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Methylene Arenium Cations via Quinone Methides and Xylylenes Stabilized by Metal Complexation

Arkadi Vigalok,[†] Linda J. W. Shimon,[‡] and David Milstein*,[†]

Contribution from the Departments of Organic Chemistry and Chemical Services, The Weizmann Institute of Science, Rehovot 76100, Israel

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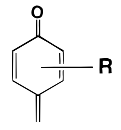
Abstract: The quinone methide (QM) rhodium complex of 3,5-bis(di-*tert*-butylphosphinomethyl)-2,6-dimethyl-4-methylene-3,5-cyclohexadien-1-one (L) (**1**) was protonated by trifluromethanesulfonic acid (triflic acid) at the quinonoid carbonyl group giving the unique methylene arenium complex (Cl)Rh[LH$^+$]$CF_3SO_3^-$ (**2**). Complexes **2** and its (trimethyl)silyl analogue (**3**) were fully characterized spectroscopically, and complex **2** was also characterized by single-crystal X-ray analysis. The crystallographic studies on **2** have revealed that the positive charge is delocalized between the carbon atoms of the ring with most of it being at the para- and ortho-carbon atoms. The electron deficient QM complex (CO)Rh$^+$[L] $CF_3SO_3^-$ (**4**), which has also been crystallographically characterized, is less basic, requiring excess of triflic acid to obtain the methylene arenium complex (CO)Rh$^+$[LH$^+$]2$CF_3SO_3^-$ (**5**), demonstrating a dramatic effect of the electron density on the metal center on the stability of the methylene arenium species. When **1** was reacted with 2−3 equiv of MeLi formation of two complexes, MeRh[3,5-bis(di-*tert*-butylphosphinomethyl)-2,6-dimethyl-4-methylene-3,5-cyclohexadien-1-en] (**6**) and its ortho-xylylene isomer (**7**), took place. Complexes **6** and **7** represent the first example of thermally stable xylylenes coordinated via only one of the exocyclic double bonds. Both **6** and **7** undergo protonation by CF_3SO_3H giving as a single product the arenium complex CF_3SO_3Rh[3,5-bis(di-*tert*-butylphosphinomethyl)-1,2,6-trimethyl-4-methylene-3,5-cyclohexadienyl]$^+CF_3SO_3^-$ (**8**). ^{13}C NMR studies performed on the arenium complexes shows no para-substituent effect on the chemical shift of the coordinated CH_2 group and that this group does not participate in the positive charge delocalization. Thus, the reported methylene arenium compounds can be viewed as a resonance form of a benzyl cation stabilized by metal complexation.

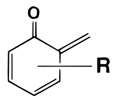
Introduction

Quinone methides (QMs) are postulated as intriguing transients in various biochemical transformations and are of general importance in modern organic chemistry.[1,2] Substitution of one of the carbonyl groups in benzoquinones for a methylene creates highly reactive species, which, in contrary to the parent quinones, undergo spontaneous oligomerizarion that prevents their isolation from solution.[3]

Most of these compounds have only been observed in dilute solutions. So far, no simple QMs, i.e., not bearing substituents at the methylene group, have been isolated, except in two cases when fused aromatics are involved, making the quinonoid structure negligible.[4] Even those having stabilizing substituents at the methylene group are known to undergo fast reactions with both nucleophiles and electrophiles giving products of 1,6-addition. For example, rapid formation of the corresponding phenols takes place when QMs are reacted at room temperature with water or alcohols even at low concentration in solution.[5] This general instability is attributed to a high tendency of QMs to undergo aromatization.



p- quinone methide



o- quinone methide

We have recently demonstrated that metal coordination to the exocyclic methylene group in a chelating PCP-type ligand system makes the QM moiety remarkably stable toward reactions with nucleophiles and electrophiles.[6] Complex **1** does not react with water or alcohols even upon heating. Its high thermal stability has also been noted.

Here we present the results of our studies on the reactivity of the QM complex **1** toward *strong* electrophiles and nucleo-

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[†] Department of Organic Chemistry.

[‡] Department of Chemical Services.

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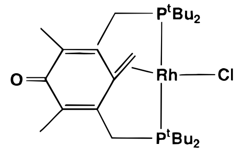

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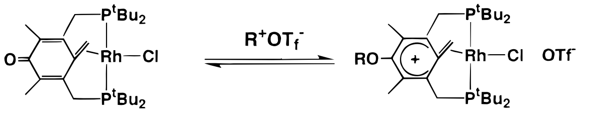
philes. Interestingly, electrophilic attack on the quinonoid oxygen atom produces a unique methylene arenium species stabilized by metal complexation, while reaction of **1** with MeLi results in unusually thermally stable metal *xylylene* complexes in which the metal is bound to only one double bond. The latter can also be converted into the methylene arenium metal complexes. Although numerous examples of isolated arenium σ-complexes (Wheland complexes), crucial intermediates in electrophilic aromatic substitution, have been reported,[7] those having an sp^2 hybridized ipso-carbon atom (i.e., methylene arenium resonance form of a benzyl cation) are yet unknown. Metal complexation allowed us to stabilize and crystallographically characterize such a species.

Results and Discussion

1. Reaction of the Quinone Methide Complex 1 with Strong Electrophiles. When a toluene solution of the red complex **1** was treated with 1 equiv of triflic acid (HOTf, $HOSO_2CF_3$), formation of green crystals of the proton adduct **2** took place in quantitative yield. Similarly, reaction of **1** with Me_3SiOTf resulted in formation of the silylated adduct **3** (eq 1). Multinuclear NMR spectroscopy of **2** and **3** and X-ray crystallographic analysis of **2** proved these adducts to be the *first known arenium compounds with an sp^2 hybridized ipso-carbon atom*. Protonation of **1** is a reversible process, and addition of a base such as NaOAc to a solution of **2** results in complete deprotonation of the latter to give **1**. No protonation of **1** with 1 equiv of *p*-toluene sulfonic acid took place, indicating that the pK_a of **2** is lower than that of this acid (< -7).[8]



(1)

1 **2, 3**

R= H (2); SiMe$_3$ (3)

