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Synthesis and Reactivity of the Methylene Arenium Form of a Benzyl Cation, Stabilized by Complexation

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Benzyl cations are highly reactive compounds involved as key intermediates in various chemical and biochemical processes.[1] They can be stabilized at low temperatures under super-acidic conditions.[2] The structural and electronic properties of these compounds is a subject of fundamental importance. Experimental observations,[2,3] supported by high level ab initio calculations,[4] indicate that the nonaromatic, “methylene arenium” resonance form (B, Figure 1) can contribute significantly to the general energy of the benzyl cation.

However, discrete methylene arenium compounds, i.e., compounds with an sp^2 *ipso* carbon atom and ring-localized charge, are unknown, except when cramped in a pincer-ligand framework.[5,6] We report here the generation and stabilization of a simple methylene arenium (MA) molecule, stabilized by coordination to a metal center. The MA complex was fully characterized, including by X-ray diffraction. Its reactivity is strongly influenced by the arenium character of the ring. Being coordinated to a metal center via the exocyclic double bond, controlled release of the methylene arenium moiety into solution was possible, where it demonstrated benzyl cation reactivity.

Utilizing our method for the generation and stabilization of quinone methides,[7] the complex (tmeda)Pd(BHT−OSiMe$_3$)Br **1**[7] was reacted with the ligand dtpp (dtpp = bis(di-*tert*-butylphosphino)propane) in THF solution at −30 °C, yielding the new, stable complex **2** of the quinone methide BHT-QM (Scheme 1).

Complex **2** was fully characterized by multinuclear NMR and IR spectroscopies[8] and by a single-crystal X-ray diffraction study. It is similar to an analogous bis(diphenyphosphino)ethane complex,[7] except for effects of the bulkiness and electron-donating properties of the dtpp ligand (Figure 2).

Significantly, upon electrophilic attack of methyl triflate on complex **2**, *an unprecedented methylene arenium compound, stabilized only by coordination of the exocyclic double bond*, was obtained, complex **3** (Scheme 1), as proven by multinuclear NMR spectroscopy and X-ray structural characterization.

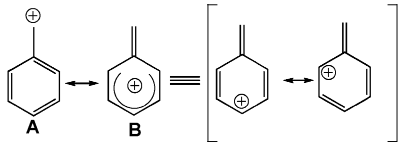
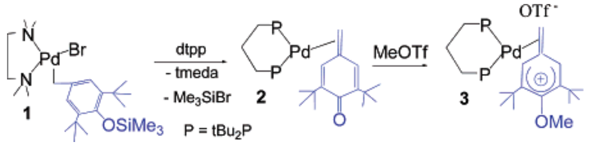


Figure 1. Resonance forms of a benzyl cation.

Scheme 1



Both the NMR and X-ray data strongly support sp^2 hybridization of the *ipso* carbon and positive charge concentration in the arenium ring. The ^{31}P NMR spectrum of **3** shows two doublets at 52.91 and 39.05 ppm (J_{P-P} = 20 Hz) for the nonequivalent phosphine groups. The methoxy group gives rise to singlets at 4.22 and 62.89 ppm in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively. It is noteworthy that the exocyclic methylene group remains almost the same as in complex **2**. In the ^{1}H NMR spectrum it gives rise to a signal which is only slightly downfield shifted (by 0.07 ppm), while in the ^{13}C{^{1}H} NMR spectrum its signal is slightly shifted upfield to 45.89 (d, J_{P-C} = 34 Hz) vs 47.67 (d, J_{P-C} = 33 Hz) in complex **2**. On the other hand, the positive charge has a strong effect on the arenium ring, as evidenced by ^{13}C NMR. As expected, the signal due to the carbonyl group disappears and is replaced by a signal of C−O−CH$_3$ at 166.08 ppm (dd, J_{P-C} = 7 Hz, 1 Hz). The other ring signals are all downfield shifted with respect to anisole (129−114 ppm) and to the related benzylic complex **4** (see later), and demonstrate a nonhomogeneous distribution of the positive charge. Notably, the *ortho* carbons appear at 139.88 ppm, while the *meta* carbons are only slightly deshielded (129.14 ppm). Due to the positive charge in the ring, the signal of the *ipso* carbon is strongly downfield shifted relative to the parent QM complex (107.51 instead of 78.12 ppm in **2**). These data clearly indicate that the positive charge is localized predominantly in the ring, distributed mainly at the *para* and *ortho* positions, and almost none at the exocyclic methylene (or metal center, see below, complex **4**). For comparison, the documented NMR data for benzyl cations (form **A**)[2,3] show that the methylene groups are strongly deshielded (appearing in the range of 150−300 ppm), while the ring is only moderately affected, indicating that the charge is mostly localized at the methylene group.

