ORGANOMETALLICS

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Benzyl Cation Stabilized by Metal Complexation. Relative Stability of Coordinated Methylene Arenium, π-Benzylic, and σ-Benzylic Structures

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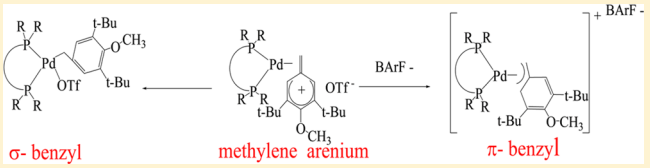
Supporting Information

ABSTRACT: Benzyl cations are highly reactive compounds involved as intermediates in various chemical and biochemical processes. In this work metal coordination was utilized to stabilize different coordinated modes of benzyl cations, including methylene arenium (MA), π-benzyl, and σ-benzyl complexes. Two bidentate ligand frameworks, diphenylphosphinoethane (dppe) and di-*tert*-butylphosphinopropane (dtpp), were studied. η^2-Coordination to Pd(II) allows for the characterization and studies of the reactivity of the otherwise unobserved methylene arenium species under ambient conditions. The relative stability and electronic structure of the three forms of the coordinated benzyl molecule, η^2-MA, η^1-σ-benzylic, and η^3- π-benzylic, were investigated experimentally and computationally. The MA and π-benzylic structures are preferred in the absence of counteranions, while the dtpp bulky ligand contributes to stabilization of the methylene arenium form. Counteranions have a significant influence on the relative stability. The triflate anion stabilizes the σ-benzylic form upon coordination to the metal center or the methylene arenium form as a result of compensation of positive charge on the MA ring. Use of the noncoordinating BArF counteranion promotes conversion to the π-benzylic form.



INTRODUCTION

Benzyl cations are highly reactive compounds involved as intermediates in various chemical and biochemical processes.[1] Benzyl cation precursors are utilized as latent initiators in cationic polymerization processes[2] and as potent alkylating agents.[3] They are postulated as key intermediates in oxidation of vitamin E[4] and lignin degradation.[5] Characterization of benzyl cations is challenging because of their high reactivity. Numerous fast UV[6] and gas-phase ion[7] studies provide evidence for formation of short-lived benzyl cations. Following Olah's discovery that unstable carbocations may be stabilized under superacidic conditions, benzyl cations were stabilized and characterized at low temperatures for the first time.[8]

Quantum chemical calculations at the MP4/6-31G*//MP2/6-31G* level indicate that the two extreme resonance forms **A** and **B** contribute to the total benzyl cation structure (Figure 1).[9] According to the calculations, delocalization of positive charge into the ring contributes significantly to the stabilization of the benzyl cation, and it can be best described by the methylene-arenium structure **B**. This is especially true for "simple" (bearing a nonsubstituted methylene group) benzyl cations, while in the case of benzyl cations having alkyl-substituted methylene groups, hyperconjugation stabilizes the positive charge on this group and lowers the contribution of resonance stabilization by the benzene ring.

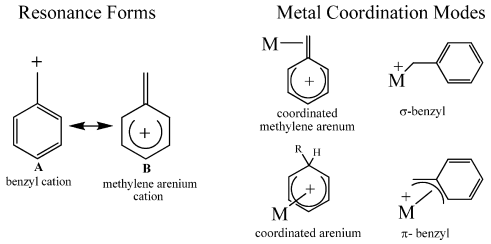
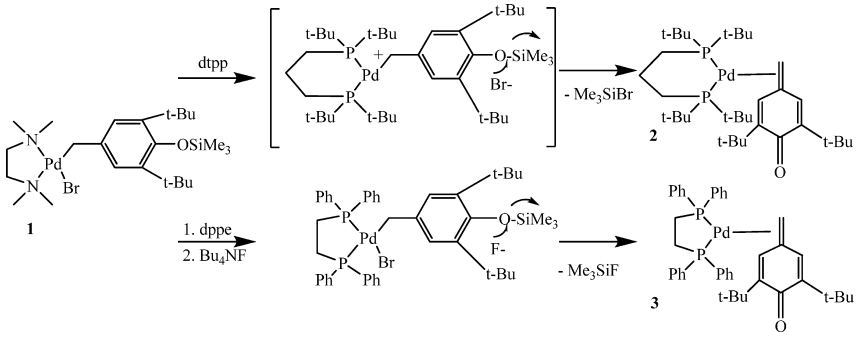


Figure 1. Benzyl cation and arenium compounds.