Green crystals of complex **2** have been obtained by slow evaporation of a CH_2Cl_2 solution of **2** at room temperature. A perspective view of a molecule of **2** is shown in Figure 1. Selected bond distances and bond angles are presented in Table 1. The X-ray structure of **2** demonstrates substantial averaging of the carbon−carbon bond distances of the pseudo-aromatic ring in comparison with the ones in the parent complex **1**. The incomplete averaging indicates asymmetric charge distribution inside the ring with most of the charge being localized on the ortho- and para-carbon atoms. Similar observations were recently reported regarding the structure of the cumyl cation.[9,10]

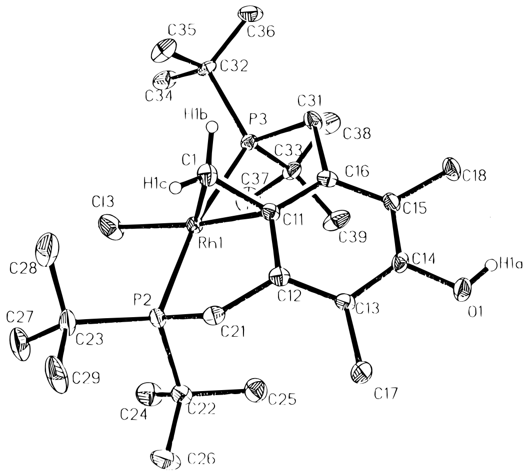


Figure 1. ORTEP view of a cation of **2** with the thermal ellipsoids at 50% probability. The hydrogen atoms (except H(1a), H(1b) and H(1c)) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**

(a) Bond Lengths			
Rh(1)−C(1)	2.032 (5)	C(11)−C(12)	1.446 (6)
Rh(1)−C(11)	2.229 (4)	C(12)−C(13)	1.373 (6)
C(1)−C(11)	1.452 (6)	C(13)−C(14)	1.416 (6)
Rh(1)−Cl(3)	2.3063 (13)	C(14)−C(15)	1.415 (6)
Rh(1)−P(2)	2.3438 (13)	C(15)−C(16)	1.382 (6)
Rh(1)−P(3)	2.3426 (13)	C(11)−C(16)	1.441 (6)
C(13)−C(17)	1.503 (6)	C(14)−O(1)	1.338 (5)
(b) Angles			
P(2)−Rh(1)−P(3)	168.28 (4)	C(1)−C(11)−Rh(1)	62.9 (2)
P(2)−Rh(1)−C(1)	88.4 (2)	C(12)−C(11)−C(16)	120.0 (4)
P(2)−Rh(1)−C(11)	85.23 (12)	C(13)−C(14)−C(15)	123.9 (4)
C(1)−Rh(1)−C(11)	39.5 (2)	C(11)−C(12)−C(13)	119.8 (4)
Rh(1)−C(1)−C(11)	77.6 (3)	C(12)−C(13)−C(14)	118.2 (4)

Importantly, the C(14)−O(1) bond distance of 1.338(5) Å no longer represents a double bond, and it is just slightly shorter than that in phenol (1.368 Å).[11] This bond length compares well with the value of 1.348 Å calculated for the *p*-hydroxybenzyl cation.[12] Significantly, the arenium ring has little effect on the methylene double bond length (1.452(6) Å) which is within the range expected for a coordinated double bond (cf. 1.441(8) Å in **1**),[13] whereas the Rh−C(11) distance has become somewhat longer than that in **1** (2.229(4) Å vs 2.183(5) Å, respectively). Notably, the bond angles at C(11) are almost perfectly trigonal, indicating that the system should be viewed as a methylene arenium complex rather than a metallacyclopropane arenium. The Rh−C(12) distance of 3.0135 Å excludes the possibility of a π-allylic interaction.

The ^{31}P NMR spectrum of **2** shows a doublet at 26.23 ppm with $J_{RhP} = 104.4$ Hz. It is noteworthy that this chemical shift,

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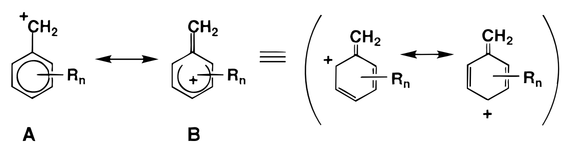
which is in the range of the free ligand, is surprisingly low for the five−six-membered ring chelates of this particluar system (compare with 40.35 ppm in **1**). The coordinated methylene group protons give rise to a triplet at 4.90 ppm ($J_{PH} = 5.8$ Hz) in ^{1}H NMR. It is also significant that protonation of the carbonyl oxygen atom in **1** to give the cationic complex **2** does not result in charge localization on the methylene carbon atom as evidenced by the ^{13}C NMR spectrum of **2**. Only a slight downfield shift of its signal in comparison to that in **1** was observed (44.15 vs 41.95 ppm, respectively), indicating that the positive charge is delocalized between the carbon atoms of the arenium ring.[14]

It was demonstrated, most notably by Olah and co-workers, that each of the two major resonance forms, **A** and **B**, contributes significantly to the total structure of the benzyl cation.[15−17] It was also shown that the presence of bulky substituents (e.g., adamantyl) on the benzylic carbon removes it from the aromatic plane and leads to localization of most of the positive charge on the methylene carbon (form **A**).[18] On the other hand, cationic σ-complexes (arenium or Wheland complexes) are known as transient intermediates in electrophilic aromatic substitution reactions (alkylation, acylation, halogenation, nitration, etc.),[19,7] and in a few cases they can be isolated in a crystalline form.[20] However, all the known examples involve formation of an *sp³ ipso-carbon atom*, and no methylene arenium compounds (i.e. resonance form **B** of a benzyl cation) have been reported. Complex **2** represents such a compound, stabilized by complexation to a late transition metal center.



A **B**

Although methylene arenium cations can be expected to have a high tendency to aromatize to the benzyl cation (form **A**), complexation to a metal center makes this process unfavorable. No reaction resulting in aromatization of **2** was observed, this complex being stable at room-temperature both in the solid state and in solution. It is worth noting that while numerous examples of transition metal complexes containing charge delocalized (prearomatic) ligands are reported, they all involve *direct* metal coordination to the aromatic ring.[21] In contrast, the metal in **2** is coordinated to an *exocyclic* methylene group connected to the prearomatic cation.

