A Novel Approach Towards Intermolecular Stabilization of *para*-Quinone Methides. First Complexation of the Elusive, Simplest Quinone Methide, 4-Methylene-2,5-cyclohexadien-1-one

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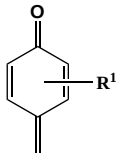
Abstract: A novel approach towards the intermolecular stabilization of "simple" (i.e. methylene-unsubstituted) *p*-quinone methides (QMs) by their coordination to a transition-metal center is described. 4-Bromomethyl phenols, protected by a silyl group, were employed as the QM precursors and *cis*-chelating diphosphine Pd^0 complexes were chosen as the metal precursors, since they have strong back-bonding interactions with the electron-poor QM moiety. Removal of the silyl protecting-group from the corresponding [LPd(benzyl)Br] complex (L = bisphosphine) with fluoride results in the spontaneous rearrangement of the unobserved zwitterionic Pd^{II} complex into the QM – Pd^0 complex. The feasibility of this approach was demonstrated in the synthesis of the structurally characterized Pd^0 complex of BHT-QM (**4**), a biologically relevant metabolite of 2,6-di-*tert*-butyl-*p*-cresol, and the synthesis of the complex of 4-methylene-2,5-cyclohexadien-1-one (**11**), the simplest, and so far unobserved QM molecule. These complexes exhibit a remarkable thermal stability and do not react with alcohol or water. In both cases, the use of an appropriate incoming ligand allowed the release of the coordinated QM into the reaction media in which it was effectively trapped by added nucleophiles.

Keywords: ligand exchange reactions · palladium · P ligands · quinone methides · synthesis design

Introduction

Otherwise inaccessible reactive molecules or molecular fragments can often be stabilized by coordination to metal centers[1] to provide unique opportunities for their characterization by spectroscopic methods and the elucidation of their structure by X-ray crystallography. Furthermore, under appropriate conditions these species may be chemically modified or displaced from the metal. Carbanions, carbenes, ylides, xylylenes, cyclobutadienes, and benzyne are some examples of elusive organic transients, the metal complexes of which have been investigated. Surprisingly, metal complexes of quinone methides (QMs) have so far attracted scarce attention. Os^{II} complexes of *ortho*-QMs that contained stabilizing substituents on the methylene group were reported.[2] By means of an approach often applied to the preparation of the closely related metal–xylylene complexes, Ir complexes of *ortho*-QMs, in which the metal center is coordinated in an η^4 fashion to the two *endo*-cyclic double bonds, were recently prepared.[3] The quinonoid ring in the resulting complexes exhibits a large distortion from planarity; this is reflected in the reactivity of the QM moiety. We have already reported the characterization of two Rh complexes of simple QMs, in which the QM moiety is a part of a bis-chelating PCP-type ligand system.[4] In none of the reported metal complexes could the QM species be removed from the coordination sphere of the metal.



QMs, especially the simple ones (i.e. those which do not have substituents on the exocyclic methylene group), are highly reactive organic intermediates, which are often very difficult to isolate in a pure form as they rapidly polymerize when their dilute solutions are concentrated.[5] Reactions with the medium or self-condensations to give the corresponding phenols are evidently driven by aromatization. Despite this instability, reactive QMs have been extensively studied on account of their importance in many chemical and biochemical processes.[6] For example, the biosynthesis of the natural polymers melanin and lignin involves *para*-QM intermediates.[7] The mechanism of action of several antitumor drugs is believed to proceed via the formation of QMs.[8] Various QMs act as alkylating agents and form covalent bonds with

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functional groups of biopolymers.[9] Elegant syntheses of natural products that involve transient *para*-QM intermediates have also been developed.[10] Moreover, studies with alkyl-substituted phenols revealed that QMs are responsible for the toxicity of these compounds.[11] Metabolic oxidation of these phenols results in the formation of QM derivatives which are attacked by cellular nucleophiles. Most of the toxicology-related studies have involved the use of 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) and its derivatives.[12] This compound is widely used as an industrial antioxidant to prevent deterioration of food products, as a radical scavenger, and as an oxygen-reducing agent. Thus, the metabolism of this compound and the toxicological effects of its metabolites, primarily the quinone methide derivative BHT-QM, are of great interest. Yet, the study of the reactivity of QMs in biotic systems is seriously obstructed by the instability of these compounds and their incompatibility with protic media.