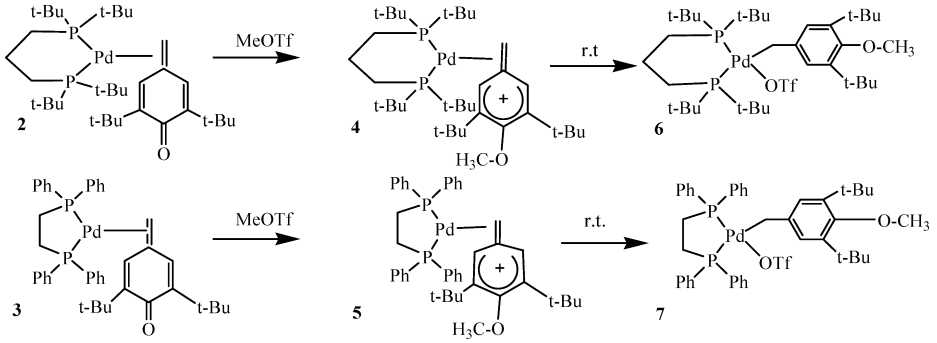
Although experimental studies also support the importance of resonance contribution from form **B**,[10,11] this limiting structure remained unobserved, while the structures corresponding to the aromatic form **A**, especially with out-of-plane methylene groups, are well documented.[12] In addition, several examples of arenium (Wheland) complexes, crucial intermediates in electrophilic aromatic substitution, were reported,[13] and in a few cases they were isolated in crystalline form.[14] Thus, all known examples of arenium complexes involve the formation of a coordinated arenium structure that includes an sp^3 ring carbon, while discrete coordinated methylene arenium compounds, i.e., compounds with an sp^2 *ipso* carbon atom

Received: June 7, 2013
Published: August 21, 2013

Scheme 1. Formation of the Quinone-Methide Complexes 2 and 3 Based on dtpp and dppe Ligands



Scheme 2. Formation and Reactivity of the Methylene Arenium Complexes Based on dtpp and dppe Ligands



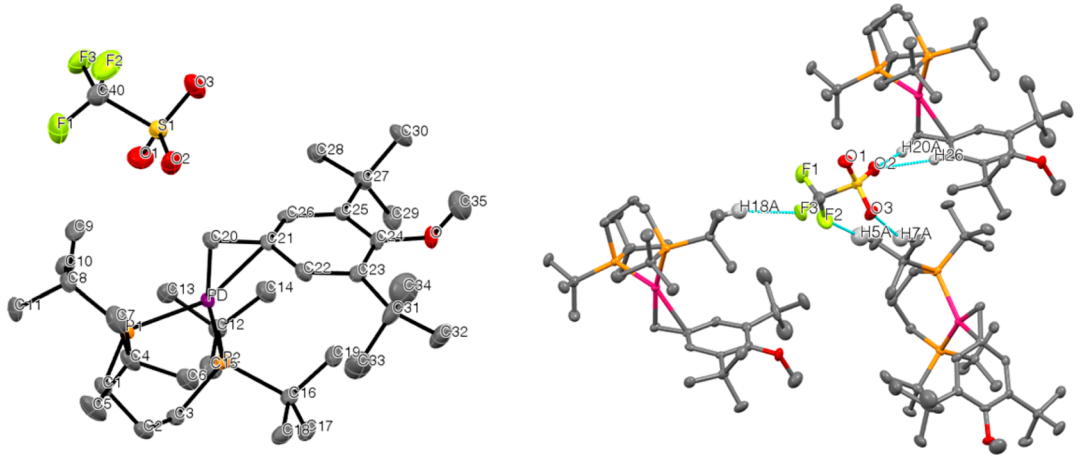


Figure 2. Left: ORTEP view of a molecule of complex **4** at the 50% ellipsoid probability level. Hydrogen atoms are omitted for clarity. Right: Interactions of complex **4** with the triflate anion.

and ring-localized charge (see Figure 1), are unknown, except when part of a pincer-ligand framework, severely limiting its relevance and preventing the release of such a chemical species.[15]

Another mode of stabilization of benzyl cations is by η^3-coordination to a metal center. Indeed, π-benzyl complexes play key roles in many catalytic and stoichiometric reactions that involve organometallic complexes, and their formation and characterization are of interest.[16,17]

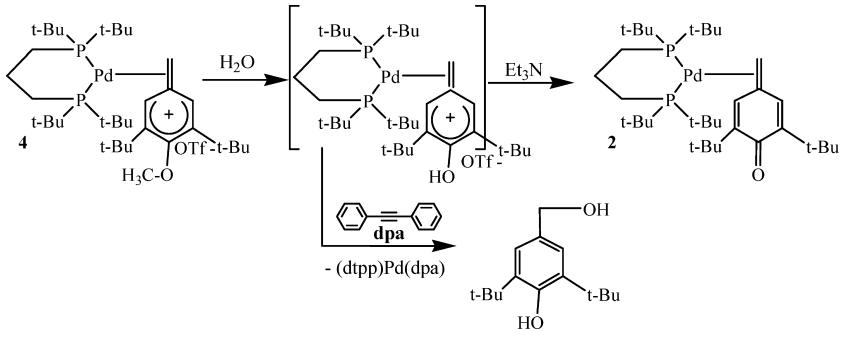
In this paper the three forms of a coordinated benzyl cation, η^2-methylene arenium (MA), η^1- benzylic, and η^3-benzylic forms, were prepared and characterized. Part of this work, including isolation of a η^2-coordinated methylene arenium palladium complex (resonance form **B**), has already been communicated by us.[18] In this work we are interested in the preparation, characterization, and evaluation of the relative stability of the three types of coordinated benzyl cations and in the factors that promote their interconversion. Both experimental and theoretical studies are described.