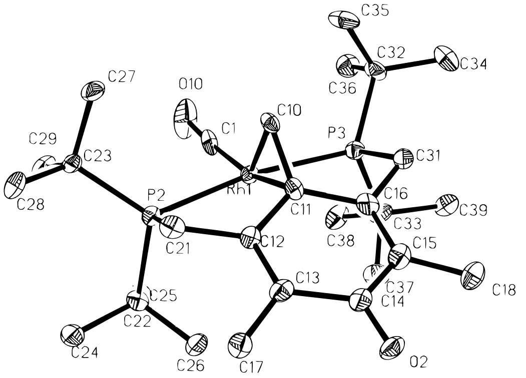
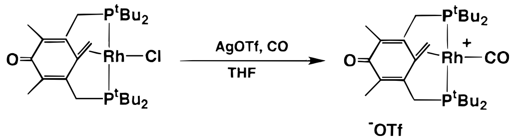


Figure 2. ORTEP view of a cation of **4** with the thermal elipsoids at 50% probability. The hydrogen atoms are omitted for clarity.

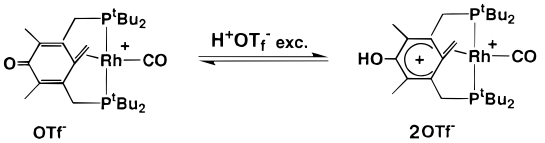
To probe the effect of the electron density on the rhodium atom on the stability of the methylene arenium carbocation relative to that of the parent quinone methide complex, the cationic Rh(I) carbonyl complex **4** has been prepared (eq 2).



(2)

1 **4**

Complex **4** could not be protonated with 1 equiv of HOTf, i.e., the protonated rhodium complex **5** has a pK_a value lower than that of triflic acid (eq 3). Protonation of **4** was achieved in situ by using 5 equiv of triflic acid, although the resulting adduct **5** could not be isolated in the solid state. Thus, complex **5** is one of the strongest stable acids. The higher basicity of **1** as compared with **4** correlates well with the much lower back-bonding from the metal to the alkene in the latter, as evidenced by X-ray analysis and by the ^{1}H NMR spectrum of **4**.



(3)

4 **5**

Orange crystals of complex **4**, suitable for an X-ray crystallographic analysis, have been obtained by slow crystallization from a solution in dichloromethane−THF (1:1). Figure 2 shows a perspective view of a molecule of **4**. Selected bond lengths and bond angles are given in Table 2. The bond lengths between the rhodium atom and both carbon atoms of the coordinated double bond are longer than those in the parent QM **1** (Rh(1)−C(10) of 2.127(8) Å and Rh(1)−C(11) of 2.258(8) Å, vs 2.052(6) Å and 2.183(5) Å in **1**, respectively), showing little back-bonding to the coordinated double bond in **4**. This also agrees well with the C(10)−C(11) bond distance of 1.402(11) Å, being slightly shorter than that in **1** (1.441(8) Å). The bond distances between the carbon atoms of the cyclohexadienyl moiety are comparable with those of **1**.

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(14) Theoretical calculations on *p*-hydroxybenzyl cations predict an approximately equal charge distribution between the exocyclic methylene and the ring (mainly at the para carbon atom): (a) Semenov, S. G.; Shevchenko, S. M. *Chem. Papers* **1991**, *45*, 289. (b) Shevchenko, S. M.; Elder, T. J.; Semenov, S. G.; Zarubin, M. Ya. *Res. Chem. Intermed.* **1995**, *21*, 413.

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Scheme 1

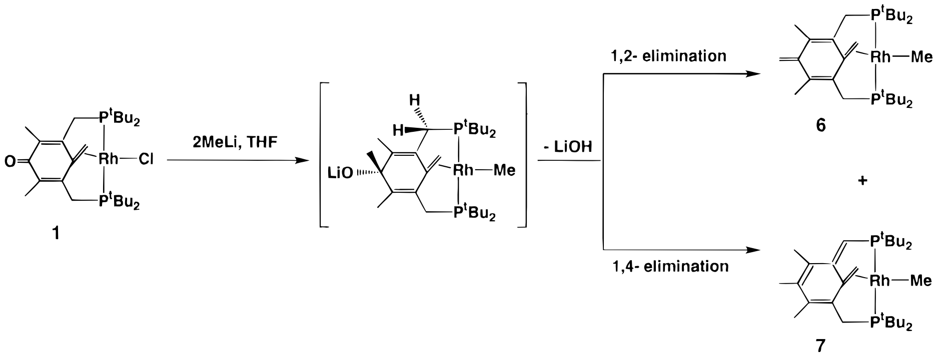


Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4**

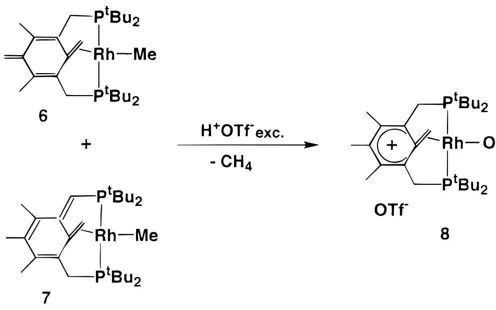
(a) Bond Lengths

Rh(1)−C(10)	2.127 (8)	C(11)−C(12)	1.485 (11)
Rh(1)−C(11)	2.258 (8)	C(12)−C(13)	1.359 (13)
C(10)−C(11)	1.402 (11)	C(13)−C(14)	1.488 (12)
Rh(1)−C(1)	1.903 (10)	C(14)−O(15)	1.476 (12)
Rh(1)−P(2)	2.345 (2)	C(15)−O(16)	1.359 (12)
Rh(1)−P(2)	2.353 (2)	C(11)−C(16)	1.491 (11)
C(1)−O(10)	1.129 (11)	C(14)−O(2)	1.241 (10)

