′)); 155.1 (*s*, C(2)); 153.6 (*s*, C(6′)); 149.3 (*s*, C(6)); 146.7 (*s*, C_b); 143.3 (*s*, C_{od}); 142.2 (*s*, C(4′)); 141.6 (*s*, C(4)); 140.8 (*s*, C_{ou}); 140.2 (*s*, C_i); 136.7 (*s*, C_p); 134.9 (*s*, C_A); 134.0 (*s*, C_B); 133.4 (*s*, C_i); 130.5 (*s*, C_o,

C_D); 130.1 (*s*, $C_{p'}$); 130.0 (*s*, C_m); 128.4 (*s*, C(5′)); 126.9 (*s*, C_C); 126.6 (*s*, C(5)); 125.6 (*s*, C_{mu}); 125.3 (*s*, C_{md}); 124.4 (*s*, C(3′)); 123.6 (*s*, C(3)); 29.1 (*s*, CH_d); 28.7 (*s*, CH_u); 24.8 (*s*, Me_{uf}); 24.6 (*s*, Me_{df}); 22.7 (*s*, Me_{ub}); 22.5 (*s*, Me_{db}). ^{19}F-NMR (CD_2Cl_2, 217 K): −152.49 (*s*, [$^{10}BF_4$]$^-$); −152.54 (*s*, [$^{11}BF_4$]$^-$). Anal. calc. for $C_{36}H_{34}BF_4N_3OPd \cdot 0.5$ MeOH (733.92): C 59.73, H 4.94, N 5.73; found: C 59.71, H 4.97, N 5.77.

*{*N,N′*-(1,2-Dimethylethane-1,2-diylidene)bis[2,6-dimethylbenzenamine-*κ*N]}{2-[1-(ethylimino-*κ*N)-2-oxo-2-phenylethyl]phenyl-*κ*C}palladium(1+) Tetrafluoroborate(1−)* (**7**). As described for **6**, with **1** (150 mg, 0.20 mmol), (2,6-$Me_2C_6H_3$)N=C(Me)−C(Me)=N(2,6-$Me_2C_6H_3$) (87.3 mg, 0.40 mmol), CH_2Cl_2 (5 ml), and Ag[BF_4] (77.3 mg, 0.40 mmol). From *ca.* 1 ml, addition of hexane caused the precipitation of the product: 189 mg (73%) of **7**. ^{1}H-NMR (CD_2Cl_2, 230 K): 7.88 (br., H_o); 7.77 (*t*, $^3J_{p,m}$ = 7.6, H_p); 7.59 (*t*, $^3J_{m,p} = {}^3J_{m,o}$ = 7.6, H_m); 7.38 (*t*, ^3J(8,7) = ^3J(8,7′) = 7.4, H−C(8)); 7.31 (*m*, H−C(7), H−C(7′)); 7.20 (*m*, H−C(3), H−C(3′), H−C(4)); 6.87 (*dt*, $^3J_{C,B} = {}^3J_{C,D}$ = 7.4, $^4J_{C,A}$ = 0.6, H_C); 6.72 (*dd*, $^3J_{D,C}$ = 7.4, $^4J_{D,B}$ = 1.3, H_D); 6.69 (*dt*, $^3J_{B,C} = {}^3J_{B,A}$ = 7.4, $^4J_{B,D}$ = 1.3, H_B); 5.10 (*d*, $^3J_{A,B}$ = 8.1, H_A); 2.49 (*m*, MeCH_2); 2.46 (*s*, Me(14)); 2.39 (*s*, Me(11) or Me(12)); 2.35 (*s*, Me(13)); 2.34 (*s*, Me(15)); 2.33 (*s*, Me(12) or Me(11)); 2.31 (*s*, Me(16)); 2.07 (*m*, MeCH_2); 0.76 (*t*, ^3J = 6.9, *Me*CH_2). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 230 K): 192.9 (*s*, C_d); 184.3 (*s*, C_c); 182.2 (*s*, C(9) or C(10)); 178.3 (*s*, C(10) or C(9)); 154.6 (*s*, C_a); 146.8 (*s*, C_b); 143.93 (*s*, C(1)); 143.88 (*s*, C(5)); 136.9 (*s*, C_p); 133.3 (*s*, C_i); 131.0 (*s*, C(6)); 130.9 (*s*, C_B); 130.5 (*s*, C(6′)); 130.4 (*s*, C_A); 130.2 (*s*, C_m); 129.8 (*s*, C(7) or C(3)); 129.7 (*s*, C(3) or C(7)); 129.6 (*s*, C(3′) and C(7′)); 129.3 (*s*, C(2) or C(2′)); 129.0 (*s*, C_D); 128.9 (*s*, C(8)); 128.4 (*s*, C(4)); 126.5 (*s*, C_C); 49.3 (*s*, Me*C*H_2); 21.3 (*s*, C(11) or C(12)); 20.3 (*s*, C(12) or C(11)); 18.8 (*s*, C(14)); 18.76 (*s*, C(13), C(15)); 18.54 (*s*, C(16)); 16.2 (*s*, *Me*CH_2). ^{19}F-NMR (CD_2Cl_2, 230 K): −151.36 (*s*, [$^{10}BF_4$]$^-$); −151.54 (*s*, [$^{11}BF_4$]$^-$). Anal. calc. for $C_{36}H_{38}BF_4N_3OPd$ (721.9310): C 59.89, H 5.31, N 5.82; found: C 59.77, H 5.25, N 5.96.

