Synthesis of a Novel α-Diimine Palladium(II) Complex Bearing an η^3-Allyl γ-Lactone Ligand, a Key Intermediate in Alkyne Cyclocarbonylation Processes

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*Summary: Reactivity of [Pd(CH$_3$)(CO)(Pr^{i}DAB)]$^+$[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^-$ (**1**), where Pr^{i}DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene, toward alkynes and carbon monoxide was investigated. While the reaction of **1** with phenylacetylene produced stereoregular homopolymer, a stoichiometric insertion of 1-phenyl-1-propyne and 2-butyne into the Pd−acyl bond yielded the palladacycles **2** and **3**; subsequent reaction with CO resulted in the formation of novel complexes **4** and **5**, which represent the first experimental evidence of a key intermediate in alkyne cyclocarbonylation processes.*

The insertion of alkynes into the palladium−carbon bond represents an important reaction involved in the synthesis of organic molecules as well as in polymerization processes.[1] Cationic Pd(II) complexes have been employed in the homopolymerization of acetylenes,[2] even if more reactive catalytic systems are based on tungsten, molybdenum, and rhodium.[3] With regard to the alternating copolymerization of alkynes and carbon monoxide, only a few examples exist in the literature.[4] Moreover, reactions of acetylenes with CO by the catalysis of palladium(II) complexes have been established as a powerful methodology for the synthesis of linear and cyclic carbonyl compounds[1a] such as esters and lactones.[5] Although the above cited reactions produce a wide variety of interesting molecules, there is little mechanistic information concerning the details of such processes.[6]

Recently we developed catalytic systems based on Pd(II) complexes with bidentate nitrogen ligands for the stereospecific styrene/CO copolymerization.[7] To gain further information on the chain growth mechanism, we studied stepwise insertion of the comonomers in the catalysts [Pd(CH$_3$)(CO)(N−N)]$^+$[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^-$ with N−N = α-diimine[7b,c] or bioxazoline ligand.[7a] Using a similar approach, an investigation of the reactivity of complex [Pd(CH$_3$)(CO)(Pr^{i}DAB)]$^+$[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^-$ (**1**), where Pr^{i}DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene, toward alkynes and CO was carried out.

In studying phenylacetylene insertion in complex **1**, highly stereoregular polyphenylacetylene (PPA) with cis−transoidal structure was obtained. Due to the high reactivity of this alkyne, it was not possible to isolate the first intermediates because the reaction evolves rapidly. Indeed, the addition of an equimolecular amount of phenylacetylene to a CD_2Cl_2 solution of **1**, even at very low temperature (−80 °C), resulted in the formation of oligomers; homopolymer in moderate yield with a molecular weight of 54 000 was obtained using an alkyne/Pd molar ratio of 80:1 (Scheme 1). Attempts to synthesize phenylacetylene/CO copolymer, in operating conditions analogous to that previously reported for styrene/CO polymerization,[7a,b] gave no results.

Isolation of organopalladium complexes deriving from the stoichiometric insertion of alkynes in the Pd−acyl

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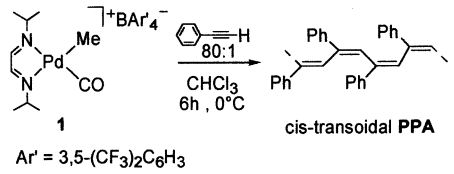
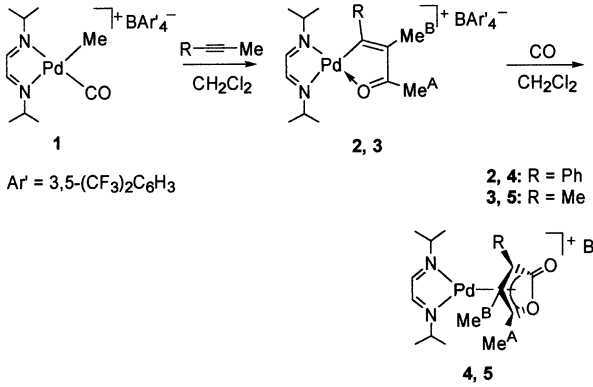
Scheme 1



Scheme 2



bond was achieved by using 1,2-substituted acetylenes. Thus, the reaction of 1-phenyl-1-propyne or 2-butyne with a dichloromethane solution of **1** gave the corresponding five-membered palladacycle **2** or **3** (Scheme 2), which were isolated as yellow powders.

