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

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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. η2-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, η2-MA, η1-σ-benzylic, and η3-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. Benzyl cation precursors are utilized as latent initiators in cationic polymerization processes and as potent alkylation agents. They are postulated as key intermediates in oxidation of vitamin E and lignin degradation. Characterization of benzyl cations is challenging because of their high reactivity. Numerous fast UV and gas-phase ion 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. 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). 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.

Although experimental studies also support the importance of resonance contribution from form B, this limiting structure remained unobserved, while the structures corresponding to the aromatic form A, especially with out-of-plane methylene groups, are well documented. In addition, several examples of arenium (Wheland) complexes, crucial intermediates in electrophilic aromatic substitution, were reported, and in a few cases they were isolated in crystalline form. Thus, all known examples of arenium complexes involve the formation of a coordinated arenium structure that includes an sp3 ring carbon, while discrete coordinated methylene arenium compounds, i.e., compounds with an sp3 ipso carbon atom

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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 $\eta^3$-coordination to a metal center. Indeed, $\pi$-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, $\eta^2$-methylene arenium (MA), $\eta^1$-benzylic, and $\eta^3$-benzylic forms, were prepared and characterized. Part of this work, including isolation of a $\eta^2$-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
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. When substituting tmeda by the dppe ligand under analogous conditions, addition of nBu4NF was required in order to remove the Me3Si protecting group and form the reported quinone methide complex 3 (Scheme 1). 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 Me3Si, not requiring the use of fluoride protection. An additional reason can be the higher electron donating ability of the dppe 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. 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 13C{1H} NMR spectra, respectively). 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). The exocyclic methylene is bent out of the pseudoaromatic ring plane by 6.1°, owing to strong back-bonding from the metal center.

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 is fully characterized by multinuclear NMR. The 31P{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 steric hindrance. In analogy with the dppe-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–C = 4 Hz) and 50.99 ppm (dd, J P–C = 37 Hz) in the 1H and 13C{1H} NMR spectra, correspondingly, while the C-O-CH3 carbon appears at 152.32 ppm in the 13C{1H} NMR spectrum. Comparing these NMR data to those reported for the benzyl cations, 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. Removal of the methyl group in anisole is a difficult process that requires activation with strong Lewis acids. However, scission of the C–O bond at the para position of the methylene arenium ring was observed immediately upon reaction with 4 with water at room temperature, leading to the corresponding phenolic complex. Further addition of Et3N 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 and for aromatic compounds in general. The single-site coordination mode of the methylene arenium moiety allows also its controlled release. 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).

**α-Benzyl Complexes.** At room temperature the methylene arenium complexes 4 and 5 undergo conversion to the α-benzylcyclohexadienyl complexes 6 and 7 (Scheme 2). In the case of the dtpp-based complexes the conversion is slow (about 20 h). The bulky tert-buty1 substituents together with the enhanced electron donation properties of the dppe 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 α-benzylcyclohexadienyl complexes. Complex 7 gives rise to two doublets in the 31P{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. The benzylic carbon Pd-CH3 is slightly upfield shifted relative to the exocyclic methylene arenium carbon 50.28 (d, J P–C = 34 Hz) and 3.40 (d, J P–H = 10 Hz, 3 Hz) in complex 7 vs 50.99 (d, J P–C = 37 Hz) and 3.45 ppm (d, J P–H = 7 Hz, J P–C = 4 Hz) in complex 5 in the 1H and 13C{1H} NMR spectra, respectively. Ring signals
definitely indicate conversion to aromaticity from 149.51 (C-O-CH3) 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.

**π-Benzylic Complexes.** Interestingly, attempts to synthesize the methylene arenium compound starting from the benzylic bromide complex 8, by substitution of the bromide ligand with the noncoordinating BArF counterion, BArF = B-(C6H4(CF3)2)4, led to formation of the π-benzylic 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-benzylic pattern with broad, nonsymmetric signals in the 1H and 13C{1H} NMR spectra. The 31P{1H} NMR spectrum of complex 9 shows signals at 51.24 and 41.61 (d, JP−Pa = 42 Hz) ppm, while the outer-sphere BArF counterion gives rise to a singlet at −62.24 ppm in the 19F{1H} NMR spectrum.

Complex 9 is remarkably stable: it does not convert to the σ-benzyl form, even upon addition of ligands such as CH3CN and CO. However addition of one equivalent of triethylphosphine to a benzene solution of the complex results in rearrangement to the benzene to a benzene solution of the π-benzylic structure and CO. However addition of one equivalent of triethylphosphine to the noncoordinating BArF counterion, BArF = B-(C6H4(CF3)2)4, led to formation of the π-benzylic 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-benzylic pattern with broad, nonsymmetric signals in the 1H and 13C{1H} NMR spectra. The 31P{1H} NMR spectrum of complex 9 shows signals at 51.24 and 41.61 (d, JP−Pa = 42 Hz) ppm, while the outer-sphere BArF counterion gives rise to a singlet at −62.24 ppm in the 19F{1H} NMR spectrum.