*{*N,N′*-(Acenaphthylene-1,2-diylidene)bis[2,6-dimethylbenzenamine-*κ*N]}{2-[1-(ethylimino-*κ*N)-2-oxo-2-phenylethyl]phenyl-*κ*C}palladium(1+) Tetrafluoroborate(1−)* (**8**). As described for **6**, with **1** (150 mg, 0.20 mmol), (2,6-$Me_2C_6H_3$)N=C(R)−C(R)=N(2,6-$Me_2C_6H_3$) (R−R = naphthalene-1,8-diyl; 161 mg, 0.42 mmol), CH_2Cl_2 (5 ml), and Ag[BF_4] (77.6 mg, 0.40 mmol). From *ca.* 1 ml, addition of hexane caused the precipitation of the product: 235 mg (67%) of **8**. ^{1}H-NMR (CD_2Cl_2, 230 K): 8.30 (*d*, ^3J(25, 25) = 8.1, H−C(25)); 8.27 (^3J(22,23) = 8.0, H−C(23)); 7.95 (br., H_o); 7.80 (*tt*, $^3J_{p,m}$ = 7.5, $^4J_{p,o}$ = 1.3, H_p); 7.61 (*m*, H_m, H−C(8), H−C(26), H−C(22)); 7.49 (*d*, ^3J(7,8) = ^3J(7′,8) = 7.9, H−C(7), H−C(7′)); 7.38 (*m*, H−C(4), H−C(3′), H−C(3)); 6.97 (*t*, $^3J_{C,B} = {}^3J_{C,D}$ = 7.6, H_C); 6.79 (*m*, H_D, H_B); 6.58 (*d*, ^3J(21, 22) = 6.9, H−C(21)); 6.52 (*d*, ^3J(26,27) = 6.9, H−C(27)); 5.45 (*dd*, $^3J_{A,B}$ = 7.9, $^4J_{A,C}$ = 0.6, H_A); 2.84 (*m*, MeCH_2); 2.64 (*m*, MeCH_2); 2.44 (*s*, Me(14)); 2.37 (*s*, Me(13)); 2.33 (*s*, Me(15)); 2.32 (*s*, Me(16)); 0.78 (*t*, ^3J = 7.0, *Me*CH_2). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 230 K): 192.8 (*s*, C_d); 184.5 (*s*, C_c); 176.2 (*s*, C(10) or C(9)); 172.5 (*s*, C(10) or C(9)); 152.3 (*s*, C_a); 147.0 (*s*, C_b); 146.8 (*s*, C(28)); 143.7 (*s*, C(1)); 143.1 (*s*, C(5)); 137.0 (*s*, C_p); 134.2 (*s*, C(25)); 133.7 (*s*, C(23)); 133.4 (*s*, C_i); 131.43 (*s*, C(24)); 131.37 (*s*, C_B); 130.84 (*s*, C(6)); 130.77 (*s*, C(6′)); 130.56 (*s*, C(7), C(7′)); 130.42 (*s*, C(3), C(3′)); 130.2 (*s*, C_m and C(8) or C(26) or C(22)); 130.12 (*s*, C(8) or C(26) or C(22)); 130.02 (*s*, C(8) or C(26) or C(22)); 129.39 (*s*, C_D); 129.21 (*s*, C(4)); 129.09 (*s*, C(2)); 129.01 (*s*, C(2′)); 128.98 (*s*, C_A); 126.88 (*s*, C_C); 126.78 (*s*, C(27)); 126.34 (*s*, C(21)); 125.55 (*s*, C(11) or C(12)); 125.18 (*s*, C(12) or C(11)); 49.8 (*s*, Me*C*H_2); 18.76 (*s*, C(14)); 18.75 (*s*, C(13)); 18.65 (*s*, C(15)); 18.59 (*s*, C(16)); 15.76 (*s*, *Me*CH_2). ^{19}F-NMR (CD_2Cl_2, 230 K): −153.07 (*s*, [$^{10}BF_4$]$^-$); −153.14 (*s*, [$^{11}BF_4$]$^-$). Anal. calc. for $C_{44}H_{38}BF_4N_3OPd$ (818.02): C 64.60, H 4.68, N 5.14; found: C 64.72, H 4.72, N 5.19.