RESULTS AND DISCUSSION

Quinone Methide Complexes. Following the strategy developed in our laboratory,[19,20] quinone methide complexes coordinated via the exocyclic C=C bond were prepared as precursors of methylene arenium complexes. Thus, the trimethylsilyl ether derivative of the widely utilized food antioxidant 2,6-di-*tert*-butyl-4-methyl phenol (BHT) was used to form the known complex (tmeda)Pd-benzyl bromide (**1**)[19] (tmeda = tetramethylethylenediamine) followed by substitution of tmeda by bidentate phosphine ligands. Two ligand

dx.doi.org/10.1021/om400523f | *Organometallics* 2013, 32, 4813−4819

Scheme 3. Reactivity of the Methylene Arenium Complex 4



frameworks, 1,2-bis(diphenylphosphine)ethane (dppe) and 1,3-bis(di-*tert*-butylphosphine)propane (dtpp), were studied in this work. When complex **1** was reacted with the dtpp ligand, the reported quinone methide complex **2** was formed in a one-step reaction.[18] When substituting tmeda by the dppe ligand under analogous conditions, additon of nBu_4NF was required in order to remove the Me_3Si protecting group and form the reported quinone methide complex **3** (Scheme 1).[19] The difference in reactivity is perhaps due to the increased bulk of the dtpp ligand, which promotes bromide dissociation from the unobserved intermediate, followed by bromide attack on Me_3Si, not requiring the use of fluoride deprotection. An additional reason can be the higher electron donating ability of the dtpp ligand and correspondingly higher electron density on the Pd atom in the former case (see below).

Methylene Arenium Complexes. We have communicated that electrophilic attack of methyl triflate on the quinone-methide complex **2** resulted in formation of the methylene arenium complex **4**[18] (Scheme 2). Due to the positive charge in the ring, the *ipso* carbon is strongly downfield shifted relative to the starting complex **2** (107.51 instead of 78.12 ppm), while the chemical shift of the exocyclic methylene group remains practically unchanged (2.97 and 45.89 ppm in complex **4** vs 2.90 and 47.67 ppm in complex **2**, in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra, respectively).[21] We have reported the X-ray single-crystal analysis of complex **4**, which revealed an asymmetric charge distribution on the quinoid ring, reflected by incomplete bond length averaging and elongation of Pd-coordinated C20−C21(1.46 Å vs 1.44 Å in **2**) and Pd−C21(2.36 Å vs 2.27 Å in **2**) bonds (Figure 2).[18] The exocyclic methylene is bent out of the pseudoaromatic ring plane by 6.1°, owing to strong back-bonding from the metal center.[22,20,23,24]

An analogous reaction took place when the dppe-based quinone methide complex **3** was reacted with one equivalent of MeOTf at −30 °C (Scheme 2). Due to the lower steric hindrance and lower electron donation ability of the dppe ligand, electrophilic attack on the quinone methide was faster. Thus, after 30 min full conversion of **3** to the new methylene arenium complex **5** was observed. Complex **5** was fully characterized by multinuclear NMR. The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits two broad, unresolved singlets at 42.10 and 32.70 ppm exhibiting higher rotation of the double bond compared to **4**, where the singlets are resolved on the NMR time scale, a result that is probably largely due to sterics. In analogy with the dtpp-based complex **4**, the positive charge is located in the ring and not on the exocyclic methylene group, resulting in the methylene signals appearing at 3.45 ppm (dd, J_{P-H} = 7 Hz, J_{P-H} = 4 Hz) and 50.99 ppm (d, J_{P-C} = 37 Hz) in the ^1H and $^{13}C\{^1H\}$ NMR spectra, correspondingly, while the *C*-O-CH_3 carbon appears at 152.32 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Comparing these NMR data to those reported for the benzyl cations,[8−10] it is possible to reach some conclusions. In the aromatic resonance form **A**, the methylene group is exceptionally deshielded (150−300 ppm), since substantial positive charge is concentrated on it; the ring is only moderately affected in comparison with neutral benzyl compounds. In our case another extreme resonance form of the benzyl cation, with positive charge that is mainly delocalized between the carbon atoms of the arenium ring, is evidenced.

The presence of a positive charge localized in the aromatic ring of the methylene arenium ligand is also revealed by its electrophilic reactivity. The reactivity of complex **4** was communicated by us.[18] Removal of the methyl group in anisole is a difficult process that requires activation with strong Lewis acids.[25] However, scission of the C−O bond at the *para* position of the methylene arenium ring was observed immediately upon reaction of **4** with water at room temperature, leading to the corresponding phenolic complex. Further addition of Et_3N led to deprotonation of the phenolic proton, resulting in the initial quinone methide complex **2** (Scheme 3). Such reactivity is unusual for benzyl cation precursors[26] and for aromatic compounds in general. The single-site coordination mode of the methylene arenium moiety allows also its controlled release.[18] As we have reported, the MA ligand can be substituted by diphenylacetylene (dpa), followed by its reaction with water, to give 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, as expected from typical benzyl cation reactivity (Scheme 3).[18]