Yellow X-ray quality crystals of **3** were obtained by slow diffusion of pentane into its toluene solution at −20 °C. As expected from a methylene arenium resonance structure, the X-ray structure of **3** (Figure 2) indicates averaging of the carbon−carbon bond distances of the quinonoid ring in comparison with those in the quinone methide complex **2**. The asymmetric charge distribution is reflected by incomplete averaging. According to the resonance forms, most of the positive charge is expected to be localized at the *ortho*- and *para*-carbon atoms. This is supported by recent observations regarding the X-ray structure of the cumyl cation[9] and the methylene arenium moiety incorporated in PCP-type ligand structures,[5] the only crystallographic examples of related compounds. Our structure is in agreement with this, the charge being localized mostly in the *para* position: C22−C23 (1.387 Å) is shorter than the rest of the distances in the ring, while C23−C24 (1.423 Å) is the longest bond. The *tert*-butyl substituents in the ring preclude C21−C22 from being the longest bond, which is what is expected in an unsubstituted ring. The C23−C24 bond was initially much longer than other ring distances (1.488 Å in parent

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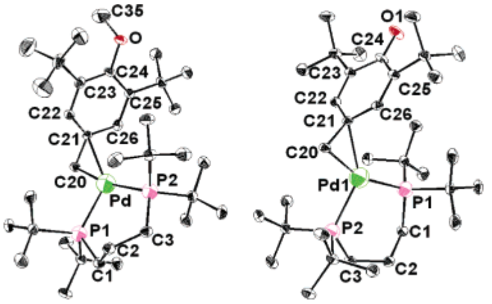
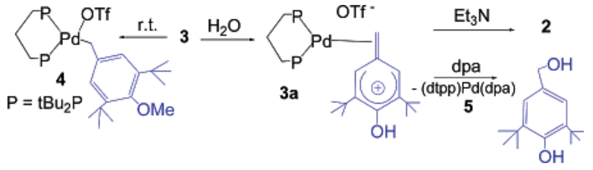


Figure 2. ORTEP views of complexes **3** (left) and **2** (right) at 50% probability. Hydrogen atoms are omitted for clarity.

Scheme 2



complex **2**), whereas the C24−C25 bond (symmetric to C23−24) is the second longest distance in both **3** (1.415 Å) and **2** (1.461 Å). Similarly to **2**, the quinonoid ring is not symmetric in complex **3**. Notably, the C−C bond lengths of the ring are longer than average bond lengths in aromatic compounds,[9] as expected for a methylene arenium structure.

The Pd-coordinated C20−C21 (1.459 Å) bond is elongated as compared with the corresponding bond in **2** (1.439 Å) as a result of more back-bonding from the Pd center to the electron-deficient exocyclic bond. This value is in the range of other bond distances of alkenes coordinated to Pd(0).[5,10] Interestingly, the Pd−C21 distance is also longer than the corresponding bond in **2** (2.360 vs 2.274 Å), probably as a result of diminished π-donation from the electron-deficient methylene arenium group to the Pd−C bond. This value is comparable with values reported for palladium complexes of nonsymmetric olefins bearing an electron-withdrawing group.[11] As a result of strong back-bonding,[12] the exocyclic methylene is bent out of the pseudo-aromatic ring plane by 6.1° (compared with 2.5° in the parent complex). No interaction between the metal and the pseudo-aromatic ring is indicated. Pd−C22 (3.150 Å) and Pd−C26 (2.884 Å) distances exclude the possibility of a π-benzylic interaction. As expected, the C24−O bond distance of 1.384 Å no longer indicates a double bond. For comparison, C−O bond length of anisole in the gas phase is 1.357 Å.[13]

The positive charge delocalization within the aromatic ring of the methylene arenium compound is also evidenced by its reactivity. Thus, upon addition of water to a methylene chloride solution of **3**, immediate hydrolysis of the methoxy group in the *para* position took place. Further deprotonation with Et_3N resulted in quantitative formation of the parent quinone methide complex **2** (Scheme 2).