(b) Angles

P(2)−Rh(1)−P(3)	167.05 (8)	C(10)−C(11)−Rh(1)	66.3 (4)
P(2)−Rh(1)−C(10)	88.3 (2)	C(12)−C(11)−C(16)	118.9 (7)
P(2)−Rh(1)−C(11)	83.7 (2)	C(11)−C(12)−C(13)	120.1 (7)
C(10)−Rh(1)−C(11)	37.1 (3)	C(12)−C(13)−C(14)	120.1 (8)
C(11)−C(10)−Rh(1)	76.5 (5)	C(14)−C(15)−C(16)	120.0 (8)

Scheme 2



The signal due to the coordinated methylene group at 5.23 ppm in the ^{1}H NMR spectrum of **4** has practically the same chemical shift as that of free ethylene, while in **1** it appears in a significantly higher field (3.13 ppm). The IR spectrum of **4** exhibits two strong bands at 2019 and 1608 cm^{-1} due to the coordinated CO and the quinonoid carbonyl group, respectively. Interestingly, the signal of the methylene carbon atom in the ^{13}C NMR spectrum of the methylene arenium species **5** is shifted *upfield* in comparison with that of **4** (67.7 vs 76.7 ppm, respectively). This surprising apparent higher "shielding" indicates that the methylene carbon atom does not participate in the delocalization of the positive charge. Moreover, protonation of the quinonoid carbonyl group in **4** also leads to a shift of the Rh−C≡O band in the IR spectrum to a higher frequency (2060 cm^{-1} in **5** vs 2019 cm^{-1} in **4**), indicating a decrease in the back-bonding interaction between the metal center and the coordinated CO. Significantly, even in an electron poor species such as **5** no aromatization takes place via metal slippage to the methylene group to form the benzyl rhodium complex.

2. Metal Stabilized Xylylenes. When the QM rhodium complex **1** was reacted with 2−3 equiv of MeLi in THF, two products were isolated after extraction with pentane, which have been assigned as the *p*- and *o*-xylylene rhodium(I) complexes **6** and **7**, respectively (Scheme 1). The ratio between the two varied slightly depending on the reaction conditions, being in general 1:1. The mechanism of this process probably involves nucleophilic attack at the quinonoid carbonyl followed by competitive 1,2- and 1,4-elimination of LiOH leading to **6** and **7**, respectively. Parallelly, methylation of the rhodium takes place. The ^{31}P{^{1}H} NMR spectrum of **6** exhibits a doublet at 50.26 ppm with J_{RhP} of 148.1 Hz; **7** exhibits an AB pattern centered at 52.12 ppm ($J_{RhPa} = 148.7$ Hz, $J_{RhPb} = 142.9$ Hz, $J_{PaPb} = 354.7$ Hz). The ^{1}H NMR spectrum of the mixture of **6** and **7** shows a singlet at 5.32 ppm due to the methylene group in **6** and a doublet at 5.25 ppm ($J_{PH} = 3.9$ Hz) for the only proton of the exocyclic double bond in **7**. Similarly, the ^{13}C{^{1}H} NMR spectrum of this mixture exhibits a broad singlet at 99.62 ppm for the exocyclic noncoordinated methylene carbon in **6** (below the baseline in the ^{13}C{^{1}H} DEPT NMR spectrum) and a doublet of multiplets for the "side-arm" double bond carbon atom in **7** at 97.50 ppm (above the baseline in the ^{13}C DEPT NMR spectrum).

Complexes **6** and **7** represent unique examples of thermally stable xylylene molecules. *p*- and *o*-Xylylenes are highly reactive species which undergo spontaneous polymerization even at very low temperatures.[22] It has been calculated that the energy difference between the ground (dimethylene cyclohexadiene) state and the transition (biradical of dimethylene benzene) state is less than 6 kcal/mol, and therefore these compounds cannot be isolated under normal conditions.[1c,23] Although it is sometimes difficult to distinguish between the dienyl and dibenzyl coordination mode, transition metal complexes of *o*-xylylenes where the metal center is coordinated to the both of exocyclic methylene groups have been reported.[24] It is, therefore, noteworthy that in both **6** and **7** the metal center is coordinated in an η^2 fashion to only *one* of the exocyclic double bonds. The stabilization here is achieved due to a combination of factors, among which the phosphine chelation effect and the distortion from planarity seem to be the most important.

When a mixture of **6** and **7** in dichloromethane was treated with an excess of triflic acid, formation of the green methylene arenium complex **8** took place in a quantitative yield (Scheme 2). The ^{1}H NMR spectrum of **8** shows a triplet at 4.79 ppm ($J_{PH} = 6.6$ Hz) due to the coordinated double bond. This very large downfield shift as compared with the parent QM was observed also in the analogous methylene arenium complex **2**. The ^{13}C{^{1}H} NMR spectrum of **8** is indicative of the high

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Table 3. Comparison of Selected $^{13}C\{^1H\}$ NMR Chemical Shifts of Methylene Arenium Complexes vs the Parent Quinone Methide Complexes

carbon atom	δ $^{13}C\{^1H\}$ NMR, ppm	
	methylene arenium	QM
Rh (C═***C***H$_2$)	44.15 (**2**) 44.34 (**8**) 68.40 (**5**)	41.95 (**1**) 76.44 (**4**)
Rh (***C***═CH$_2$)	74.06 (**2**) 87.57 (**8**) 90.65 (**5**)	66.97 (**1**) 100.36 (**4**)
Ar***C***-O (or Ar***C***═O)	176.74 (**2**) 180.53 (**5**)	186.51 (**1**) 184.93 (**4**)

positive charge density on the prearomatic ring, with most of the charge being localized on the para- and ortho- carbon atoms (162.06 and 161.42 ppm, respectively). These chemical shifts are substantially higher than those of aromatic compounds but still lower than that of positively charged arenium compounds.[25] Similarly to **2**, the coordinated methylene group appears as a doublet of triplets at 44.34 ppm (J_{RhC} = 24.2 Hz, J_{PC} = 3.0 Hz) showing no influence of the para-substituent on the chemical shift in the methylene arenium complex (i.e., OH vs CH$_3$).