*{*N,N′*-(1,2-Dimethylethane-1,2-diylidene)bis[2,6-diisopropylbenzenamine-*κ*N]}{2-[1-(ethylimino-*κ*N)-2-oxo-2-phenylethyl]phenyl-*κ*C}palladium(1+) Tetrafluoroborate(1−)* (**9**). As described for **6**, with **1** (100 mg, 0.13 mmol), (2,6-^{i}Pr$_2$$C_6H_3$)N=C(Me)−C(Me)=N(2,6-^{i}Pr$_2$$C_6H_3$) (112 mg, 0.27 mmol), CH_2Cl_2 (5 ml), and Ag[BF_4] (53 mg, 0.27 mmol). From *ca.* 1 ml, addition of hexane caused the precipitation of the product: 142.8 mg (63%) of **9**. ^{1}H-NMR (CD_2Cl_2, 230 K): 7.87 (br., H_o); 7.77 (*t*, $^3J_{p,m}$ = 7.5, H_p); 7.58 (*t*, $^3J_{m,p} = {}^3J_{m,o} = {}^3J_{p,m}$ = 7.5, H_m); 7.54 (*t*, ^3J(4,3) = ^3J(4,3′) = 7.4, H−C(8)); 7.44 (*dd*, ^3J(3,4) = 7.4, ^4J(3,3′) = 0.97, H−C(7)); 7.34 (*m*, H−C(3), H−C(3′), H−C(4), H−C(7′)); 6.85 (*dt*, $^3J_{C,D} = {}^3J_{C,B}$ = 7.4, $^4J_{C,A}$ = 0.68, H_C); 6.69 (*dd*, $^3J_{D,C}$ = 7.4, $^4J_{D,B}$ = 1.5, H_D); 6.65 (*dt*, $^3J_{B,A} = {}^3J_{B,C}$ = 7.4, $^4J_{B,D}$ = 1.5, H_B); 5.06 (*d*, $^3J_{A,B}$ = 7.4, H_A); 3.34 (*sept.*, ^3J(13,17) = 6.7, H−C(13)); 3.14 (*m*, H−C(14), H−C(16)); 3.04 (*sept.*, ^3J(15, 19) = 6.9, H−C(15)); 2.66 (*m*, ^3J = 7.1, MeCH_2); 2.45 (*s*, Me(12)); 2.42 (*s*, Me(11)); 2.27 (*m*, ^3J = 7.1, MeCH_2); 1.45 (*d*, ^3J(17f,13) = 6.7, Me(17f)); 1.27 (*m*, Me(18f), Me(18b), Me(20b), Me(19b), Me(19f)); 1.15 (*d*, ^3J(17b,13) = 6.7, Me(17b)); 0.86 (*d*, ^3J(20f,16) = 6.7, Me(20f)); 0.58 (*t*, ^3J = 7.1, *Me*CH_2).

$^{13}C\{^1H\}$-NMR (CD_2Cl_2, 230 K): 192.6 (*s*, C_d); 185.5 (*s*, C_c); 181.7 (*s*, C(10)); 177.9 (*s*, C(9)); 156.0 (*s*, C_a); 146.7 (*s*, C_b); 142.1, 141.8, 140.35, 139.34, 138.9, 138.7 (*s*, C(1), C(2), C(2′), C(5), C(6), C(6′)); 136.9 (*s*, C_p); 133.1 (*s*, C_i); 132.3 (*s*, C_A); 130.5 (*s*, C_B); 130.1 (*s*, C_m); 129.8 (*s*, C(8)); 129.3 (*s*, C(4)); 128.8 (*s*, C_D); 126.4 (*s*, C_C); 125.7, 125.5 (*s*, C(3), C(3′), C(7′)); 125.2 (*s*, C(7)); 49.5 (*s*, Me*C*H_2); 29.9 (*s*, C(13)); 29.5 (*s*, C(15)); 29.3 (*s*, C(14)); 28.9 (*s*, C(16)); 24.4 (*s*, C(17b)); 23.3 (*s*, C(17f)); 24.3, 23.9, 23.8, 23.4, 22.9 (*s*, C(18b), C(18f), C(19b), C(19f), C(20b)); 22.7 (*s*, C(12)); 22.6 (*s*, C(20f)); 22.3 (*s*, C(11)); 16.3 (*s*, *Me*CH_2). ^{19}F-NMR (CD_2Cl_2, 230 K): −151.36 (*s*, $[^{10}BF_4]^-$); −151.42 (*s*, $[^{11}BF_4]^-$). Anal. calc. for $C_{44}H_{54}BF_4N_3OPd$ (834.14): C 63.35, H 6.53, N 5.04; found: C 63.22, H 6.41, N 5.01.