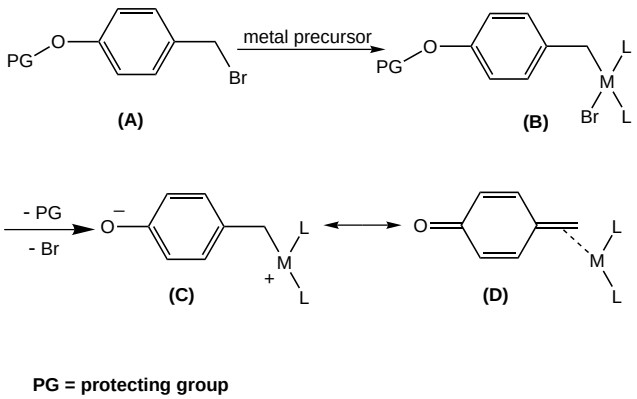
We report here on a novel general approach towards the generation, characterization, and reactivity studies of metal complexes of QM. The complexation of simple quinone methides and their controlled release have been accomplished for the first time. Specifically, we report on the generation, stabilization, and properties, including the controlled displacement, of BHT-QM and the even more reactive, so far elusive, unsubstituted QM analogue. Part of this work has already been communicated.[13]

Results and Discussion

General considerations: Our synthetic strategy is based on the notion that the desired product, the η^2 methylene-coordinated, *p*-quinone methide-metal complex, can be also regarded as a zwitterionic η^1-methylene-*p*-phenoxy metal complex (Figure 1). The outline of the synthesis is depicted in

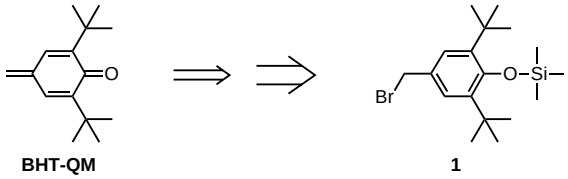
Figure 1. Quinone methide form and the zwitterionic form of *p*-quinone methide in the metal complex.

Scheme 1. The oxidative addition of a QM precursor **A** to a metal complex would result in complex **B**. This complex is then modified to generate the zwitterionic complex **C**, which is expected to rearrange to the final QM metal complex **D**. Since 4-(bromomethyl)phenols, the QM precursors, are unstable and tend to eliminate HBr to form the corresponding unstable QMs, the phenolic group was protected by a silyl group. *cis*-Chelating diphosphine Pd complexes were chosen as the metal precursors, since they are expected to have strong backbonding interactions with the electron-poor QM moiety in the final product **D**, which enhances the stability of the complex.[14]



Scheme 1. Synthetic strategy to produce η^2 methylene-coordinated, *p*-quinone methide-metal complexes.