σ-Benzyl Complexes. At room temperature the methylene arenium complexes **4** and **5** undergo conversion to the σ-benzylic complexes **6**[18] and **7** (Scheme 2). In the case of the dtpp-based complexes the conversion is slow (about 20 h). The bulky *tert*-butyl substituents together with the enhanced electron donation properties of the dtpp ligand contribute to the stability of this reactive electron-deficient moiety. In the case of the dppe ligand conversion to the benzyl triflate Pd(II) complex **7** was faster; after 2 h at rt complex **7** was obtained as a major product. Complexes **6** and **7** have NMR spectra characteristic of σ-benzyl-Pd(II) complexes. Complex **7** gives rise to two doublets in the $^{31}P\{^1H\}$ NMR spectrum at 52.56 and 42.57 ppm with a P−P coupling of 41 Hz. The coupling constant is in good agreement with reported values for square planar *cis*-diphosphine Pd(II) complexes.[17] The benzylic carbon Pd-CH_2 is slightly upfield shifted relative to the exocyclic methylene arenium carbon 50.28 (d, J_{P-C} = 34 Hz) and 3.40 (dd, J_{P-H} = 10 Hz, 3 Hz) in complex **7** vs 50.99 (d, J_{P-C} = 37 Hz) and 3.45 ppm (dd, J_{P-H} = 7 Hz, J_{P-H} = 4 Hz) in complex **5** in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. Ring signals

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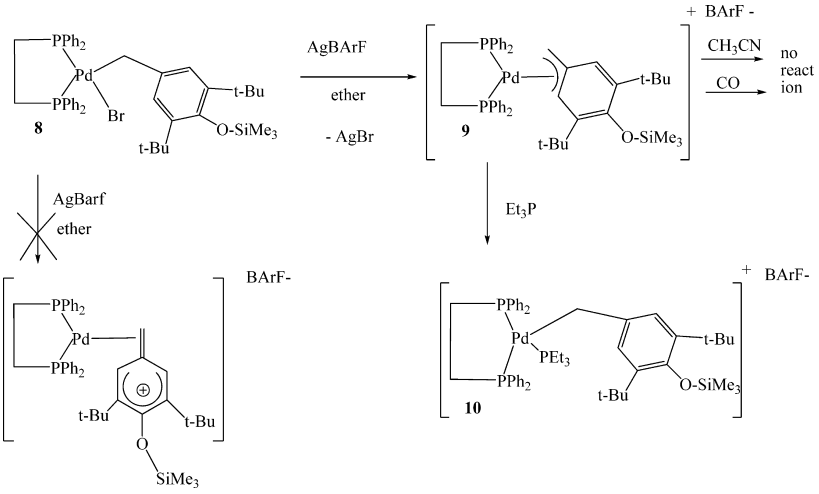
Scheme 4. Formation and Reactivity of the π-Benzyl Complex 9



definitely indicate conversion to aromaticity from 149.51 (*C*-O-CH_3) in **5** to 124.88 ppm in complex **7**. A similar tendency is observed when dtpp-based methylene arenium complex **4** converts to σ-benzyl complex **6**.[18]

π-Benzyl Complexes. Interestingly, attempts to synthesize the methylene arenium compound starting from the benzyl bromide complex **8**, by substitution of the bromide ligand with the noncoordinating BArF counteranion, BArF = B-$(C_6H_3(CF_3)_2)_4$, led to formation of the π-benzyl complex **9**, in which case the methylene arenium structure was not observed (Scheme 4). Complex **9** was fully characterized by multinuclear NMR. It exhibits a characteristic π-benzyl pattern with broad, nonsymmetric signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{31}P{^{1}H} NMR specrum of complex **9** shows signals at 51.24 and 41.61 (d, J_{P-P} = 42 Hz) ppm, while the outer-sphere BArF counteranion gives rise to a singlet at −62.24 ppm in the ^{19}F{^{1}H} NMR spectrum.

Complex **9** is remarkably stable: it does not convert to the σ-benzylic form, even upon addition of ligands such as CH_3CN and CO. However addition of one equivalent of triethylphosphine to a benzene solution of the π-benzylic complex **9** did result in rearrangement to the σ-benzylic structure **10**, giving rise to three characteristic signals in the ^{31}P{^{1}H} NMR spectrum, 49.50 (dd, $J_{Pc\text{-}Pb}$ = 338 Hz, J_{Pa-Pb} = 32 Hz, P_b), 41.40 (dd, $J_{Pc\text{-}Pa}$ = 42 Hz, J_{Pb-Pa} = 32 Hz, P_a), and 11.50 (dd, $J_{Pb\text{-}Pc}$ = 338 Hz, $J_{Pa\text{-}Pc}$ = 42 Hz, P_c) for the phosphrous atoms of dppe (a, b) and of Et_3P (c), correspondingly.

Relative Stability of the Coordinated Benzyl Cations. We were interested in determining the relative stability of the three observed forms of the coordinated benzyl molecule. Two series of complexes based on dtpp and dppe ligands were studied using DFT calculations, with the starting geometries defined as methylene arenium, σ-benzyl, and π-benzyl. Only one minimum was found on each potential energy surface, i.e., optimization from all three "initial guess" geometries converged to the same structure in each case (Figure 3). For the bulky dtpp ligand, geometry optimization led to the MA complex, whereas in the case of the dppe compound, the π-benzylic structure was preferred. DFT calculations of the dtpp-based complex are in good agreement with X-ray and NMR studies of **4**. The optimized geometry of this complex has a trigonal shape around the metal atom with bond lengths and angles very similar to those found by the X-ray studies of **4** (see Supporting Information).