Spectroscopic data of these compounds reveal a structure similar to that recently reported for insertion products of alkynes in a Pd(II) complex bearing a phosphine-imine ligand.[6a] In the ^{13}C NMR spectra of both **2** and **3** the signal due to one of the two olefin carbons appears at high frequency, more than 190 ppm; in addition, in the IR spectrum, the C═O stretching band is observed at around 1570 cm^{-1}, a value lower than those reported for analogous styrene insertion products.[7a,b,8] These two pieces of evidence could be ascribed to the charge distribution in the conjugated carbonyl system so that the olefin carbon in α-position to palladium is considerably deshielded and C═O has a partial character of single bond. Another feature of the ^1H NMR spectrum of **2** is the extremely different chemical shift of the two isopropyl C*H* (2.11 and 3.93 ppm). Such a difference was not observed for the two *CH* signals (3.92 and 4.19 ppm) of compound **3**. One can assume that, in complex **2**, the proton at 2.11 ppm lies in the shielding region of the phenyl, due to the preferred orientation of the aromatic ring, nearly perpendicular to the Pd coordination plane.

It has been reported that the palladacycle complexes, isolated as intermediates in styrene/CO copolymerization, readily react with carbon monoxide to yield open chain products.[7a,b,9] To check this kind of reactivity with analogous complexes deriving from alkyne insertions, **2** and **3** were dissolved at −30 °C in dichloromethane previously saturated with CO. The resulting products were isolated as dark yellow powders and were identified as the novel compounds **4** and **5** (Scheme 2). The ^{13}C spectra show in both cases just one signal in the

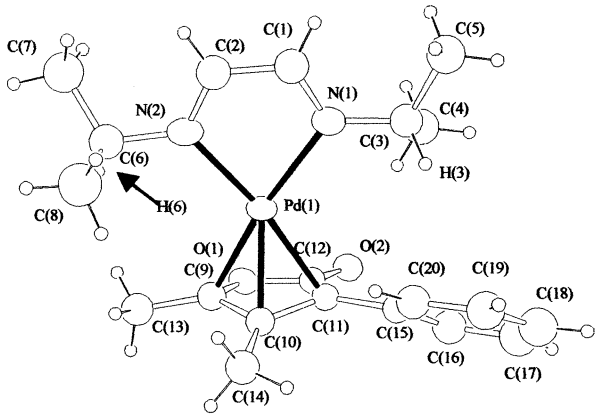


Figure 1. ORTEP view of the complex cation of **4**. All atoms are drawn at 50% probability except for hydrogens, which have been assigned arbitrary thermal parameters. Selected bond lengths (Å) and angles (deg): Pd(1)−N(1) = 2.132(5), Pd(1)−N(2) = 2.107(5), Pd(1)−C(9) = 2.199(6), Pd(1)−C(10) = 2.152(6), Pd(1)−C(11) = 2.171(6); N(1)−Pd(1)−N(2) = 78.6(2), N(1)−Pd(1)−C(9) = 167.0(2), N(1)−Pd(1)−C(10) = 141.2(2), N(1)−Pd(1)−C(11) = 109.8(2), N(2)−Pd(1)−C(9) = 110.5(2), N(2)−Pd(1)−C(10) = 132.4(2), N(2)−Pd(1)−C(11) = 170.8(2), C(9)−Pd(1)−C(10) = 37.6(2), C(9)−Pd(1)−C(11) = 61.9(2), C(10)−Pd(1)−C(11) = 38.4(2).