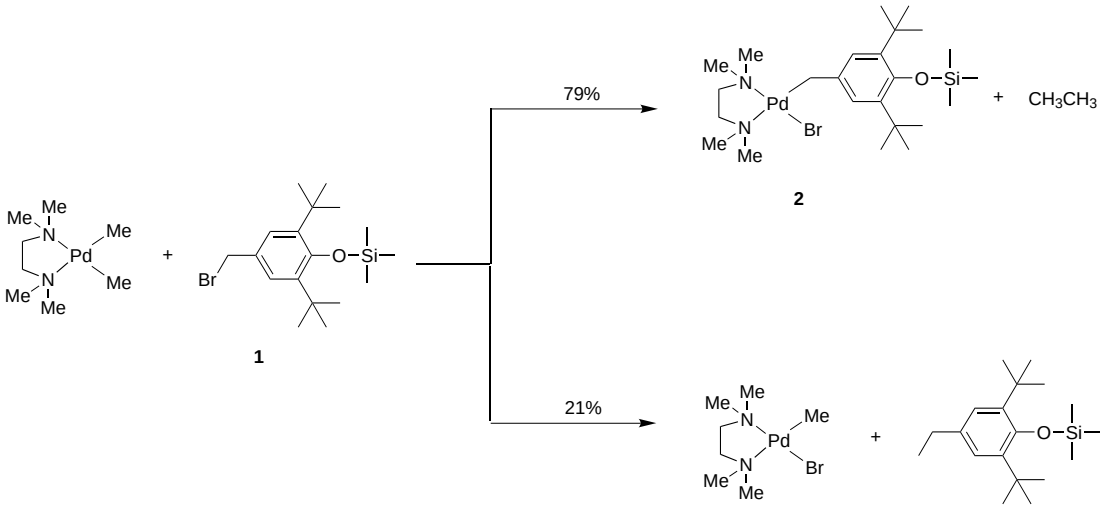
Synthesis of the BHT-QM palladium complex: The precursor selected for BHT-QM was the corresponding trimethylsilyl (TMS) ether of 4-bromomethyl-2,6-di-*tert*-butylphenol (**1**, Scheme 2). The phenolic function of the commercially



Scheme 2. BHT-QM and its precursor **1**.

available 2,6-di-*tert*-butyl-4-methylphenol (BHT) was silylated by refluxing with hexamethyldisilazane in DMF.[15] The resulting silyl ether was brominated with NBS in CCl_4 under intense illumination to give **1**. Compound **1** is a white powder which can be stored in the solid state at room temperature for weeks with only slight decomposition. The benzylic CH_2Br group in **1** gives rise to a singlet at $\delta = 4.49$ in the ^{1}H NMR spectrum and a singlet in the ^{13}C NMR spectrum at $\delta = 35.27$.

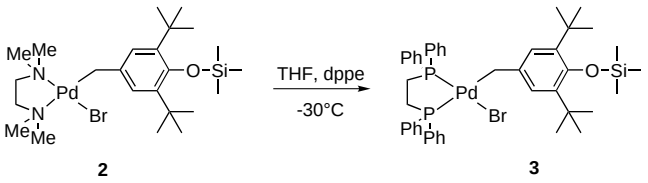
Initially, we tried to oxidatively add the benzyl bromide **1** to chelated diphosphine Pd^0 complexes. Reaction of [(dppp)Pd(dba)][16] (dba = dibenzylidene acetone; dppp = 1,3-bis(diphenylphosphino)propane)) with three equivalents of **1** at room temperature in acetone resulted in oxidative addition; however, the final product could not be separated from DBA by extraction with common organic solvents. The separation from DBA appeared to be crucial in later stages (vide infra). The complex [(dippp)Pd(dba)] (dippp = 1,3-bis(diisopropylphosphino)propane) did not react with three equivalents of **1** under the same conditions, probably because of the tighter binding of DBA in this electron-rich complex. When the mixture was heated at 90 °C, the product from the oxidative addition was obtained in low yield (≈10 %). The major product was [(dippp)$PdBr_2$],[17] as detected by ^{31}P NMR spectroscopy. We attributed this reactivity to electron-transfer processes that involve the electron-rich zero-valent metal center and the benzyl bromide. Because of these drawbacks, we decided to apply a slightly different approach that utilized Pd^{II} precursors. It was demonstrated that benzyl bromide oxidatively adds to [(tmeda)$PdMe_2$] (TMEDA = *N*,*N*,*N*′,*N*′-



Scheme 3. Reaction of **1** with [(tmeda)PdMe$_2$].

tetramethyl-1,2-ethanediamine) to give, after reductive elimination of ethane, [(tmeda)Pd(Br)(CH$_2$Ph)] in good yield.[18] Exchange of tmeda by an appropriate bisphosphine was expected to be a facile step.