{N,N′-(Acenaphthylene-1,2-diylidene)bis[2,6-diisopropylbenzenamine-κN]}{2-[1-(ethylimino-κN)-2-oxo-2-phenylethyl]phenyl-κC}palladium(1+) Tetrafluoroborate(1−) (**10**). As described for **6**, with **1** (150 mg, 0.20 mmol), (2,6-^{i}Pr$_2$C$_6$H$_3$)N=C(R)−C(R)=N(2,6-^{i}Pr$_2$C$_6$H$_3$) (R−R = naphthalene-1,8-diyl; 220 mg, 0.44 mmol), CH_2Cl_2 (5 ml), and Ag[BF_4] (78 mg, 0.40 mmol). From *ca.* 1 ml, addition of hexane caused the precipitation of the product. Further purification by crystallization from CH_2Cl_2/Et_2O yielded **10** (371 mg, 94%). ^1H-NMR (CD_2Cl_2, 230 K): 8.31 (*d*, ^3J(25,26) = 8.3, H−C(25)); 8.28 (*d*, ^3J(23,22) = 8.2, H−C(23)); 7.95 (br., H_o); 7.82 (*t*, $^3J_{p,m}$ = 7.5, H_p); 7.78 (*t*, ^3J(8,7) = ^3J(8,7′) = 7.5, H−C(8)); 7.63 (*t*, $^3J_{m,p}$ = $^3J_{m,o}$ = 7.5, H_m); 7.61 (*t*, ^3J(26,25) = ^3J(26,27) = 8.3, H−C(26)); 7.59 (*t*, ^3J(22,23) = ^3J(22,21) = 8.2, H−C(22)); 7.59 (*d*, overlapped by H−C(22) and H−C(26), H−C(7)); 7.57 (*t*, overlapped by H−C(22), H−C(4)); 7.55 (*d*, overlapped by H−C(4) and H−C(22), H−C(7′)); 7.49 (*d*, ^3J(3,4) = 7.7, H−C(3)); 7.47 (*d*, ^3J(3′,4) = 7.7, H−C(3′)); 6.96 (*t*, $^3J_{C,B}$ = $^3J_{C,D}$ = 7.2, H_C); 6.82 (*dd*, $^3J_{D,C}$ = 7.2, $^4J_{D,B}$ = 1.5, H_D); 6.79 (*dt*, $^3J_{B,C}$ = $^3J_{B,A}$ = 8.1, $^4J_{B,D}$ = 1.5, H_B); 5.57 (*d*, $^3J_{A,B}$ = 8.1, H_A); 3.33 (*m*, H−C(14), H−C(13), H−C(15), H−C(16)); 2.95 (*m*, Me*C*H_2); 2.77 (*m*, Me*C*H_2); 1.47 (*d*, ^3J(17,13) = 6.7, H−C(17f)); 1.41 (*d*, ^3J(18, 14) = 6.7, H−C(18f)); 1.27 (*d*, ^3J(19,18) = 6.7, H−C(19f)); 1.06 (*d*, ^3J(20,16) = 6.7, H−C(20f)); 1.03 (*d*, ^3J(18,14) = 6.7, H−C(18b)); 1.00 (*d*, ^3J(19,15) = 6.7, H−C(19b)); 0.97 (*d*, ^3J(20,16) = 6.7, H−C(20b)); 0.87 (*d*, ^3J(17,13) = 6.7, H−C(17b)); 0.75 (*t*, ^3J = 7.2, *Me*CH_2). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 230 K): 192.5 (*s*, C_d); 185.2 (*s*, C_c); 176.1 (*s*, C(10)); 172.9 (*s*, C(9)); 153.7 (*s*, C_a); 146.8 (*s*, C_b); 146.6 (*s*, C(28)); 142.4 (*s*, C(1)); 141.2 (*s*, C(5) or C(2) or C(2′)); 140.5 (*s*, C(6) or C(6′)); 140.2 (*s*, C(6) or C(6′)); 138.8 (*s*, C(5) or C(2) or C(2′)); 138.7 (C(5) or C(2) or C(2′)); 137.1 (*s*, C_p); 134.3 (*s*, C(25)); 133.8 (*s*, C(23)); 133.2 (*s*, C_i or C(12) or C(11)); 131.7 (*s*, C(24)); 131.0 (*s*, C_B); 130.7 (*s*, C(8)); 130.6 (*s*, C_A); 130.2 (*s*, C_m); 129.95 (*s*, C(7′) or C(7) or C(4)); 129.91 (*s*, C(7′) or C(7) or C(4)); 129.88 (*s*, C(7′) or C(7) or C(4)); 129.3 (*s*, C_D); 127 5 (*s*, C(27)); 127.2 (*s*, C(21)); 126.9 (*s*, C_C); 126.22 (*s*, C(22) or C(27)); 126.19 (*s*, C(3)); 126.15 (*s*, C(22) or C(27)); 125.90 (s , C_i or C(11) or C(12)); 125.87 (*s*, C(3′)); 125.76 (*s*, C_i or C(11) or C(12)); 49.3 (*s*, Me*C*H_2); 30.2 (*s*, C(13)); 29.8 (*s*, C(14)); 29.7 (*s*, C(15)); 29.6 (*s*, C(16)); 24.8 (*s*, C(17b)); 24.4 (*s*, C(18b)); 24.3 (*s*, C(19b)); 23.8 (*s*, C(20b)); 23.4 (*s*, C(17f)); 23.3 (*s*, C(18f)); 22.9 (*s*, C(19f)); 22.9 (*s*, C(20f)); 16.2 (*s*, *Me*CH_2). ^{19}F-NMR (CD_2Cl_2, 230 K): −153.01 (*s*, $[^{10}BF_4]^-$); −153.06 (*s*, $[^{11}BF_4]^-$). Anal. calc. for $C_{52}H_{54}BF_4N_3OPd$ (930.23): C 67.14, H 5.85, N 4.52; found: C 67.28, H 5.93, N 4.42.