carbonyl region and three signals in the range from 71 to 122 ppm. The carbonyl resonance at around 165 ppm and the IR stretching band for the C═O at around 1790 cm^{-1} are compatible with a γ-lactone species. The remaining three resonances were ascribed to the Pd-coordinated η^3-allyl fragment of the heterocycle. Evidently, the formation of **4** and **5** takes place through the insertion of CO in the palladium vinyl bond of **2** and **3**, followed by a cyclization reaction. A similar cyclocarbonylation process was observed in the synthesis of a molybdenum complex containing an η^3-allyl butyrolactone ligand.[10] The structure proposed for complex **4** is in agreement with the NOEs detected between one isopropyl C*H* of the nitrogen ligand and the Me^A and between the other isopropyl C*H* and the ortho protons of the phenyl ring. Complexes **4** and **5** resulted in being very stable in the solid state as well as in dichloromethane solution.

The structure of complex **4** was confirmed by X-ray diffraction[11] (Figure 1). The palladium ion is coordinated to the γ-lactone moiety in η^3-fashion and to the nitrogen atoms of the Pr^iDAB ligand in a distorted square-planar arrangement, assuming that C(9) and C(11) are two of the four donors. The average Pd−C separation (2.17 Å) is a little larger than those found in Pd η^3-coordinated complexes, with nitrogen atoms in trans positions provided by a NCCN moiety (average 2.12 Å).[12] The Pd(II) ion is 1.95 Å out of the mean plane described by the γ-lactone ring, the latter forming an angle of 82.9(3)° with the N═C−C═N mean plane. The C−C bond distances in the η^3-allyl system are comparable (within 3σ, average 1.41 Å) and the ring of the phenyl

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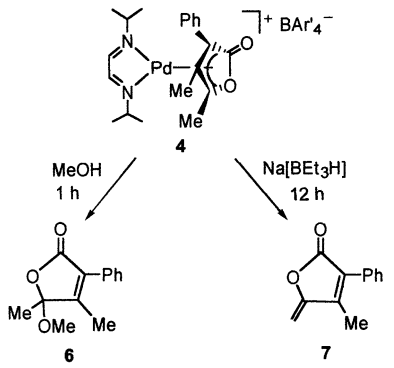
Scheme 3



substituent is tilted by 30.3(2)° with respect to the heterocyclic ring. The steric hindrance exerted by the γ-lactone substituents seems to influence the conformation of the isopropyl groups of the α-diimine ligand in such a way that both methyne hydrogen atoms are gauche to the Pd(II); the resulting geometry is in agreement with the NOE experiments mentioned above.[13] To our knowledge palladium complexes analogous to **4** and **5** have never been described in the literature; however they had been hypothesized as intermediates in the Pd-catalyzed synthesis of lactones starting from alkynes and carbon monoxide.[5g−l]

Cleavage of the η^3-allyl palladium carbon bond was performed in two different ways. Thus, by dissolving complex **4** in methanol a selective nucleophilic attack of the solvent occurred with quantitative formation of the α,β-unsaturated γ-lactone **6**. On the other hand, reaction of a dichloromethane solution of **4** with an equimolecular amount of $Na[BEt_3H]$ produced compound **7**, through proton abstraction from the methyl in the 5 position (Scheme 3).