3. Comments on Charge Delocalization in the Metal Stabilized Methylene Arenium Complexes. The chemistry of carbocations is an important and flourishing area in modern organic chemistry.[26] Among other carbocations, benzyl cations, which exhibit a high degree of charge delocalization, are of particular interest in various fields of chemistry.[27] One of the most important questions is the relative contribution of each of the resonance forms **A** and **B** to the overall energy of the cation. As in many cases the X-ray structures of these highly reactive species are unavailable, ^{13}C NMR has become the most powerful tool in determining the charge distribution in the system.[28] It was shown that in planar benzyl cations the substituents in the para position to the exocyclic methylene group dramatically influence its chemical shift in the ^{13}C NMR spectrum through the shared system of conjugated bonds.[29] As expected, introducing donor substituents into the para position results in the upfield shift of this signal, while electron withdrawing groups in the para position decrease the contribution of the resonance form **B** and lead to the downfield shift of the signal. On the other hand, in nonplanar benzyl cations the effect of the para substituent on the chemical shift of the methylene group is negligible, as most of the charge is localized at this carbon atom with no contribution of the methylene arenium form.[17] To our knowledge, no methylene arenium compound (i.e., resonance form **B**) has so far been reported. Table 3 presents ^{13}C NMR chemical shifts of the coordinated CH$_2$ group of the methylene arenium metal complexes (**2** and **8**, **5**) and the parent quinone methides (**1** and **4**, respectively). The most important features here are that within each series there is practically no effect of the ring charge on the chemical shift of the methylene carbon atom in ^{13}C NMR (i.e., the signal in compounds **2** and **8** is only slightly shifted downfield from that in **1**, whereas in the CO-containing dicationic complex **5** it is even shifted upfield in comparison to that in **4**). Moreover, substitution of the very strong electron releasing OH group in **2** ($\sigma = -0.37$; $\sigma^+ = -0.92$) for a very mild donor CH$_3$ ($\sigma = -0.17$; $\sigma^+ = -0.31$)[30] in **8** has evidently *no* effect on the chemical shift of the methylene group signal in the ^{13}C NMR spectrum, showing no participation of this group in the overall charge delocalization in the methylene arenium complexes. By comparison, the quarternary carbon atom chemical shift *is* affected by the substituent in the para-position in an expected way, i.e., more than 13 ppm downfield when OH is substituted by Me (87.57 ppm in **8** vs 74.06 ppm in **2**), clearly indicating that positive charge is ring localized. In the parent QM complex **1** this signal appears at 66.97 ppm. Table 3 also demonstrates a high degree of charge localization at the para-carbon atom of the ring. The chemical shift of this atom in the ^{13}C NMR spectra of the methylene arenium complexes is only slightly upfield from that of parent QM complexes (176.74 (**2**) and 180.53 (**5**) vs 186.51 (**1**) and 184.93 (**4**), respectively), although one would expect more dramatic changes upon substitution of **C**═O for **C**−OH. For comparison, the ^{13}C NMR signal of the **C**−OH group in the neutral organometallic phenol ClRh(CH$_3$)[HO−C$_6$(CH$_3$)$_2$-(CH$_2$P(t-Bu)$_2$)$_2$][6] appears at 153.78 ppm.

In summary, we have prepared rare examples of stable quinone methides and xylylenes stabilized by metal complexation and have shown that they can be converted to methylene arenium complexes. The latter compounds are unexpectedly stable and have been fully characterized, including by X-ray analysis. The electron density on the metal center strongly influences the stability of these species in comparison to the parent quinonoid compounds. Surprisingly, even in the electron poor dicationic complexes no metal slippage to the methylene carbon atom to produce benzyl metal complexes takes place, showing that the methylene arenium resonance form of a benzyl cation coordinated to a metal center is preferred over the aromatic structure with the positive charge localized at the metal. Moreover, no effect of the para substitutent on the chemical shift of the exocyclic methylene group in ^{13}C NMR was observed, indicating lack of conjugation of this group with the ring. Thus, the reported methylene arenium compounds can be viewed as a "discrete resonance" form of a benzyl cation in which the charge is ring-localized, stabilized by metal complexation. Further investigations on the metal- and ligand-centered reactivity of these interesting complexes are in progress.

Experimental Section

General Procedures. All operations were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier). All solvents were reagent grade or better. Pentane, benzene, and THF were distilled over sodium/benzophenone ketyl. All solvents were degassed and stored under high-purity nitrogen after distillation. All deuterated solvents (Aldrich) were stored under high-purity nitrogen on molecular sieves (3 Å). Trifluoromethanesulfonic acid was purchased from Aldrich (99+ %) and used as it is.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent h_1 (7.24 ppm chloroform-d, 7.15 ppm benzene-d_6) and all-d solvent peaks (77.00 ppm chloroform, 128.00 ppm benzene), respectively. ^{31}P chemical shifts are in ppm downfield from H$_3$PO$_4$ and referenced to an external 85% phosphoric acid sample. All measurements were performed at 21 °C unless otherwise specified.

Synthesis and Characterization of Compounds 2−8. Compound 2. To a solution of **1**[6] (20 mg, 0.034 mmol) in 1 mL of toluene was

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added 3.5 μL ($\approx$1.2 equiv) of HOTf at -30 °C. Immediate color change from red to dark green took place with the formation of a green crystalline precipitate. The mixture was allowed to stay at -30 °C for 3 h after which formation of green crystals of **2** was completed. The solvent was removed by decantation, and the crystals were washed with pentane and dried in vacuum to quantitatively yield **2**.