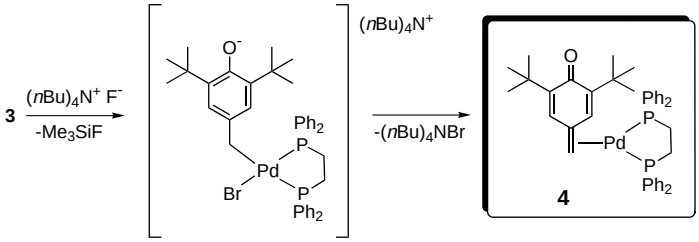
Indeed, reaction of **1** with [(tmeda)PdMe$_2$] resulted in a mixture of the benzyl complex **2** (79%) and [(tmeda)PdMe(Br)] (21%) (Scheme 3). Complex **2** was readily extracted with diethyl ether and was fully characterized by NMR spectroscopy. The CH$_2$ group bound to the metal center gives rise to a singlet at $\delta = 2.84$ in the ^{1}H NMR spectrum and to a singlet at $\delta = 14.84$ in the ^{13}C NMR spectrum. The two amine groups of the tmeda ligand are chemically nonequivalent and show four signals in both ^{1}H and ^{13}C NMR spectra. The benzyl bromide complex **2** was treated with a series of chelating bisphosphine ligands in order to exchange the tmeda ligand. The most efficient ligand-exchange reaction was obtained with dppe (bis(diphenylphosphino)ethane) (Scheme 4), and the conditions were optimized to achieve the quantitative and clean



Scheme 4. Exchange reaction of the tmeda ligand with dppe.

formation of the bisphosphine benzyl complex **3**. The ^{31}P NMR spectrum of **3** in C$_6$D$_6$ exhibits two doublets of equal intensities at $\delta = 30.12$ and 52.90 [J(P,P) = 40.6 Hz], corresponding to the two nonequivalent phosphorus atoms of the chelating ligand. The benzylic protons appear in the ^{1}H NMR spectrum as a doublet of doublets at $\delta = 3.94$ [J(P,H) = 10.5 and 5.4 Hz] as a result of coupling to the phosphines. Good exchange results were also obtained with dippp, dppp, and dtbpp (1,3-bis(di-*tert*-butyl-phosphino)propane), but other minor products, which appeared as singlets in the ^{31}P NMR spectra, were also formed. When dmpe (1,2-bis(dimethylphosphino)ethane) was added to **2**, no desired exchange product was observed. The ^{31}P NMR spectrum showed a singlet at $\delta = -1.56$ and a broad signal at 21.70. Apparently, the small size of the phosphine ligand allows more than one molecule to interact with the metal center.

Remarkably, when **3** was treated with one equivalent of nBu$_4$NF in THF, the quinone methide complex [(dppe)Pd(BHT-QM)] (**4**) was obtained in 91% yield (Scheme 5). The ammonium phenoxy intermediate formed by the cleavage of the Si–O bond, spontaneously disproportionated to give **4** and nBu$_4$NBr. Alternatively, when **3** was



Scheme 5. Formation of the quinone methide–metal complex **4** with nBu$_4$NF.

treated with one equivalent of silver trifluoromethanesulfonate (triflate, AgOTf) in wet THF in the dark, complexes **5** and **6** were formed (Scheme 6) as evidenced by ^{31}P and ^{1}H NMR analyses. Complex **5** is completely hydrolyzed into **6** within 48 hours at room temperature. Complexes **5** and **6** possess similar NMR features (see Experimental Section), except that the ^{1}H NMR spectrum of **6** lacks the pattern characteristic of the silyl protecting-group. Addition of an equimolar amount of base (tBuOK) to a solution of **6** in THF resulted in the clean formation of **4** (Scheme 6).