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−Cortho distance is shown in the inset panel.

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-benzyllic 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).

| Table 1. Optimized Pd−C Bond Lengths and Wiberg Bond Indexes in the MA-dtpp and π-Benzyllic-dppe Complexes |
|-----------------|-----------------|
|                 | interatomic distance | WBI |
| Pd−C(sp²)       | 2.063            | 0.468 |
| Pd−C(sp²⁻)      | 2.311            | 0.255 |
| Pd−C(sp³)       | 2.916            | 0.226 |

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benzyl-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 significant Pd → benzyl electron transfer, the quantity of this transfer is considerably different: NBO analysis yields total charges on the benzyl ligand in the dtpp 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 OCH3 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(sp3) 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-benzylc ring by forming metal–ligand bonds to the metal center. This was experimentally demonstrated by formation of the stable σ-benzylc 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 benzylc pincer ligand.27 Notably, when a small excess of NaBArF was added to a CH2Cl2 solution of the methylene arenium complex 4 (the dtpp-based complex was chosen due to its higher stability), immediate conversion to the π-benzylc 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 (JP= 42 Hz) ppm in the 31P{1H} NMR spectrum. As in the case of 9, complex 11 exhibits a broad and nonsymmetric pattern of the η2-coordinated benzylc ring in the 1H and 13C{1H} NMR spectra, the Pd-CH2 group giving rise to the corresponding signals at 2.56 (bs) and 41.92 (dd, JP-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 η2-MA and η2-π-benzylc complexes. In the presence of coordinated OTf−, formation of the σ-benzylc 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-benzylc form is more stable than the MA-dtpp and π-benzylc-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-benzylc-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 η2 and η' to the η1 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-benzylc forms of the coordinated benzylc 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. Commericially available reagents were used as received. Complexes 19, 21-24, 5, 6, and 8 were prepared according to the literature procedures. NMR spectra were recorded at 400(1H), 100 (13C), and 162 (31P) MHz using a Bruker AMX-400 NMR spectrometer and at 500 (1H), 126 (13C), and 202 (31P) using a Bruker DXP 500 spectrometer. All spectra were recorded at 23 °C unless otherwise specified. 1H NMR and 31P{1H} NMR chemical shifts are reported in parts per million downfield from internal standards.

#### General Procedures.

A toluene solution (1 mL) of (dppe)PdQM (3) (3 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 31P{1H} NMR spectrum revealed...
quantitative formation of complex 5. Since conversion of 5 to 7 takes place at room temperature, complex 5 was characterized at ~30 °C.

\[^{1}H\] NMR (d4-toluene): 7.50–7.60 (aromatic signals of dppe) 6.94 (bs, 2H, MA-ring), 3.45 (dd, JP-H = 7 Hz, JP-H = 4 Hz, 2H, exocyclic), 2.87 (s, 3H, O-CH3), 1.41 (m, 4H, dppe), 1.61 (s, 18H, tBu), 1.23 (d, JP-c = 4 Hz, 2H, CH2), 0.92 (s, 18H, tBu). The reaction mixture was allowed to stand at room temperature (in CD2Cl2), the [13C] 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 3. The reaction mixture was protected from light and stirred for 1 h at rt, followed by filtration and the complex was purified by chromatography on silica gel (230–400 mesh). The yield of the isolated complex 7 was determined by 1H NMR (CD2Cl2): 7.50 (aromatic signals of dppe and BArF), 162.72 (bs, C(8-toluene): 75.55 (s)).

Computational Methods. All electronic structure calculations were carried out using the Gaussian09 package. Structure optimizations and evaluation of harmonic frequencies have been performed at the density functional theory (DFT)29,30 level using the PBE0 hybrid density functional29 in conjunction with the PC-1 basis set. The latter consists of the SDD basis set32 with an added f function for palladium (exponent 1.170, the geometric mean of the two f exponents given by Martin and Sundermann33), 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 (IEFPQM) as it is implemented in Gaussian09. Dispersion interactions were included by adding Grimme’s empirical dispersion correction term37 with cutoff function inspired by Becke and Johnson38 (D3BJ). Full topological analysis was performed using the program A-MMALL.39 Natural bond orbital (NBO) calculations were performed using NBO.40 Unless stated otherwise, energy 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, methylenecarbene, π-benzyl, and σ-benzyl cations, were prepared and studied. Two bidentate ligand frameworks, the bulky dppe and the less bulky dtpp, were utilized in this study. The π-metal coordination mode allowed for the isolation and reactivity studies of the otherwise unstable methylenecarbene 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-benzyl one, whereas the bulky dppe ligand framework contributes to stabilization of the methylenecarbene, 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 tri fluoride counteranion enables the stabilization of either the σ-benzyl form upon coordination to the metal center or the methylenecarbene form upon compensation of positive charge on the MA ring. Use of the non-coordinating, bulky BARF anion resulted in conversion to the π-benzyl 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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Author Contributions
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.

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