$^{31}P\{^1H\}NMR$ (δ, ppm) ($CDCl_3$) 26.23 (d, $J_{RhP} = 104.4$ Hz). *^1H NMR* (δ, ppm) 12.00 (br s, 1H, O**H**), 4.90 (t, $J_{PH} = 5.8$ Hz, 2H, C=C**H**$_2$), 2.85 (AB quart. $J_{HH} = 16.7$ Hz, 4H, C**H**$_2$$-$P), 2.25 (s, 6H, Ar$-$C**H**$_3$), 1.51 (vt, $J_{PH} = 6.9$ Hz, 18H, *t*-Bu), 1.34 (vt, $J_{PH} = 6.8$ Hz, 18 H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (δ, ppm) 176.74 (s, **C**-OH), 165.00 (s, **Ar**), 126.85 (t, $J_{PC} = 4.4$ Hz, **Ar**), 74.06 (br d, $J_{RhC} = 7.4$ Hz, **C**=CH$_2$), 44.15 (br d, $J_{RhC} = 23.3$ Hz, C=**C**H$_2$), 37.24 (t, $J_{PC} = 6.6$ Hz, **C**(CH$_3$)$_3$), 37.12 (t, $J_{PC} = 6.7$ Hz, **C**(CH$_3$)$_3$), 30.48 (t, $J_{PC} = 2.2$ Hz, C(**C**H$_3$)$_3$), 29.34 (s, C(**C**H$_3$)$_3$), 22.40 (t, $J_{PC} = 6.7$ Hz, **C**H$_2$$-$P), 13.61 (s, Ar$-$**C**H$_3$).

Elemental Analysis: Found (Calc.): C 45.29 (45.50), H 6.53 (6.68).

Compound 3. Complex **3** was prepared in situ by the addition of 9 μL ($\approx$1.2 equiv) of Me$_3$SiOTf to a CDCl$_3$ solution of **1** (20 mg, 0.034 mmol) at room temperature. The green solution of **3** was immediately formed, and the NMR spectra showed complete disappearance of **1**. The silyl group in **3** undergoes rapid hydrolysis to give **2**. At room temperature the ^{31}P{^{1}H} NMR spectrum of complex **3** shows a broad hill at 23.5 ppm. Well resolved NMR spectra of **3** have been recorded at -30 °C.

$^{31}P\{^1H\}NMR$ (δ, ppm) ($CDCl_3$) 22.77 (d, $J_{RhP} = 101.1$ Hz). *^1H NMR* (δ, ppm) 4.45 (t, $J_{PH} = 5.6$ Hz, 2H, C=C**H**$_2$), 2.81 (AB quart. $J_{HH} = 16.9$ Hz, 4H, C**H**$_2$$-$P), 2.14 (s, 6H, Ar$-$C**H**$_3$), 1.39 (vt, $J_{PH} = 6.8$ Hz, 18H, *t*-Bu), 1.20 (vt, $J_{PH} = 6.5$ Hz, 18 H, *t*-Bu), 0.21 (s, 9H, Si(CH$_3$)$_3$). *$^{13}C\{^1H\}$ NMR* (δ, ppm) 172.56 (s, **C**-OSi), 166.32 (s, **Ar**), 130.83 (t, $J_{PC} = 3.8$ Hz, **Ar**), 79.90 (br d, $J_{RhC} = 8.6$ Hz, **C**=CH$_2$), 45.42 (br d, $J_{RhC} = 22$ Hz, C=**C**H$_2$), 37.00 (m, 2 overlapped **C**(CH$_3$)$_3$), 30.31 (s, C(**C**H$_3$)$_3$), 29.26 (s, C(**C**H$_3$)$_3$), 23.00 (t, $J_{PC} = 7.8$ Hz, **C**H$_2$$-$P), 14.65 (s, Ar$-$**C**H$_3$), 1.11 (s, Si(**C**H$_3$)$_3$).

Compound 4. To a solution of **1** (20 mg, 0.034 mmol) in THF (1 mL) a solution of 9 mg of AgOTf in 1 mL of THF was added at room temperature. After 1 h in the dark, the solution was filtered to remove silver chloride. Carbon monoxide was then briskly bubbled through the resulting brown solution causing the precipitation of **4** as an orange powder. The product was filtered through a cotton pad, washed with benzene, and redissolved in CH$_2$Cl$_2$. Evaporation of the solvent gave pure **4** as an orange solid (22 mg, 86%).

$^{31}P\{^1H\}NMR$ (δ, ppm) ($CDCl_3$) 64.78 (d, $J_{RhP} = 95.0$ Hz). *^1H NMR* (δ, ppm) 5.23 (td, $J_{PH} = 4.2$ Hz, $J_{RhH} = 3.3$ Hz, 2H, C=C**H**$_2$), 3.38 (AB quart. $J_{HH} = 16.8$ Hz, 4H, C**H**$_2$$-$P), 2.04 (d, $J_{PH} = 1.2$ Hz, 6H, Ar$-$C**H**$_3$), 1.44 (vt, $J_{PH} = 7.5$ Hz, 18H, *t*-Bu), 1.28 (vt, $J_{PH} = 7.1$ Hz, 18 H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (δ, ppm) 187.20 (dt, $J_{RhC} = 79.3$ Hz, $J_{PC} = 13.3$ Hz, Rh-**C**O), 184.93 (s, **C**=O), 144.60 (s, **Ar**), 132.73 (t, $J_{PC} = 5.2$ Hz, **Ar**), 100.36 (br m, **C**=CH$_2$), 76.44 (dt, $J_{RhC} = 15.0$ Hz, $J_{PC} = 1.7$ Hz, C=**C**H$_2$), 37.84 (t, $J_{PC} = 8.7$ Hz, **C**(CH$_3$)$_3$), 36.93 (td, $J_{PC} = 8.9$ Hz, $J_{RhC} = 1.5$ Hz, **C**(CH$_3$)$_3$), 30.62 (t, $J_{PC} = 1.9$ Hz, C(**C**H$_3$)$_3$), 28.85 (t, $J_{PC} = 1.8$ Hz, C(**C**H$_3$)$_3$), 21.68 (t, $J_{PC} = 9.6$ Hz, **C**H$_2$$-$P), 13.23 (s, Ar$-$**C**H$_3$). IR (chloroform, cm^{-1}) 2019 (s), 1608 (s).

Elemental Analysis: Found (Calc.): C 48.38 (47.67), H 7.03 (6.62).

Compound 5. Complex **5** was prepared in situ by the addition of 21 μL (5.2 equiv) of HOTf to a CD$_2$Cl$_2$ solution of **4** (20 mg, 0.027 mmol) at room temperature. Color change from orange to yellow was observed immediately.