{[1-(Benzoyl-κO)-2,3-dihydro-2-isopropyl-3-oxo-1H-isoindol]carbonyl-κC}(2,2′-bipyridine-κN^2, κN^2)palladium(1+) Hexafluorophosphate(1−) (**14**). A 5-mm NMR tube equipped with a PTFE-*J. Young* valve was charged with **5** (*ca.* 10 mg) and then connected to the high-vacuum line and evacuated to *ca.* 10^{-5} Torr. CD_2Cl_2 (*ca.* 0.5 ml) was condensed into the tube by using a liq. N_2 bath. The tube was allowed to reach r.t. in order to completely dissolve **5**, the soln. was frozen again and evacuated to *ca.* 10^{-5} Torr. The tube was filled with CO while the soln. was frozen, and then allowed to slowly reach r.t. by using an EtOH/liq. N_2 bath. A small amount of a light-brown precipitate was observed. Compound **14** (> 90% of the mixture) was identified by NMR spectroscopy. It was not possible to experimentally discriminate between the two inequivalent pyridine rings of the coordinated bpy ligand; the resonance at higher frequency was assigned to H−C(6′) in agreement with a similar observation in [Ru(acetyl)] complexes with pyrazolyl ligands [3b]. ^1H-NMR (CD_2Cl_2, 298 K): 9.16 (*ddd*, ^3J(6′,5′) = 5.2, ^4J(6′,4′) = 1.6, ^5J(6′,3′) = 0.8, H−C(6′)); 9.07 (*ddd*, ^3J(6,5) = 5.6, ^4J(6,4) = 1.6, ^5J(6,3) = 0.7, H−C(6)); 8.42 (*m*, H−C(3), H−C(3′)); 8.37 (*dt*, ^3J(4′,5′) ≈ ^3J(4′,3′) = 7.5, ^4J(4′,6′) = 1.6, H−C(4′)); 8.30 (*dt*, ^3J(4,5) ≈ ^3J(4,3) = 7.7, ^4J(4,6) = 1.6, H−C(4)); 8.05 (*ddd*, $^3J_{A,B}$ = 7.6, $^4J_{A,C}$ = 1.3, $^5J_{A,D}$ = 0.8, H_A); 7.96 (*ddd*, ^3J(5′,4′) = 7.7, ^3J(5′,6′) = 5.2, ^4J(5′, 3′) = 1.3, H−C(5′)); 7.94 (*dd*, $^3J_{o,m}$ = 8.6, $^4J_{o,p}$ = 1.3, H_o); 7.91 (*dt*, $^3J_{D,C}$ = 7.6, $^4J_{D,B}$ + $^5J_{D,A}$ = 1.8, H_D); 7.85 (*tt*, $^3J_{p,m}$ = 7.5, $^4J_{p,o}$ = 1.3, H_p); 7.75 (*ddd*, ^3J(5,4) = 7.6, ^3J(5,6) = 5.6, ^4J(5,3) = 1.4, H−C(5)); 7.72 (*dt*, $^3J_{B,A}$ ≈ $^3J_{B,C}$ = 7.5, $^4J_{B,D}$ = 1.0, H_B); 7.65 (*dt*, $^3J_{C,B}$ ≈ $^3J_{C,D}$ = 7.6, $^4J_{C,A}$ = 1.3, H_C); 7.57 (*dd*, $^3J_{m,o}$ = 8.6,

$^3J_{m,p}$ = 7.5, H_m); 3.98 (*sept.*, ^3J = 6.7, Me_2CH); 1.30, 1.20 (*d*, ^3J = 6.7, Me_2CH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 209.9 (*s*, C_d); 206.0 (*s*, C_f); 168.6 (*s*, C_e); 156.3 (*s*, C(2)); 153.5 (*s*, C(2′)); 150.5 (*s*, C(6′)); 149.9 (*s*, C(6)); 142.3 (*s*, C(4′)); 142.0 (*s*, C(4)); 139.2 (*s*, C_b); 138.9 (*s*, C_p); 133.7 (*s*, C_C); 131.8 (*s*, C_o); 131.6 (*s*, C_B); 131.0 (*s*, C_a); 130.3 (*s*, C_m); 129.9 (*s*, C_i); 128.2 (*s*, C(5′)); 127.6 (*s*, C(5)); 125.9 (*s*, C_A); 124.1, 123.5 (*s*, C(3), C(3′)); 122.0 (*s*, C_D); 100.7 (*s*, C_c); 49.1 (*s*, Me_2CH); 20.7, 20.6 (*s*, Me_2CH). ^{19}F-NMR (CD_2Cl_2, 298 K): −73.17 (*d*, ^1J(F,P) = 710, $[PF_6]^-$).