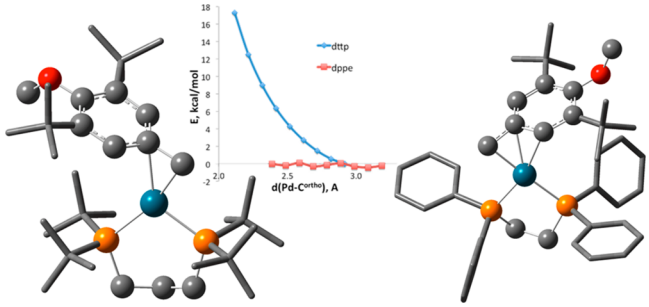


Figure 3. Optimized geometries of the complexes based on dtpp (left) and dppe (right) ligands to which the initial structures converged in the absence of a coordinated counterion. Hydrogen atoms are omitted for clarity. Deformation energy as a function of the Pd−C^{ortho} distance is shown in the inset panel.

Relaxed scan of the potential energy surface of the dttp-based complex showed a systematic increase in energy with decreasing distance between Pd and C^{ortho} atoms below the optimized value of 2.916 Å. An increase of the Pd−C^{ortho} bond length in the dppe-based complex caused simultaneous Pd bonding with the second C^{ortho} atoms. Thus, a relaxed PES scan of the dppe-based complex showed a negligible barrier between the two symmetric η^3-π-benzylic structures and did not lead to an η^2-MA structure (Figure 3, inset). Thus, according to the calculations, preference toward the MA or π-benzylic structure depends on the auxiliary ligand properties, while the σ-benzylic form is unfavorable in the absence of a coordinating counteranion.

The optimized Pd−C bond lengths and Wiberg bond indexes, based on NBO analysis listed in Table 1, indicate that the strengths of the interactions between the metal atom and the methylene group are similar in the MA-dtpp and π-

Table 1. Optimized Pd−C Bond Lengths and Wiberg Bond Indexes in the MA-dtpp and π-Benzylic-dppe Complexes

	interatomic distance		WBI	
	MA-dtpp	π-benzylic-dppe	MA-dtpp	π-benzylic-dppe
Pd−C(sp^3)	2.063	2.099	0.468	0.498
Pd−C(sp^2-*ipso*)	2.311	2.230	0.255	0.267
Pd−C(sp^2)	2.916	2.387	0.226	0.338

dx.doi.org/10.1021/om400523f | *Organometallics* 2013, 32, 4813−4819

benzylic-dppe complexes, whereas the Pd interaction with the aromatic ring is much stronger in the latter case.

Analysis of the electronic structure of the two complexes using NBO and QTAIM approaches yields partial atomic charges shown in Figure 4. Although both methods indicate

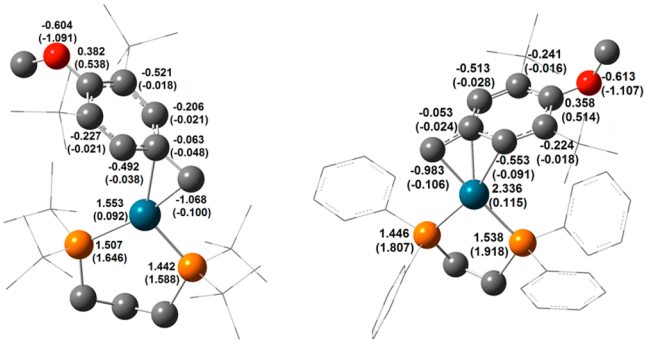


Figure 4. Atomic charges based on NBO and QTAIM (in parentheses) analyses in the MA-dtpp (left) and π-benzylic-dppe (right) complexes. Hydrogen atoms are omitted for clarity.

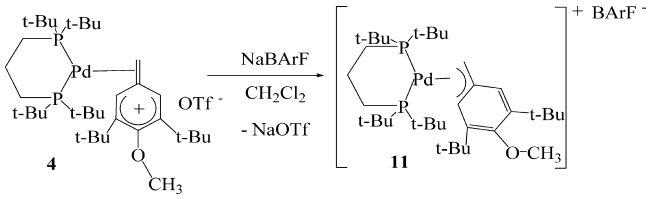
significant Pd → benzyl electron transfer, the quantity of this transfer is considerably different: NBO analysis yields total charges on the benzyl ligand in the dttp and dppe complexes of −1.18 and −1.21, respectively, of which −0.47 and −0.37 are on the methylene group. In contrast, QTAIM gives total charges of 0.11 and 0.08 including −0.07 and −0.04 on the methylene group, respectively. In both approaches, only the *para*-C atom bound to the OCH_3 group retains a positive charge in both complexes, while other atoms of the aromatic ring bear negative partial charges. Apparently, the methoxy group stabilizes the positive charge on the carbon to which it is bound, while steric repulsion with the two tBu groups probably pushes the methoxy group out of the ring plane, resulting in lack of resonance effect on the other ring atoms.