In conclusion, in studying the reactivity of complex **1** toward alkynes, it has been observed that the nature of the products, either polymers or organic molecules, depends mainly on the substituents present on the triple bond. Moreover, we have isolated and fully charachterized the new complexes **4** and **5**, which represent the first experimental evidence of a key intermediate in alkyne cyclocarbonylation processes.[5g−l] The formation of compounds **4** and **5** seems to preclude the synthesis of alternating alkyne/CO copolymers, although the use of alkynes with electron-withdrawing substituents might shift the process toward the formation of copolymers. Further studies are in progress to develop a catalytic cycle for the production of optically active lactones by using a chiral oxazoline ligand.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen. Complex $[Pd(CH_3)(CO)(Pr^iDAB)]^+[BAr'_4]^-$ (**1**) (Pr^iDAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene; Ar′ = 3,5-$(CF_3)_2C_6H_3$) was synthesized as previously reported in the literature.[7b] Phenylacetylene, 1-phenyl-1-propyne, and 2-butyne were used after distillation over calcium hydride. Carbon monoxide (Cp grade 99.99%) was supplied by Air Liquide. Elemental analyses (C, H, N) were carried out with a Fisons Instruments 1108 CHNS-O elemental analyzer. Infrared spectra were measured in the range 4000−600 cm^{-1} on a Nicolet FT-IR Avatar 360 spectrometer. NMR spectra were measured on a Bruker AC200 spectrometer with a multinuclear 5 mm probehead. ^1H and ^{13}C NMR chemical shifts are relative to TMS and were measured using the residual proton or carbon resonance of the deuterated solvents. NOE measurements were performed using Bruker NOEDIFF pulse program, with irradiation times of 3 s and power 40 L. The molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of polyphenylacetylene were determined by gel permeation chromatography versus 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 and chloroform as solvent (flow rate 0.6 mL/min).

Synthesis of Polyphenylacetylene (PPA). Complex **1** (42.1 mg, 0.036 mmol) was dissolved in 1 mL of chloroform; after addition of 320 μL (2.9 mmol) of phenylacetylene (alkyne/palladium molar ratio 80:1) at −30 °C the solution color changed from yellow to dark red. The reaction mixture was slowly warmed at 0 °C and stirred for 6 h. The resulting yellow polymer was precipitated with methanol (5 mL) and washed with methanol. To remove metallic palladium traces, it was redissolved in chloroform and filtered through Celite, giving, after evaporation of solvent, 75.5 mg (20 g of polymer/g Pd) of PPA. IR (Nujol, cm^{-1}): 754, 739, 696. ^1H NMR ($CDCl_3$, 20 °C): 7.07−6.87 (m br, 3H, Ph-H_m, Ph-H_p); 6.65 (d, J = 4.7 Hz, 2H, Ph-H_o); 5.86 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 20 °C): 142.9 (Ph-C=CH); 139.3 (Ph-C_i); 131.8 (Ph-C=CH); 127.8, 127.5 (Ph-C_o, Ph-C_m); 126.7 (Ph-C_p). Anal. Calcd for $(C_8H_6)_n$: C, 94.08; H, 5.92. Found: C, 93.70; H, 6.10. M_w = 54 000; M_w/M_n = 2.0.

$[Pd(C(Ph)=C(CH_3)C(O)CH_3)(Pr^iDAB)]^+[BAr'_4]^-$ (2). A 20 μL (0.160 mmol) sample of 1-phenyl-1-propyne was added at −50 °C to a dichloromethane solution (4 mL) of **1** (185 mg, 0.160 mmol). The reaction mixture was warmed at 0 °C within 2 h. After filtration through Celite, solvent was evaporated and the resulting solid was washed with hexane (4 × 4 mL) to give 191 mg (0.151 mmol, 94%) of the yellow compound **2**. IR (Nujol, cm^{-1}): 1612 (C=N), 1570 (C=O). ^1H NMR (CD_2Cl_2, −30 °C): δ 7.89 (s, 1H, CH=N); 7.67 (s, 8H, Ar′-H_o); 7.62 (s, 1H, CH=N); 7.50 (s, 4H, Ar′-H_p); 7.33−7.24 (m, 3H, Ph-H_m, Ph-H_p); 7.10−7.03 (m, 2H, Ph-H_o); 3.93 (sept, J = 6.5 Hz, 1H, CH(CH_3)$_2$); 2.33 (s, 3 H, C(O)(CH_3)); 2.11 (sept, J = 6.5 Hz, 1H, CH(CH_3)$_2$); 1.60 (s, 3 H, PdC(Ph)=C(CH_3)); 1.31, 0.76 (d, J = 6.5 Hz, 6H each, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, −30 °C): δ 223.8 (C(O)); 194.0 (PdC(Ph)=C(CH_3)); 163.3, 159.0 (C=N); 162.0 (q, $^1J_{CB}$ = 49.5 Hz, Ar′-C_i); 144.7 (PdC(Ph)=C(CH_3)); 142.1 (Ph-C_i); 134.9 (Ar′-C_o); 129.2, 124.9 (Ph-C_m, Ph-C_o); 128.9 (q, $^2J_{CF}$ = 32.0 Hz, Ar′-C_m); 128.5 (Ph-C_p); 124.7 (q, $^1J_{CF}$ = 270.6 Hz, CF_3); 117.7 (Ar′-C_p); 63.3, 56.0 (CH(CH_3)$_2$); 27.3 (C(O)-(CH_3)); 22.0, 21.2 (CH(CH_3)$_2$); 15.4 (PdC(Ph)=C(CH_3)). Anal. Calcd for $C_{51}H_{39}BF_{24}N_2OPd$: C, 48.27; H, 3.10; N, 2.21. Found: C, 48.62; H, 2.78; N, 2.25.