$^{31}P\{^1H\}NMR$ (δ, ppm) (CD_2Cl_2) 47.77 (d, $J_{RhP} = 83.6$ Hz). *^1H NMR* (δ, ppm) 5.20 (td, $J_{PH} = 5.2$ Hz, $J_{RhH} = 2.2$ Hz, 2H, C=C**H**$_2$), 3.62 (AB quart. $J_{HH} = 17.4$ Hz, 4H, C**H**$_2$$-$P), 2.40 (s, 6H, Ar$-$C**H**$_3$), 1.49 (vt, $J_{PH} = 8.1$ Hz, 18H, *t*-Bu), 1.30 (vt, $J_{PH} = 7.5$ Hz, 18 H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (δ, ppm) 185.26 (dt, $J_{RhC} = 83.0$ Hz, $J_{PC} = 11.0$ Hz, Rh-**C**O), 180.53 (s, **C**-OH), 162.86 (s, **Ar**), 129.11 (t, $J_{PC} = 4.7$ Hz, **Ar**), 90.65 (br dt, $J_{RhC} = 6.6$ Hz, $J_{PC} = 1.9$ Hz, **C**=CH$_2$), 68.40 (br d, $J_{RhC} = 20.7$ Hz, C=**C**H$_2$), 39.33 (t, $J_{PC} = 8.2$ Hz, **C**(CH$_3$)$_3$), 37.25 (t, $J_{PC} = 7.6$ Hz, **C**(CH$_3$)$_3$), 30.41 (s, C(**C**H$_3$)$_3$), 27.91 (s, C(**C**H$_3$)$_3$), 22.77 (t, $J_{PC} = 10.1$ Hz, **C**H$_2$$-$P), 12.88 (s, Ar$-$**C**H$_3$). IR (chloroform, cm^{-1}) 2060 (m).

Compounds 6 and 7. To a solution of **1** (20 mg, 0.034 mmol) in THF (2 mL) was added 60 μL of a 1.4 M solution of MeLi in diethyl ether at -30 °C. The solution immediately turned dark red. The reaction mixture was allowed to reach room temperature and solvent was evaporated. Pentane (2 mL) was added to the resulting solid, the precipitate was isolated by filtration and washed with 2 × 2 mL of pentane, and the washings were combined with the filtrate. After removal of the solvent under vacuum, an approximately 1:1 mixture of complexes **6** and **7** was obtained as an air-sensitive red solid. Yield 14 mg (72%).

6: *$^{31}P\{^1H\}NMR$ (δ, ppm) (C_6D_6)* 50.26 (d, $J_{RhP} = 148.1$ Hz). *^1H NMR* (δ, ppm) 5.32 (s, 2H, C=C**H**$_2$), 2.94 (td, $J_{PH} = 5.2$ Hz, $J_{RhH} = 2.0$ Hz, 2H, Rh$-$(C=C**H**$_2$)), 2.64 (AB quart. $J_{HH} = 15.6$ Hz, 4H, C**H**$_2$$-$P), 1.92 (d, $J_{PH} = 0.9$ Hz, 6H, Ar$-$C**H**$_3$), 1.15 (td, $J_{PH} = 5.6$ Hz, $J_{RhH} = 2.2$ Hz, 3H, Rh$-$C**H**$_3$), signals due to *t*-Bu groups overlapped with those of **7**. *$^{13}C\{^1H\}$ NMR* (δ, ppm) 99.62 (br s, C=**C**H$_2$, “down” in ^{13}C{^{1}H} DEPT NMR), 46.25 (dt, $J_{RhC} = 17.0$ Hz, $J_{PC} = 2.9$ Hz, Rh$-$(C=**C**H$_2$)), 30.32 (br t, C(**C**H$_3$)$_3$), 29.75 (br t, C(**C**H$_3$)$_3$), 21.92 (t, $J_{PC} = 8.6$ Hz, **C**H$_2$$-$P), 16.72 (s, Ar$-$**C**H$_3$), -7.85 (m, Rh-**C**H$_3$, overlapped with that of **7**).

7: *$^{31}P\{^1H\}NMR$ (δ, ppm) (C_6D_6)* 52.12 (AB quart., $J_{RhPa} = 148.7$ Hz, $J_{RhPb} = 142.9$ Hz, $J_{PaPb} = 354.7$ Hz). *^1H NMR* (δ, ppm) 5.25 (d, $J_{PH} = 3.9$ Hz, 1H, C=C**H**-P), 3.37 (AB quart., 1H, Rh$-$(C=C**H**$_2$)), 2.64 (AB quart. $J_{HH} = 15.6$ Hz, 2H, C**H**$_2$$-$P), 1.96 (s, 3H, Ar$-$C**H**$_3$), 1.82 (s, 3H, Ar$-$C**H**$_3$), 1.74 (br s, 3H, Ar$-$C**H**$_3$), signal due to Rh$-$C**H**$_3$ overlapped with those the *t*-Bu groups of **6** and **7**. *$^{13}C\{^1H\}$ NMR* (δ, ppm) 97.50 (dm, C=**C**H$-$P, “up” in ^{13}C{^{1}H} DEPT NMR), 63.81 (dt, $J_{RhC} = 13.5$ Hz, $J_{PC} = 3.3$ Hz, Rh$-$(C=**C**H$_2$)), 31.11 (d, $J_{PC} = 1.9$ Hz, C(**C**H$_3$)$_3$), 30.57 (d, $J_{PC} = 2.2$ Hz, C(**C**H$_3$)$_3$), 30.07 (d, $J_{PC} = 1.8$ Hz, C(**C**H$_3$)$_3$), 29.60 (d, $J_{PC} = 1.9$ Hz, C(**C**H$_3$)$_3$), 24.25 (d, $J_{PC} = 10.2$ Hz, **C**H$_2$$-$P), 17.22 (br d, Ar$-$**C**H$_3$), 16.95 (br d, Ar$-$**C**H$_3$), 15.70 (s, Ar$-$**C**H$_3$).