The NBO charge on the *para*-C atom in complex **4** (+0.38) is well consistent with the experimental estimation (+0.36). Moreover, NBO analysis indicates significant bonding between Pd and one (in the dtpp complex) or two (in the dppe complex) C atoms of the aromatic ring, whereas QTAIM reveals bond critical points only for the Pd−C(sp^3) interactions in both complexes.

Counteranion Interplay. The counteranion plays an important role in benzyl complexation. Coordinating counteranions such as triflate can decrease the energy of the σ-benzylic form by binding to the metal center. This was experimentally demonstrated by formation of the stable σ-benzylic complexes **6** and **7**. The effect of coordinating and noncoordinating counteranions was previously observed with Rh complexes, where substitution of the coordinating counteranion by the noncoordinating counteranion led to the dearomatization of the benzylic pincer ligand.[27] Notably, when a small excess of NaBArF was added to a CH_2Cl_2 solution of the methylene arenium complex **4** (the dtpp-based complex was chosen due to its higher stability), immediate conversion to the π-benzylic complex **11** was observed (Scheme 5).

Complex **11** was fully characterized by multinuclear NMR. It gives rise to two doublets at 66.33 and 41.87 (J_{P-P} = 42 Hz) ppm in the $^{31}P\{^1H\}$ NMR spectrum. As in the case of **9**, complex **11** exhibits a broad and nonsymmetric pattern of the η^3-coordinated benzylic ring in the ^1H and $^{13}C\{^1H\}$ NMR

Scheme 5. Conversion of the Methylene Arenium Complex 4 to the π-Benzyl Complex 11 upon Substitution of the Triflate Anion with the Bulky BArF Counteranion



spectra, the Pd-CH_2 group giving rise to the corresponding signals at 2.56 (bs) and 41.92 (dd, J_{P-C} = 42, 8 Hz) ppm.

DFT calculations show that in solution the triflate counterion is directly coordinated to the Pd atom as the most electrophilic center in both η^2-MA and η^3 π-benzylic complexes. In the presence of coordinated OTf^-, formation of the σ-benzylic form becomes energetically preferred by 2.7 and 6.8 kcal/mol for the dtpp and dppe complexes, respectively, in dichloromethane at rt. In toluene, the σ-benzylic form is more stable than the MA-dtpp and π-benzylic-dppe structures by 25.1 and 28.3 kcal/mol, respectively. This order of stability is consistent with the relative rates of formation of σ-complexes **6** and **7** (*vide supra*).

Thus, we have found that the interaction between the MA-dtpp and π-benzylic-dppe cations with the triflate counterion results in the formation of a Pd−OTf bond. Coordination of the counteranion changes the mode of coordination of the benzyl cation from η^2 and η^3 to the η^1 σ coordination mode. Use of an excessively bulky counteranion that does not approach the metal center leads to the formation of the MA or π-benzylic forms of the coordinated benzyl cation, depending on the nature of the ligand.

EXPERIMENTAL SECTION

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. Complexes **1**,[19] **2**,[18] **3**,[19] **4**,[18] **6**,[18] and **8**[19] were prepared according to the literature procedures. NMR spectra were recorded at 400(^1H), 100 (^{13}C), and 162 (^{31}P) MHz using a Bruker AMX-400 NMR spectrometer and at 500 (^1H), 126 (^{13}C), and 202 (^{31}P) using a Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C unless otherwise specified. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (2.09 ppm, toluene; 5.32 ppm, CH_2Cl_2; and 7.24 ppm, $CDCl_3$). In $^{13}C\{^1H\}$ NMR measurements the signals of d_8-toluene (20.09 ppm), CD_2Cl_2 (53.80 ppm), and $CDCl_3$ (77.00 ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.

Formation of (dppe)Pd(methylene arenium) (5). To a toluene solution (1 mL) of (dppe)Pd(QM) (**3**) (36 mg, 0.05 mmol) precooled to −30 °C was added MeOTf (5 μL, 0.05 mmol). The reaction mixture was kept at −30 °C for 10 min and then warmed to room temperature. After 30 min the $^{31}P\{^1H\}$ NMR spectrum revealed

dx.doi.org/10.1021/om400523f | *Organometallics* 2013, 32, 4813−4819

quantitative formation of complex **5**. Since conversion of **5** to **7** takes place at room temperature, complex **5** was characterized at −30 °C.