$[Pd(C(CH_3)=C(CH_3)C(O)CH_3)(Pr^iDAB)]^+[BAr'_4]^-$ (3). Complex **3** was synthesized according to the procedure described for **2** using 55.0 mg (0.048 mmol) of **1** and 8 μL (0.102 mmol) of 2-butyne. A 42.3 mg (0.035 mmol, 73%) sample of **3** was collected as a yellow powder. IR (Nujol, cm^{-1}): 1611 (C=N), 1569 (C=O). ^1H NMR (CD_2Cl_2, −30 °C): δ 7.94, 7.81 (s, 1H each, CH=N); 7.68 (s, 8H, Ar′-H_o); 7.51 (s, 4H, Ar′-H_p); 4.19, 3.92 (sept, J = 5.9 Hz, 1H each, CH(CH_3)$_2$); 2.20 (s, 3H, C(O)(CH_3)); 1.85 (s, 3H, PdC(CH_3)=C(CH_3)); 1.70 (s, 3H, PdC-(CH_3)=C(CH_3)); 1.25 (d, J = 5.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, −30 °C): δ 221.2 (C(O)); 199.3 (PdC(CH_3)=C(CH_3)); 163.2, 158.8 (C=N); 162.0 (q, $^1J_{CB}$ = 49.3 Hz, Ar′-C_i); 144.7 (PdC(CH_3)=C(CH_3)); 134.9 (Ar′-C_o); 129.0 (q, $^2J_{CF}$ = 31.2 Hz, Ar′-C_m); 124.7 (q, $^1J_{CF}$ = 270.8 Hz, CF_3); 117.8 (Ar′-C_p); 62.9,

(13) Given the limitation that hydrogens were introduced in calculated positions and refined according to the linked atoms and, as a consequence, their corresponding C−H bond distances were not refined, it should be observed that the hydrogen atom labeled H(3) is ca. 2.6 Å from the plane of the phenyl ring, while H(6) is ca. 2.9 Å from the C(13) methyl carbon atom.

58.7 (*C*H(CH$_3$)$_2$); 26.7 (C(O)(*C*H$_3$)); 24.7 (PdC(*C*H$_3$)═C(CH$_3$)); 22.1, 21.1 (CH(*C*H$_3$)$_2$); 13.7 (PdC(CH$_3$)═C(*C*H$_3$)). Anal. Calcd for $C_{46}H_{37}BF_{24}N_2OPd$: C, 45.78; H, 3.09; N, 2.32. Found: C, 45.41; H, 3.01; N, 2.27.