The ^{31}P NMR spectrum of **4** in C$_6$D$_6$ shows two sharp doublets at $\delta = 29.07$ and 37.49 [J(P,P) = 14.2 Hz], indicative of two nonequivalent phosphorus nuclei in a mutual *cis* configuration. The upfield ^{13}C chemical shift of the carbons of the coordinated double bond and their coupling to the two nonequivalent phosphines, $\delta(CH_2) = 51.34$ [d, J(P,C) = 30.8 Hz], and $\delta(C{=}CH_2) = 82.27$ [dd, J(P,C) = 12.5 and

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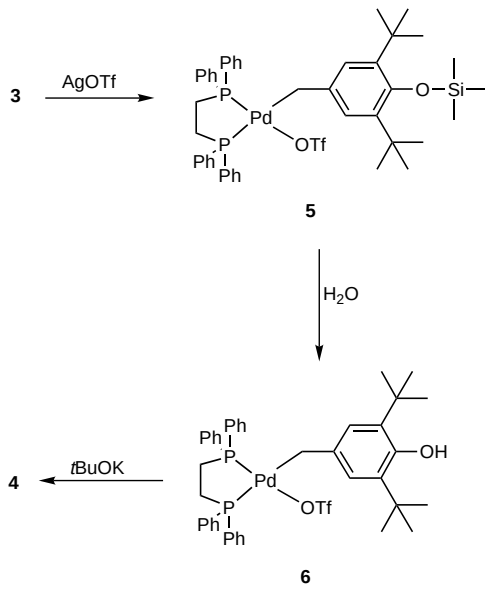


Scheme 6. Alternative formation of the quinone methide–metal complex **4** with AgOTf and subsequent hydrolysis.

4.8 Hz], as well as the doublet of doublets that originates from the benzylic protons in the ^{1}H NMR spectrum at $\delta = 3.40$ [J(P,H) = 7.2 and 3.8 Hz], indicate that coordination takes place through the exocyclic double bond. The carbonyl carbon is also coupled to the phosphorus atoms and appears as a broad doublet at $\delta = 183.96$, which is in the region observed for other 2,5-cyclohexadienones and quinones.[19] The carbonyl group of the QM moiety exhibits a characteristic, strong IR absorption band at $\tilde{\nu} = 1598\ cm^{-1}$, similar to the one reported for PCP pincer-type QM Rh^I complexes.[4]

Slow diffusion of pentane into a solution of **4** in diethyl ether resulted in orange crystals that were subjected to an X-ray diffraction study, which has already been communicated.[13] A view of a molecule of **4** is shown in Figure 2.

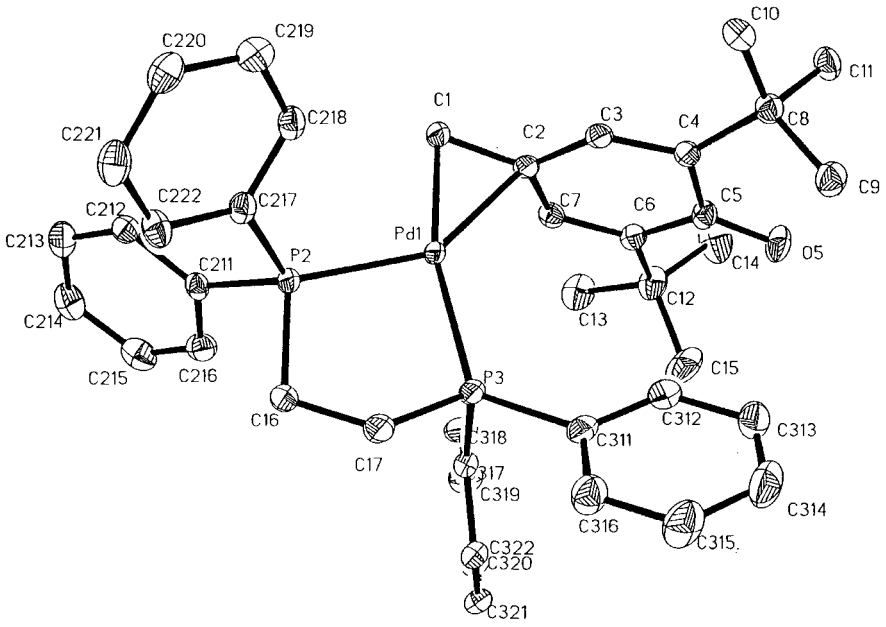


Figure 2. Crystal structure of **4**.