$^{31}P\{^1H\}$ NMR (d_8-toluene): 42.10 (bs), 32.70 (bs). ^1H NMR (d_8-toluene): 7.50−7.00 (aromatic signals of dppe) 6.94 (bs, 2H, MA-ring), 3.45 (dd, J_{P-H} = 7 Hz, J_{P-H} = 4 Hz, 2H, exocyclic), 2.87 (s, 3H, O-CH_3), 1.41 (m, 4H, dppe), 1.61 (s, 18H, tBu). $^{13}C\{^1H\}$ NMR (d_8-toluene): 152.32 (s, C-O-CH_3 of MA-ring), 142−130 (aromatic signals of dppe), 136.04 (bs, *ortho* of MA-ring), 130.72 (s, *meta* of MA-ring), 117.66 (s, $C{=}{=}CH_2$), 60.99 (s, C-O-CH_3), 50.99 (d, J_{P-C} = 37 Hz, exocyclic), 34.27 (s, $C(CH_3)_3$-MA), 29.70 (s, $C(CH_3)_3$-MA), 25.96 (m, dppe), 24.90 (m, dppe). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT and C−H correlation measurements.) $^{19}F\{^1H\}$ NMR (d_8-toluene): 75.55 (s).

When complex **5** was allowed to stand at room temperature (in CD_2Cl_2), the $^{31}P\{^1H\}$ NMR spectrum revealed formation of the new complex **7**, which became the major product after 2 h, in addition to unidentified compounds formed as a result of decomposition of complex **7**.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 52.56 (d, J_{P-P} = 41 Hz), 42.57 (d, J_{P-P} = 41 Hz). ^1H NMR (CD_2Cl_2): 7.7−6.6 (aromatic signals of dppe), 6.87 (s, 2H, Ar), 4.22 (s, 3H, O-CH_3), 3.40 (dd, J_{P-H} = 10 Hz, 3 Hz, 2H, Pd-CH_2), 2.30 (m, 4H, dppe), 1.19 (s, 18H, tBu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 151.73−125 (aromatic signals of dppe), 149.51 (s, J_{P-C} = 6 Hz, C-O-CH_3 of benzylic ring), 140.40 (s, benzylic ring), 130.00 (d, J_{P-C} = 22 Hz, benzylic ring), 124.88 (d, J_{P-C} = 9 Hz, benzylic ring), 64.48 (d, J_{P-C} = 2 Hz, C-O-CH_3), 50.28 (d, J_{P-C} = 34 Hz, Pd-CH_2), 34.83 (s, $C(CH_3)_3$), 31.21 (s, $C(CH_3)_3$), 26.13 (dd, J_{P-C} = 15 Hz, J_{P-C} = 5 Hz, dppe), 24.88 (dd, J_{P-C} = 15 Hz, J_{P-C} = 5 Hz, dppe).

Formation of (dppe)Pd(π-benzyl) (9). To an ether solution (1 mL) of complex **8** (30 mg, 0.034 mmol) was added AgBArF (BArF = $B(C_6H_3(CF_3)_2)_4$) (38 mg, 0.034 mmol). The reaction mixture was protected from light and stirred for 1 h at rt, followed by filtration through Celite and evaporation to give 51 mg (0.029 mmol, 85% yield) of complex **9**.

$^{31}P\{^1H\}$ NMR (C_6D_6): 51.24 (d, J_{P-P} = 42 Hz), 41.61 (d, J_{P-P} = 42 Hz). ^1H NMR (C_6D_6): 7.30−6.90 (aromatic signals of dppe) 6.51 (s, 1H, π-benzyl ring), 6.49 (bs, 1H, π-benzyl ring), 2.73 (bd, J_{P-H} = 9 Hz, 2H, Pd-CH_2), 1.89 (m, 2H, dppe), 1.67 (m, 2H, dppe), 1.21 (bs, 18 H, tBu), 0.35 (s, 9H, $(CH_3)_3Si$). $^{13}C\{^1H\}$ NMR (C_6D_6): 135−118 (aromatic signals of dppe and BArF), 162.72 (dd, J_{P-C} = 50 Hz, J_{P-C} = 49 Hz, C-O-$SiMe_3$ of π-benzyl ring) 146.39 (d, J_{P-C} = 3 Hz, *ortho* of π-benzyl ring), 146.35 (bs, *ortho* of π-benzyl ring) 119.05 (d, J_{P-C} = 1 Hz, *meta* of π-benzyl ring), 111.37 (dd, J_{P-C} = 6 Hz, J_{P-C} = 1 Hz, C-CH_2 of π-benzyl ring), 50.91 (dd, J_{P-C} = 70 Hz, J_{P-C} = 1 Hz, Pd-CH_2), 31.57 (s, $C(CH_3)_3$), 30.37 (s, $C(CH_3)_3$), 26.00 (m, dppe), 3.48 (s, $SiMe_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT and C−H correlation measurements.) $^{19}F\{^1H\}$ NMR (C_6D_6): 62.24 (s). ES-MS: m/z^+ 797.72 (M + 1) [calcd 797.49], m/z^- 863.52 BArF) [calcd 863.23].