[Pd(η^3-C(Ph)C(CH$_3$)C(CH$_3$)OC(O))(Pr^{i}DAB)]$^+$[BAr′$_4$]$^-$ (4). A 232 mg (0.183 mmol) sample of **2** was dissolved at −30 °C in 4 mL of dichloromethane previously saturated with CO. The solution was warmed at 0 °C within 2 h and then filtered through Celite. After evaporation of the solvent a dark yellow powder was obtained, which was washed with hexane (3 × 2 mL) to give 233 mg (0.180 mmol, 98%) of **4**. IR (CD_2Cl_2, cm^{-1}): 1799 (C═O), 1611 (C═N). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.97 (s, 1H, C*H*═N); 7.91−7.82 (m, 3H, Ph-*H*$_o$ and C*H*═N); 7.67 (s, 8H, Ar′-*H*$_o$); 7.49 (s, 4H, Ar′-*H*$_p$); 7.47−7.33 (m, 3H, Ph-*H*$_m$, Ph-*H*$_p$); 3.91 (sept, J = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$); 3.07 (sept, J = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$); 2.35 (s, 3 H, C(Ph)C(C*H*$_3$)); 1.67 (s, 3H, C(C*H*$_3$)O); 1.28, 1.16, 0.91, 0.70 (d, J = 6.4 Hz, 3H each, CH-(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 165.0 (OC(O)); 162.0 (q, $^1J_{CB}$ = 49.3 Hz, Ar′-*C*$_i$); 160.9, 160.7 (*C*═N); 134.9 (Ar′-*C*$_o$); 130.2 (Ph-*C*$_p$); 129.8, 129.2 (Ph-*C*$_m$, Ph-*C*$_o$); 128.9 (q, $^2J_{CF}$ = 31.9 Hz, Ar′-*C*$_m$); 128.0 (Ph-*C*$_i$); 124.7 (q, $^1J_{CF}$ = 271.0 Hz, *C*F$_3$); 121.9, 111.7, 72.3 (*C*(Ph)*C*(CH$_3$)*C*(CH$_3$)); 117.8 (Ar′-*C*$_p$); 60.9, 60.5 (*C*H(CH$_3$)$_2$); 22.8, 21.8, 20.8, 20.0 (CH(*C*H$_3$)$_2$); 14.3, 13.0 (C(*C*H$_3$)C(*C*H$_3$)O). Anal. Calcd for $C_{52}H_{39}BF_{24}N_2O_2Pd$: C, 48.15; H, 3.03; N, 2.16. Found: C, 47.78; H, 2.98; N, 2.15.

[Pd(η^3-C(CH$_3$)C(CH$_3$)C(CH$_3$)OC(O))(Pr^{i}DAB)]$^+$[B-Ar′$_4$]$^-$ (5). Complex **5** was synthesized according to the procedure described for **4** starting from 46.0 mg (0.038 mmol) of **3**. A 42.3 mg (0.034 mmol, 90%) sample of **5** was collected as a dark yellow powder. IR (Nujol, cm^{-1}): 1786 (C═O), 1610 (C═N). ^{1}H NMR (CD_2Cl_2, −30 °C): δ 7.97, 7.95 (s, 1H each, C*H*═N); 7.68 (s, 8H, Ar′-*H*$_o$); 7.51 (s, 4H, Ar′-*H*$_p$); 3.87 (sept br, J = 6.2 Hz, 2H, C*H*(CH$_3$)$_2$); 2.14 (s, 3H, C(CH$_3$)C(C*H*$_3$)C-(CH$_3$)O); 1.58 (s, 3H, C(CH$_3$)C(CH$_3$)C(C*H*$_3$)O); 1.44 (s, 3H, C(C*H*$_3$)C(CH$_3$)C(CH$_3$)O); 1.25, 1.17 (d, J = 6.2 Hz, 6H each, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, −30 °C): δ 166.8 (O*C*(O)); 162.0 (q, $^1J_{CB}$ = 49.3 Hz, Ar′-*C*$_i$); 160.8, 160.5 (*C*═N); 134.9 (Ar′-*C*$_o$); 129.0 (q, $^2J_{CF}$ = 31.2 Hz, Ar′-*C*$_m$); 124.7 (q, $^1J_{CF}$ = 270.8 Hz, *C*F$_3$); 117.8 (Ar′-*C*$_p$); 120.7, 114.9, 70.9 (*C*(CH$_3$)*C*(CH$_3$)*C*(CH$_3$)O); 117.8 (Ar′-*C*$_p$); 62.6, 60.3 (*C*H(CH$_3$)$_2$); 22.4, 22.0, 20.9, 20.6 (CH-(*C*H$_3$)$_2$); 13.8, 11.8, 9.6 (C(*C*H$_3$)C(*C*H$_3$)C(*C*H$_3$)O). Anal. Calcd for $C_{47}H_{37}BF_{24}N_2O_2Pd$: C, 45.71; H, 3.02; N, 2.27. Found: C, 45.58; H, 2.95; N, 2.24.