Selected bond distances and bond angles are given in Table 1. The Pd atom lies in a distorted trigonal-planar environment, coordinated to the two phosphorus atoms and the exocyclic double bond of the BHT-QM moiety. The

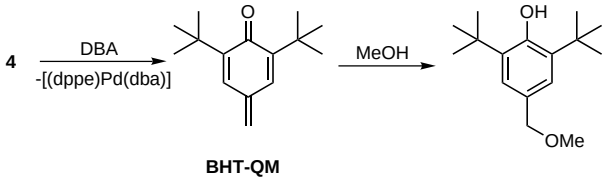
Table 1. Selected bond lengths [Å] and bond angles [°] for the crystal structure of **4**.

Pd1–C1	2.088(2)	P2-Pd1-P3	86.73(2)
Pd1–C2	2.208(2)	C1-Pd1-C2	38.97(6)
C1–C2	1.437(2)	C2-C1-Pd1	75.06(10)
C2–C3	1.443(3)	C1-C2-Pd1	65.97(10)
C3–C4	1.362(2)	C1-C2-C3	122.0(2)
C4–C5	1.474(3)	C7-C2-C3	116.7(2)
C5–C6	1.474(3)	C2-C3-C4	123.3(2)
C6–C7	1.364(3)	C3-C4-C5	118.6(2)
C2–C7	1.441(2)	C3-C4-C8	122.5(2)
C5–O5	1.251(2)	C4-C5-C6	118.1(2)
C4–C8	1.539(3)	C4-C5-O5	120.9(2)

coordinated double bond is notably elongated (1.437(2) Å) relative to that of free olefins, as a result of substantial backdonation from the metal. The quinonoid character of the ligand is reflected in the alternation of the ring bonds, whereby the C3–C4 and C6–C7 bond lengths of 1.362(2) Å and 1.364(3) Å, respectively, are noticeably shorter than the rest of the carbon–carbon bonds of the ring (cf. C2–C3 1.443(3) Å and C4–C5 1.474(3) Å). The carbonyl C5–O5 bond length of 1.251(2) Å is in the range reported for other quinonoid compounds.[20] It is noteworthy that the strong backbonding from the metal center to the QM moiety results in the loss of planarity around C2; the C1–C2 exocyclic bond is displaced out of the ring plane by 10.78° away from the palladium atom. A similar observation is reported for the structurally relevant [(PMe$_3$)$_2$Pd(pentamethylfulvene)], where the coordinated exocyclic double bond is displaced from the plane of the fulvene ring by 10.81°.[21, 22]

Complex **4** is a thermally stable compound and can be stored under a dinitrogen atmosphere for months. Remarkably, it is also stable towards gentle heating (55 °C) in benzene or even in wet MeOH, which clearly indicates that there is no spontaneous dissociation of the QM moiety from Pd. Free BHT-QM would have reacted immediately with the media were there any equilibria present involving the [P$_2$Pd] fragment and the QM moiety. Exposure of a benzene solution of **4** to air resulted in the total decomposition with quantitative formation of dppe oxide within 2 h. This oxidation process is apparently catalyzed by the metal,[23] since only partial oxidation of dppe in air was observed after heating a solution of dppe at 80 °C for 8 hours. Substitution of the