*[1-(Benzoyl-κO)-2,3-dihydro-2-isopropyl-3-oxo-1*H*-isoindol-1-yl-κC][2,2′-bipyridine-κ*$N^{2'}$*,κ*$N^{2'}$*)-palladium(1+) Hexafluorophosphate(1−)* (**16**). A dil. soln. of **14** in a 5-mm NMR tube equipped with a PTFE-*J. Young* valve and connected to the high-vacuum line, was decarbonylated by means of one freeze-pump-thaw degassing cycle. The obtained product mixture contained **16** (*ca.* 90%), residual complex **14**, and a very small amount of other minor unidentified by-products. ^1H-NMR (CD_2Cl_2, 298 K): 8.86 (*dt*, ^3J(6,5) = 5.4, ^4J(6,4) + ^5J(6,3) = 2.5, H−C(6)); 8.34 (*m*, H−C(4), H−C(3)); 8.24 (*ddd*, ^3J(3′,4′) = 8.1, ^4J(3′,5′) = 1.3, ^5J(3′,6′) = 0.7, H−C(3′)); 8.15 (*m*, H_D, H−C(4′)); 8.05 (*ddd*, $^3J_{A,B}$ = 5.7, $^4J_{A,C}$ = 3.2, $^5J_{A,D}$ = 0.7, H_A); 7.86 (*m*, H−C(5), H_p); 7.80 (*dd*, $^3J_{o,m}$ = 8.3, $^4J_{o,p}$ = 1.2, H_o); 7.66 (*m*, *ABXY*, H_C, H_B); 7.58 (*dd*, $^3J_{m,o}$ = 8.3, $^4J_{m,p}$ = 7.4, H_m); 7.45 (*ddd*, ^3J(5′,4′) = 7.6, ^3J(5′,6′) = 5.6, ^4J(5′,3′) = 1.4, H−C(5′)); 6.88 (*ddd*, ^3J(6′,5′) = 5.6, ^4J(6′,4′) = 1.5, ^4J(6′,3′) = 0.7, H−C(6′)); 4.14 (*sept.*, ^3J = 6.7, Me_2CH); 1.50, 1.36 (*d*, ^3J = 6.7, Me_2CH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 217.8 (*s*, C_d); 169.3 (*s*, C_e); 156.7 (*s*, C(2′)); 152.8 (*s*, C(2)); 150.3 (*s*, C(6)); 148.8 (*s*, C(6′)); 143.1 (*s*, C_b); 142.00 (*s*, C(4)); 141.98 (*s*, C(4′)); 138.9 (*s*, C_p); 133.3 (*s*, C_C); 131.15 (*s*, C_i); 130.5 (*s*, C_o); 130.0 (*s*, C_m); 129.8 (*s*, C_a); 128.8 (*s*, C_B); 128.4 (*s*, C(5)); 127.9 (*s*, C(5′)); 125.2 (*s*, C_A); 124.2 (*s*, C(3)); 123.7 (*s*, C(3′)); 121.5 (*s*, C_D); 50.0 (*s*, Me_2CH); 45.7 (*s*, C_c); 20.9, 20.8 (*s*, Me_2CH). ^{19}F-NMR (CD_2Cl_2, 298 K): −73.17 (*d*, ^1J(F,P) = 710, $[PF_6]^-$).

*3-Benzoyl-2-ethyl-2,3-dihydro-1*H*-isoindol-1-one* (**11**) *and 3-Benzoyl-2,3-dihydro-2-isopropyl-1*H*-isoindol-1-one* (**12**). An excess of H_2O was added to a soln. of either **16** or **14** in a 5-mm NMR tube. Over a period of hours (depending on the H_2O concentration), the quant. formation of **12** was observed, together with the precipitation of an amorphous dark solid. Complex **11** was obtained similarly by starting from **13** or **15**. Alternatively, **11** and **12** were formed from **4** or **5**, resp., by performing the carbonylation reaction in wet CD_2Cl_2 or CH_2Cl_2.

Data of **11**: ^1H-NMR (CD_2Cl_2, 298 K): 8.04 (*dd*, $^3J_{o,m}$ = 8.4, $^4J_{o,p}$ = 1.3, H_o); 7.86 (*ddd*, $^3J_{A,B}$ = 7.5, $^4J_{A,C}$ = 1.3, $^5J_{A,D}$ = 0.8, H_A); 7.74 (*tt*, $^3J_{p,m}$ = 7.5, $^4J_{p,o}$ = 1.3, H_p); 7.61 (*t*, $^3J_{m,o} \approx {}^3J_{m,o}$ = 7.9, H_m); 7.52 (*td*, $^3J_{B,C} \approx {}^3J_{B,A}$ = 7.5, $^4J_{B,D}$ = 1.0, H_B); 7.46 (*td*, $^3J_{C,D} \approx {}^3J_{C,B}$ = 7.5, $^4J_{C,A}$ = 1.3, H_C); 7.25 (*dd*, $^3J_{D,C}$ = 7.5, $^4J_{D,B}$ = 1.0, H_D); 6.18 (*s*, H_c); 4.08 (*m*, $MeCH_2$); 3.21 (*m*, $MeCH_2$); 1.25, (*t*, ^3J = 7.3, $MeCH_2$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 194.1 (*s*, C_d); 168.8 (*s*, C_e); 140.0 (*s*, C_b); 135.9 (*s*, C_i); 134.6 (*s*, C_p); 132.8 (*s*, C_a); 131.9 (*s*, C_C); 129.6 (*s*, C_m); 129.4 (*s*, C_B); 129.2 (*s*, C_o); 124.3 (*s*, C_A); 123.0 (*s*, C_D); 65.4 (*s*, C_c); 36.7 (*s*, $MeCH_2$); 13.6 (*s*, $MeCH_2$).