Reaction of Complex 4 with MeOH. A 33.6 mg (25.9 μmol) sample of **4** was dissolved in 2 mL of methanol. Formation of a black Pd precipitate was immediately observed. The reaction mixture was stirred for 1 h at 20 °C and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of hexane/ethyl acetate (6:4) as eluent to give compound **6** (4.2 mg, 19.2 μmol, 74%) as a yellow solid. IR (Nujol, cm^{-1}): 1775 (C═O). ^{1}H NMR ($CDCl_3$, 20 °C): 7.56−7.37 (m, 5H, Ph-*H*); 3.22 (s, 3H, O-C*H*$_3$); 2.13 (s, 3H, C(Ph)═C(C*H*$_3$)); 1.69 (s, 3H, C(OCH$_3$)-C(C*H*$_3$)). ^{13}C NMR ($CDCl_3$, 20 °C): 169.7; 157.8; 129.3; 129.2; 129.0; 128.9; 128.5; 107.5; 50.5; 22.7; 11.7. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.68; H, 6.56.

Reaction of Complex 4 with Na[BEt$_3$H]. A 50 μL (50 μmol) sample of Na[BEt$_3$H] (solution 1 M in THF) was added to a chloroform solution (2 mL) of **4** (54.2 mg, 41.8 μmol). The reaction mixture was stirred for 12 h at 20 °C (during this time formation of black Pd precipitate occurred) and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of hexane/ethyl acetate (6:4) as eluent to give compound **7** (3.7 mg, 19.9 μmol, 48%) as a yellow solid. IR (Nujol, cm^{-1}): 1785 (C═O). ^{1}H NMR ($CDCl_3$, 20 °C): 7.58−7.36 (m, 5H, Ph-*H*); 5.24 (d, J = 2.7 Hz, 1H, ═C*H*$_2$); 5.00 (d, J = 2.7 Hz, 1H, ═C*H*$_2$); 2.29 (s, 3H, C(Ph)═C(C*H*$_3$)). ^{13}C NMR ($CDCl_3$, 20 °C): 168.8; 155.8; 146.2; 129.5; 129.1; 129.0; 128.6; 128.3; 94.0; 11.0. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.71; H, 5.29.

X-ray Structure Determination. Crystal data for **4**: $C_{52}H_{39}BF_{24}N_2O_2Pd$, M_r 1297.08, monoclinic, space group $P2_1/n$, a = 12.408(1) Å, b = 32.054(4) Å, c = 14.877(2) Å, β = 111.760(5)°, V = 5495(1) Å^3, Z = 4, T = 200 K, Goebel mirror monochromated Cu Kα λ = 1.5418 Å, ρ_{calcd} = 1.568 Mg/m^3, μ(Cu Kα) = 3.847 mm^{-1}, F(000) = 2592, absorption corrections with SADABS,[14] Siemens SMART diffractometer, ω scan, frame width 0.3°, θ range 2.76−56.14°, 20 132 collected reflections, 6953 unique reflections (R_{int} = 0.039), data/parameters = 6207/529, structure solution by SIR97[15] and subsequent refinement by full matrix least-squares on F_o^2 with SHELX 97,[16] anisotropic thermal parameters assigned to all the atoms except carbon and hydrogen atoms because the reflections/parameters ratio observed would otherwise be too poor, hydrogen atoms introduced in calculated positions and treated as riding atoms with an isotropic temperature factor depending on that of the parent atom, several fluorine atoms of the anion were disordered and were refined in double position, R1 = 0.0653, wR2 = 0.1229, R1(all data) = 0.0712, wR2(all data) = 0.1256.

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Supporting Information Available: X-ray structure information for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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