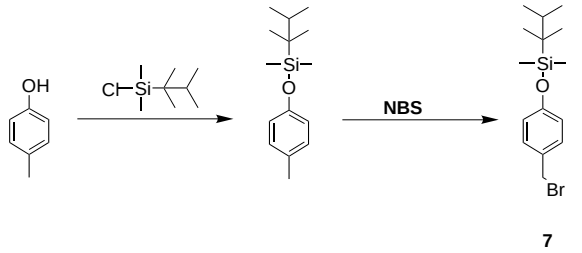
BHT-QM fragment from the metal center in **4** could not be achieved by the use of hard donor ligands, such as acetonitrile or pyridine; complex **4** remained unchanged. In contrast, reaction of **4** with the electron-deficient alkene dibenzylideneacetone (DBA) or with diphenylacetylene (DPA) resulted in the clean formation of the corresponding [P_2Pd(dba)] and [P_2Pd(dpa)] complexes. The unstable free BHT-QM was detected in a C_6D_6 reaction solution by ^{1}H NMR spectroscopy immediately after its release. When the same experiments were performed in methanol as the solvent, the free QM was trapped immediately with the formation of the 1,6-Michael-type adduct, 2,6-di-*tert*-butyl-4-methoxymethylphenol, which was detected by ^{1}H NMR spectroscopy and GC-MS (Scheme 7). Similarly, when CD_3OD was used as the solvent, a CD_3O group was incorporated into the organic product. Thus, the controlled release of free QM from the metal into solution, in which it is effectively trapped by nucleophiles, was achieved for the first time.



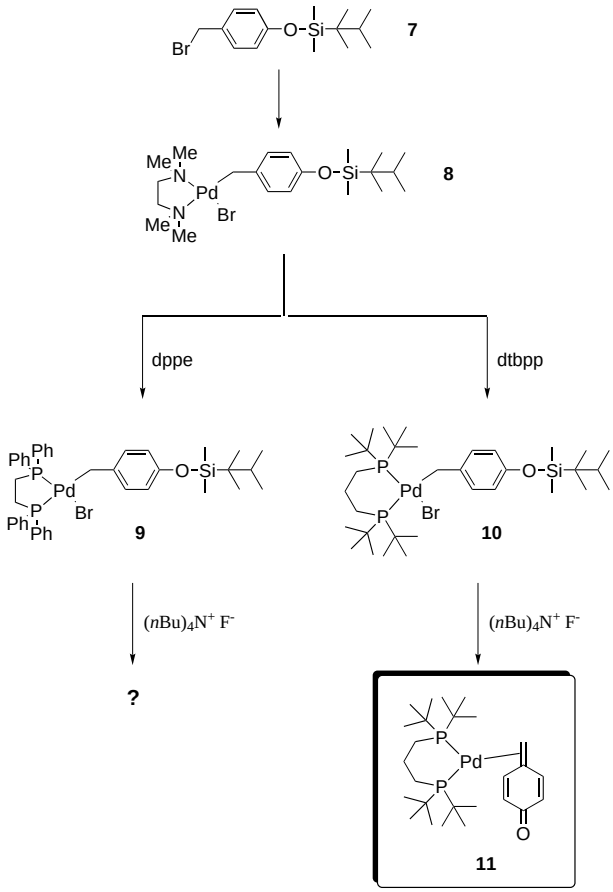
Scheme 7. Release of BHT-QM which is immediately trapped by MeOH.

Synthesis of the s-QM palladium complex: Isolation of the simplest (that is, unsubstituted) *para*-quinone methide (s-QM) can be regarded as the ultimate goal for a study which deals with stabilization of quinone methides, since it is considered as one of the most reactive members of this family of compounds. Indeed, this species reacts immediately upon formation and has never been characterized.[24] We decided to utilize the strategy outlined above to try to isolate a stable s-QM palladium complex. As in the case of BHT-QM, the trialkylsilyl ether of 4-(bromomethyl)phenol was chosen as the precursor for this quinone methide. The corresponding 4-(bromomethyl)phenyl (trimethyl)silyl ether was synthesized by silylation of *para*-cresol with Me_3SiCl followed by bromination of the product. Unfortunately, this precursor, a transparent liquid substance, rapidly decomposed to give a purple film. Presumably, hydrolysis by traces of moisture results in the unstable 4-(bromomethyl)phenol, which undergoes HBr elimination and formation of the highly reactive s-QM. In order to increase the stability of the QM precursor, we decided to use bulkier silyl protecting-groups.[25] Reaction of *p*-cresol with thexyldimethylchlorosilane (thexyl = 1,1,2-trimethylpropyl) and subsequent bromination by NBS gave 4-(bromomethyl)phenyl (thexyldimethyl)silyl ether (**7**) (Scheme 8). Neat benzyl bromide **7** also showed extensive decomposition under ambient conditions, although at a slower rate than that of the TMS analogue. Therefore, **7** was generated in a benzene solution ($\approx$0.2 M) and was kept at $-30\,^\circ$C under nitrogen. The benzene was removed under vacuum just before **7** was used.