Data of **12**: ^1H-NMR (CD_2Cl_2, 298 K): 7.97 (*dd*, $^3J_{o,m}$ = 8.4, $^4J_{o,p}$ = 1.3, H_o); 7.88 (*ddd*, $^3J_{A,B}$ = 7.5, $^4J_{A,C}$ = 1.3, $^5J_{A,D}$ = 0.8, H_A); 7.71 (*tt*, $^3J_{p,m}$ = 7.5, $^4J_{p,o}$ = 1.3, H_p); 7.57 (*t*, $^3J_{m,o} \approx {}^3J_{m,o}$ = 7.9, H_m); 7.53 (*td*, $^3J_{B,C} \approx {}^3J_{B,A}$ = 7.5, $^4J_{B,D}$ = 1.0, H_B); 7.48 (*td*, $^3J_{C,D} \approx {}^3J_{C,B}$ = 7.5, $^4J_{C,A}$ = 1.3, H_C); 7.22 (*dd*, $^3J_{D,C}$ = 7.5, $^4J_{D,B}$ = 1.0, H_D); 6.12 (*s*, H_c); 4.42 (*sept.*, ^3J = 6.8, Me_2CH); 1.39, 1.23 (*d*, ^3J = 6.8, Me_2CH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 195.4 (*s*, C_d); 169.3 (*s*, C_e); 140.8 (*s*, C_b); 135.7 (*s*, C_i); 134.6 (*s*, C_p); 133.2 (*s*, C_a); 132.0 (*s*, C_C); 129.5 (*s*, C_m); 129.4 (*s*, C_B); 129.2 (*s*, C_o); 124.1 (*s*, C_A); 122.7 (*s*, C_D); 65.0 (*s*, C_c); 46.0 (*s*, Me_2CH); 21.1, 20.3 (*s*, Me_2CH).

*(2,2′-Bipyridine-κ*N,*κ*$N^{2'}$*)[1-(ethylamino-κ*N*)-1-{2-[(1*E*)-2-(4-methylphenyl)ethenyl]phenyl}-2-oxo-2-phenylethyl-κC}palladium(1+) Hexafluorophosphate(1−)* (**17**) *and (2,2′-Bipyridine-κ*N,*κ*$N^{2'}$*)[1-(isopropylamino-κ*N*)-1-{2-[(1*E*)-2-(4-methylphenyl)ethenyl]phenyl}-2-oxo-2-phenylethyl-κC}palladium(1+) Hexafluorophosphate(1−)* (**18**). To a soln. of **5** (100 mg, 0.15 mmol) in CH_2Cl_2 (5 ml), *p*-methylstyrene (3 ml; Pd/*p*-methylstyrene mol ratio 1:150) was added. Within 16 h, the initially yellow soln. became dark yellow/orange, while a small amount of dark precipitate was formed. The soln. was filtered, and the volume was reduced to *ca.* 3.5 ml, and hexane was then added. The precipitated solid was collected by filtration and washed several times with Et_2O and hexane to remove excess *p*-methylstyrene: 106 mg (90%). Complex **17** was obtained similarly from **4**.

Data of **18**: ^1H-NMR (major isomer, *ca.* 85%; CD_2Cl_2, 298 K): 8.82 (*ddd*, ^3J(6,5) = 5.2, ^4J(6,4) = 1.6, ^5J(6,3) = 0.7, H−C(6)); 8.32 (*ddd*, $^3J_{D,C}$ = 7.8, $^4J_{D,B}$ = 1.9, $^5J_{D,A}$ = 0.4, H_D); 8.28 (*ddd*, ^3J(3,4) = 8.0, ^4J(3,5) = 1.3, ^5J(3,6) = 0.7, H−C(3)); 8.26 (*ddd*, ^3J(3′,4′) = 7.9, ^4J(3′,5′) = 1.3, ^5J(3′,6′) = 0.7, H−C(3)); 8.20