Formation of (dtpp)Pd(π-benzyl) (11). To a CD_2Cl_2 solution (1.5 mL) of complex **2** (30 mg, 0.046 mmol) was added MeOTf (5.2 μL, 0.046 mmol) at −30 °C. The reaction mixture was allowed to warm to room temperature. After 1.5 h, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR revealed formation of complex **4**. At this stage 1.5 equiv of NaBArF (0.069 mmol, 61 mg) was added, resulting in immediate formation of the new complex **11** as observed by $^{31}P\{^1H\}$ NMR. The solvent was evaporated and the complex was purified by washing with pentane and dissolution in CH_2Cl_2. Decantation and evaporation of the solvent gave clean complex **11** in 82% yield (58 mg, 0.038 mmol).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 66.33 (d, J_{P-P} = 42 Hz), 41.87 (d, J_{P-P} = 42 Hz). ^1H NMR (CD_2Cl_2): 6.06 (bs, 2H, Ar), 3.11 (d, J_{P-H} = 7 Hz 2 H, dtpp), 3.19 (s, 3H, O-CH_3), 2.56 (bs, 2H, Pd-CH_2), 1.95 (m, 2H, dtpp), 1.75 (m, 4H, dtpp), 1.50 (m, 2H, dtpp), 1.36 (s, 18H, tBu), 1.30 (d, J_{P-H} = 14 Hz, 18H, tBu-dtpp), 0.87 (d, J_{P-H} = 14 Hz, 18H, tBu-dtpp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 162.01 (dd, J_{P-C} = 39 Hz, J_{P-C} = 40 Hz, C-O-CH_3 of benzylic ring), 135.67 (dd, J_{P-C} = 4 Hz, J_{P-C} = 2 Hz, C-CH_2 of benzylic ring), 129.41 (dd, J_{P-C} = 2 Hz, J_{P-C} = 3 Hz, benzylic ring), 129.06 (dd, J_{P-C} = 2 Hz, J_{P-C} = 3 Hz, benzylic ring), 117.92 (bd, J_{P-C} = 2 Hz, benzylic ring), 117.80 (bd, J_{P-C} = 2 Hz, benzylic ring), 41.92 (dd, J_{P-C} = 42 Hz, 8 Hz, Pd-CH_2), 39.34 (d, J_{P-C} = 14 Hz, C-O-CH_3), 35.07 (d, J_{P-C} = 11 Hz, $C(CH_3)_3$-dtpp), 35.08 (d, J_{P-C} = 11 Hz, $C(CH_3)_3$-dtpp), 34.65 (s, $C(CH_3)_3$), 30.80 (d, J_{P-C} = 4 Hz, $C(CH_3)_3$-dtpp), 30.07 (d, J_{P-C} = 4 Hz, $C(CH_3)_3$-dtpp), 29.93 (s, $C(CH_3)_3$), 22.06 (d, J_{P-C} = 7 Hz, dtpp), 21.89 (d, J_{P-C} = 7 Hz, dtpp), 20.60 (d, J_{P-C} = 15 Hz, dtpp). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): 63.24 (s). ES-MS: m/z^+ 672.38 (M+) [calcd 671.81], m/z^- 864.00 (BArF) [calcd 863.23].

Computational Methods. All electronic structure calculations were carried out using the Gaussian09 package.[28] Geometry optimizations and evaluation of harmonic frequencies have been performed at the density functional theory (DFT)[29,30] level using the PBE0 hybrid density functional[31] in conjunction with the PC-1 basis set. The latter consists of the SDD basis set[32] with an added f function for palladium (exponent 1.170, the geometric mean of the two f exponents given by Martin and Sundermann[33]), together with Jensen's polarization consistent pc-1 basis set for the remaining elements.[34] This combination is of double-ζ plus polarization quality. All structures were fully optimized in the gas phase and characterized as minima by calculating the harmonic vibrational frequencies. Bulk solvent effects of the experimental dichloromethane, toluene, and ether media have been taken into account by the self-consistent reaction field (SCRF) method, using the integral equation formalism model (IEFPCM) as it is implemented in Gaussian09. Dispersion interactions were included by adding Grimme's empirical dispersion correction term[35] with cutoff function inspired by Becke and Johnson[36] (D3BJ). Full topological analysis was performed using the program AIMALL.[37] Natural bond orbital (NBO) calculations were performed using NBO5.[38] Unless stated otherwise, energetic data are presented as free energies (ΔG) at 298.15 K and include corrections for solvation and dispersion (see above).

■ SUMMARY

In summary, three forms of coordinated benzyl cations, namely, methylene arenium, π-benzyl, and σ-benzyl cations, were prepared and studied. Two bidentate ligand frameworks, the bulky dtpp and the less bulky dppe, were utilized in this study. The η^2-metal coordination mode allowed for the isolation and reactivity studies of the otherwise unstable methylene arenium cation under ambient conditions. Theoretical and experimental studies demonstrate that in the absence of counteranion MA and π-benzylic structures are preferred over the σ-benzylic one, where the bulky dtpp ligand frame contributes to stabilization of the methylene arenium form, whereas the π-benzyl form is preferred for the dppe framework. Counteranions have a significant effect on the relative stability of the three forms. Thus, the triflate counteranion enables the stabilization of either the σ-benzylic form upon coordination to the metal center or the methylene arenium form upon compensation of positive charge on the MA ring. Use of the non-coordinating, bulky BArF anion resulted in conversion to the π-benzylic form. We anticipate that the present study will contribute to the fundamental understanding of chemical and biological processes involving benzyl cation intermediates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information includes NMR spectra and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Israel Science Foundation and by the Helen and Martin Kimmel Center for Molecular Design. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry. We thank Dr. Eugene Khaskin for fruitful discussions.

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