Compound 8. To a 1:1 mixture of **6** and **7** (14 mg, 0.025 mmol) in 1 mL of CH$_2$Cl$_2$ was added 30 μL of HOTf at -30 °C. The green solution was allowed to warm to room temperature, and 2 mL of pentane was added resulting in the precipitation of a green solid. Crude **8** was filtered, washed with pentane and then benzene, and redissolved in dichloromethane. Removal of solvent under vacuum resulted in pure **8** (20 mg, 94%).

$^{31}P\{^1H\}NMR$ (δ, ppm) ($CDCl_3$) 18.55 (d, $J_{RhP} = 99.5$ Hz). *^1H NMR* (δ, ppm) 4.79 (t, $J_{PH} = 0.6.6$ Hz, 2H, C=C**H**$_2$), 2.94 (AB quart. $J_{HH} = 17.1$ Hz, 4H, C**H**$_2$$-$P), 2.47 (s, 6H, Ar$-$C**H**$_3$), 1.63 (s, 3H, Ar$-$C**H**$_3$), 1.53 (vt, $J_{PH} = 7.1$ Hz, 18H, *t*-Bu), 1.37 (vt, $J_{PH} = 6.8$ Hz, 18 H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (δ, ppm) 162.06 (s, **Ar**), 161.42 (s, **Ar**), 138.25 (t, $J_{PC} = 4.5$ Hz, **Ar**), 87.57 (dt, $J_{RhC} = 9.3$ Hz, $J_{PC} = 2.8$ Hz, **C**=CH$_2$), 44.34 (dt, $J_{RhC} = 24.2$ Hz, $J_{PC} = 3.0$ Hz, C=**C**H$_2$), 37.39 (t, $J_{PC} = 7.0$ Hz, $J_{RhC} = 0.9$ Hz, **C**(CH$_3$)$_3$), 37.21 (t, $J_{PC} = 7.7$ Hz, **C**(CH$_3$)$_3$), 30.65 (t, $J_{PC} = 2.3$ Hz, C(**C**H$_3$)$_3$), 29.28 (t, $J_{PC} = 1.9$ Hz, C(**C**H$_3$)$_3$), 23.06 (t, $J_{PC} = 8.3$ Hz, **C**H$_2$$-$P), 22.72 (s, Ar$-$**C**H$_3$), 17.01 (s, Ar$-$**C**H$_3$).

X-ray Analysis of the Structure of 2. Complex **2** was crystallized from CH$_2$Cl$_2$ at room temperature to give green crystals.

Crystal data: C$_{28}$H$_{49}$ClF$_3$O$_4$P$_2$RhS, green needle, 0.2 × 0.1 × 0.1 mm^3, monoclinic, $P2(1)/n$, $a = 8.515(2)$, $b = 27.745(6)$, $c = 13.729(3)$ Å, $\beta = 93.21$ (3) from 25 reflections, $T = 110$ K, $V = 3238.4$ (13) Å^3, $Z = 4$, $F_w = 739.03$, $D_c = 1.516$ Mg/m^3, $m = 0.822$ mm^{-1}.

Data collection and treatment: Rigaku AFC5R four-circle diffractometer, MoKα, graphite monochromator ($\lambda = 0.71073$ Å), 12 069 reflections collected, $1.47° \leq \Theta \leq 27.52°$, $-11 \leq h \leq 11$, $0 \leq k \leq 36$, $-17 \leq l \leq 8$, ω scan method, scan width = 1.2°, scan speed 8°/min, typical half-height peak width = 0.40°, three standards were collected 64 times each, with an 3% change in intensity, 7406 independent reflections (R-int = 0.0394).

Solution and Refinement. The structure was solved by Patterson method (SHELXS-92). Full-matrix least-squares refinement was based on F^2 (SHELXL-93). Idealized hydrogens were placed and refined in a riding mode, with the exception of H1A and H1B on C1 which were located in the difference map and refined independently. Parameters (383) with no restraints, final $R_1 = 0.0546$ (based on F^2) for data with $I > 2\sigma I$ and, $R_1 = 0.0959$ for all data based on 7406 reflections, goodness-of-fit on $F^2 = 1.095$, largest electron density = 0.945 e/Å^{-3}. The data were not corrected for absorption.

X-ray Analysis of the Structure of 4. Complex **4** was crystallized from CH$_2$Cl$_2$/THF 1:1 mixture at room temperature.

Crystal Data: $C_{33}H_{48}F_3O_6P_2RhS$, orange prisms, 0.1 × 0.1 × 0.1 mm^3, triclinic, P-1, $a = 10.608(2)$, $b = 12.413(2)$, $c = 15.345(3)$ Å, $\alpha = 66.92(3)$, $\beta = 93.21$ (3), $\gamma = 81.60(3)$ from 25 reflections, $T = 110$ K, $V = 1825.9(6)$ Å^3, $Z = 2$, $F_w = 794.62$, $D_c = 1.445$ Mg/m^3, $m = 0.668$ mm^{-1}.

Data collection and treatment: Rigaku AFC5R four-circle diffractometer, MoKα, graphite monochromator ($\lambda = 0.710\,73$ Å), 5825 reflections collected, $1.45° \leq \Theta \leq 24.00°$, $0 \leq h \leq 12$, $-14 \leq k \leq 14$, $-12 \leq l \leq 17$, ω scan method, scan width = 1.2°, scan speed 10°/min and, typical half-height peak width = 0.40°, two standards were collected 29 times each, with an 5% change in intensity, 5500 independent reflections (R-int = 0.0308).

Solution and Refinement. The structure was solved by Patterson method (SHELXS-92). Full-matrix least-squares refinement was based on F^2 (SHELXL-93). Idealized hydrogens were placed and refined in a riding mode with the exception of H1A and H2A at C(10) which were located independently in the difference Fourier map but refined in a riding mode with restrained C−H bond length. Parameters (402) with two restraints, final $R_1 = 0.0686$ (based on F^2) for data with $I > 2\sigma I$ and, $R_1 = 0.0980$ for all data based on 5491 reflections, goodness-of-fit on $F^2 = 1.059$, largest electron density = 2.016 e/Å^{-3}.

Note: There is one disordered THF molecule per asymmetric unit.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for complexes **2** and **4** (18 pages). See any current masthead page for ordering and Internet access instructions.

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