(*ddd*, $^3J(4,5)=9.2$, $^4J(4,3)=8.0$, $^5J(4,6)=1.6$, H–C(4)); 8.10 (*ddd*, $^3J(4',5')=9.2$, $^4J(4',3')=7.9$, $^5J(4',6')=1.6$, H–C(4')); 7.84 (*dd*, $^3J_{A,B}=8.0$, $^4J_{A,C}=1.3$, H_A); 7.78 (*ddd*, $^3J(6',5')=5.4$, $^4J(6',4')=1.6$, $^5J(6',3')=0.7$, H–C(6')); 7.69 (*ddd*, $^3J(5,4)=9.2$, $^3J(5,6)=5.2$, $^4J(5,3)=1.3$, H–C(5)); 7.67 (*dt*, $^3J_{B,A}\approx{}^3J_{B,C}=8.0$, $^4J_{B,D}=1.9$, H_B); 7.57 (*dd*, $^3J_{o,m}=8.5$, $^3J_{o,p}=1.3$, H_o); 7.53 (*tt*, $^3J_{p,m}=7.5$, $^4J_{p,o}=1.3$, H_p); 7.49 (*dt*, $^3J_{C,B}\approx{}^3J_{C,D}=7.9$, $^4J_{C,A}=1.3$, H_C); 7.30 (*m*, H–C(11), H_m); 7.24 (*ddd*, $^3J(5',4')=9.2$, $^3J(5',6')=5.4$, $^4J(5',3')=1.3$, H–C(5')); 7.18 (*d*, $^3J(12,11)=8.6$, H–C(12)); 7.05 (*s*, H–C(8), H–C(9); in $CDCl_3$ at a lower concentration, *AB*, $^3J(8,9)=16$); 6.23 (br. *d*, $^3J=6.4$, Me_2CHNH); 2.91 (*m*, Me_2CHNH); 2.38 (*s*, Me(14)); 1.47, 1.39 (*d*, $^3J=6.5$, Me_2CHNH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 188.4 (*s*, C_d); 155.4 (*s*, C(2')); 153.9 (*s*, C(2')); 152.9 (*s*, C(6)); 152.6 (*s*, C(6')); 141.1 (*s*, C(4)); 140.9 (*s*, C(4')); 139.2 (*s*, C(13)); 138.3 (*s*, C_a); 135.95 (*s*, C_D); 135.88 (*s*, C_i); 134.0 (*s*, C(10)); 133.9 (*s*, C(8) or C(9)); 133.7 (*s*, C_p); 131.5 (*s*, C_B); 130.6 (*s*, C_b); 129.9 (*s*, C(12)); 129.3 (*s*, C_o); 129.0 (*s*, C_m, C_C); 127.8 (*s*, C(5)); 127.4 (*s*, C(5')); 126.91 (*s*, C(11)); 126.87 (*s*, C_A); 123.51 (*s*, C(3')); 123.43 (*s*, C(9) or C(8)); 123.38 (*s*, C(3)); 76.6 (*s*, C_c); 50.0 (*s*, Me_2CHNH); 26.1, 22.8 (*s*, Me_2CHNH); 21.3 (*s*, C(14)). ^{19}F-NMR (CD_2Cl_2, 298 K): −73.7 (*d*, $^1J(F,P)=710$, $[PF_6]^-$).

*2-{2-[(1*E*)-2-(4-Methylphenyl)ethenyl]phenyl}-2-(isopropylimino)-1-phenylethan-1-one* (**19**). A 5-mm NMR tube equipped with a PTFE-*J. Young* valve was charged with **18** (20 mg), connected to the high-vacuum line, and evacuated to *ca.* 10^{-5} Torr. CD_2Cl_2 (*ca.* 0.5 ml) was condensed into the tube by using a liq. N_2 bath. The tube was allowed to reach r.t. to completely dissolve compound **18**, the soln. was frozen again and evacuated to *ca.* 10^{-5} Torr. The tube was filled with CO while the soln. was frozen, and then allowed to slowly reach r.t. by using an EtOH/liq. N_2 bath. A large amount of an amorphous dark precipitate formed, and **19** (>95% of the mixture) was identified by NMR spectroscopy. ^1H-NMR (CD_2Cl_2, 298 K): 8.21 (*dd*, $^3J_{o,m}=8.5$, $^3J_{o,p}=1.3$, H_o); 7.82 (*d*, $^3J_{A,B}=8.0$, H_A); 7.67 (*t*, $^3J_{p,m}=7.6$, H_p); 7.57 (*t*, $^3J_{o,m}\approx{}^3J_{m,p}=7.8$, H_m); 7.49 (*dt*, $^3J_{B,A}\approx{}^3J_{B,C}=7.9$, $^4J_{B,D}=1.4$, H_B); 7.38 (*dt*, $^3J_{C,B}\approx{}^3J_{C,D}=7.7$, $^4J_{C,A}=1.2$, H_C); 7.31 (*d*, $^3J(12,11)=8.1$, H–C(11)); 7.21 (*d*, $^3J_{C,D}=8.0$, H_D); 7.16 (*d*, $^3J(12,11)=8.1$, H–C(12)); 7.05 (AB, $^3J(8,9)\approx16$, H–C(8), H–C(9)); 3.66 (*sept.*, $^3J=6.5$, Me_2CHNH); 2.37 (*s*, H–C(14)); 1.21, (*d*, $^3J=6.5$, Me_2CHNH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): 193.0 (*s*, C_d); 164.5 (*s*, C_c); 138.5 (*s*, C(13)); 136.0 (*s*, C_i); 135.9 (*s*, C_a); 134.4 (*s*, C(10)); 134.2 (*s*, C_b); 133.6 (*s*, C_p); 131.5 (*s*, C(8) or C(9)); 131.2 (*s*, C_o); 129.7 (*s*, C(12)); 129.5 (*s*, C_B); 128.7 (*s*, C_m); 128.2 (*s*, C_D); 127.5 (C_C); 126.8 (*s*, C(11)); 125.5 (*s*, C_A); 124.9 (*s*, C(9) or C(8)); 54.8 (*s*, Me_2CHNH); 23.3 (*s*, Me_2CHNH); 21.3 (*s*, Me(14)).

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