Such reactivity is unusual for aromatic compounds in general, as well as for benzyl cation precursors.[14] For instance, hydrolysis of the methoxy group in anisole is a difficult process that requires activation with strong Lewis acids.[15] Thus, the methylene arenium structure dramatically enhances the reactivity of the Me−O bond toward nucleophilic attack, as observed also in the case of a phenoxonium complex.[16]

Significantly, the one-site coordination mode of the methylene arenium moiety makes possible its controlled release under very mild conditions, using a ligand substitution process. Thus, upon addition of diphenylacetylene (dpa) to a CD_2Cl_2 solution of complex **3a** containing 99 equiv of water at room temperature, the methylene arenium moiety dissociated from the metal center and reacted with water, giving 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, as expected from benzyl cation reactivity (Scheme 2).

Slow rearrangement of **3** to give the benzylic complex **4** takes place at room temperature (Scheme 2). **4** was fully characterized by multinuclear NMR spectroscopy. The signals due to the ring carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum clearly indicate conversion to aromaticity. For example, the *para* and *ipso* carbons in the methylene arenium ring, which significantly deviate from aromaticity in **3**, return to the normal range of a metal coordinated benzyl ligand in $^{13}C\{^1H\}$ NMR : *para* **C**−O−CH_3 (147.98 vs 166.08 ppm in **3**) and *ipso* carbon (125.45 vs 107.51 ppm in **3**).

To summarize, a methylene arenium cation, an extreme resonance form of a benzyl cation, was generated, stabilized by coordination of the exocyclic double bond, and fully characterized in solution and in the solid state. It exhibits reactivity patterns resulting from the positively charged ring, such as facile ether C−O bond hydrolysis to the corresponding alcohol, and deprotonation to form a *p*-quinone methide complex. Controlled release of the methylene arenium moiety was achieved by associative substitution, forming and trapping the benzyl cation. This approach can potentially be utilized for the delivery and controlled generation of benzyl cations.

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Supporting Information Available: Crystallographic data of **2** and **3** (CIF) and preparation and characterization of **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Olah, G. A.; Prakash, G. K. S. *Carbocation Chemistry*; Wiley & Sons: New York, 2004.
(2) (a) Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 932. (b) Bollinger, J. M.; Comisarow, M. B.; Cupas, C. A.; Olah, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 5687. (c) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044. (d) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7355.
(3) Van Pelt, P.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1057.
(4) Reindl, B.; Clark, T.; Scheleyer, P.v. R. *J. Phys. Chem. A* **1998**, *102*, 8953.
(5) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477.
(6) Transition metal stabilized arenium cations (not methylene arenium): (a) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233. (b) Keane, J. M.; Chordia, M. D.; Mocella, C. J.; Sabat, M.; Trindle, C. D.; Harman, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 6806.
(7) Rabin, O.; Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 7119.
(8) See Supporting Information.
(9) Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087.
(10) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H. J.; Krueger, C. *Organometallics* **1983**, *2*, 1369.
(11) Burrows, A. D.; Choi, N.; McPartlin, M.; Mingos, D. M. P.; Tarlton, S. V.; Vilar, R. *Organomet. Chem.* **1999**, *573*, 313.
(12) Vigalok, A. Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798.
(13) Seip, H. M.; Seip. R. *Acta Chem. Scand.* **1973**, *27*, 4024.
(14) Sneen, R. A.; Felt, G. R.; Dickason, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 638.
(15) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley & Sons: New York, 1981; p 88.
(16) Vigalok, A.; Rybtchinski, B.; Gozin, Y.; Koblenz, T. S.; Ben-David, Y.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 15692.

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