Reaction of [(tmeda)$PdMe_2$] with **7** gave the corresponding benzyl bromide adduct **8** in 35% yield (Scheme 9). Complex



Scheme 8. Synthesis of 4-(bromomethyl)phenyl (thexyldimethyl)silyl ether (**7**).



Scheme 9. Formation of the novel Pd^0 complex of s-QM (**11**).

8 and the corresponding diphosphine Pd-benzyl complexes (vide infra) undergo slow decomposition at room temperature, probably as a result of hydrolysis of the silyl protecting-group. The ^{1}H NMR spectrum of **8** in C_6D_6 shows a singlet at $\delta = 3.36$ for the benzylic protons and two doublets for the aromatic protons [$\delta = 6.77$ and 7.83, J(H,H) = 8.5 Hz]. Treatment of **8** with dppe (1 equiv) afforded the bisphosphine palladium complex **9**. As with the related complex **3**, the ^{31}P NMR spectrum of **9** in [D_6]benzene consists of two doublets characteristic of nonequivalent phosphine groups coordinated in *cis* positions. The ^{1}H NMR spectrum shows a doublet of doublets for the aromatic protons of the benzyl group, one of which shows a small splitting as a result of coupling with ^{31}P. The benzylic protons appear as a doublet of doublets at $\delta =$ 3.93 [J(P,H) = 10.6 Hz and 5.0 Hz].

Reaction of **9** with nBu$_4$NF led to the formation of a new bisphosphine palladium complex. The ^{31}P{^{1}H} NMR spectrum

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indicates the presence of an AB spin system [$\delta = 38.62$ and 56.42, $J(P,P) = 24.6$ Hz]. The signal of the benzylic protons is strongly shifted upfield to $\delta = 1.21$ and is also split by coupling to the two nonequivalent phosphorus atoms [dd, $J(P,H) = 8.0$ and 4.0 Hz]. No signals of the thexyldimethylsilyl group are observed. The IR spectrum of this compound does not contain any sharp absorption bands in the range $\nu = 1570-1670$ cm^{-1}, which indicates the absence of a carbonyl group. While the nature of this complex is not yet clear, its spectroscopic features show no similarities to those obtained for the [(dppe)Pd(BHT-QM)] complex. Since the only difference between **9** and **3** is the presence of two bulky *tert*-butyl groups on the QM moiety, the difference in the products obtained from the reactions of these complexes with nBu$_4$NF may be the result of the availability of the phenolate group for coordination or for further reaction in the case of **9**.

In order to avoid the formation of nonquinonoid products by the interaction of the phenolate group with the metal center, steric hindrance was introduced into the system by the use of the dtbpp ligand instead of dppe. Thus, addition of dtbpp (1 equiv) to a THF solution of **8** gave the benzyl complex **10** in 52% yield. The ^{31}P{^{1}H} NMR spectrum of **10** exhibits two doublets, corresponding to the phosphorus atoms of dtbpp coordinated in *cis* positions. The benzylic protons appear as a broad doublet at $\delta_H = 3.95$ [$J(P,H) = 8.1$ Hz] and one of the doublets of the aromatic AB spin system is broadened as a result of coupling to the phosphorus atoms.

Addition of nBu$_4$NF to a THF solution of **10** results in the removal of the silyl protecting-group and the clean formation of the novel Pd^0 complex of s-QM **11** (Scheme 9). This complex shows two doublets in the ^{31}P{^{1}H} NMR spectrum for its two nonequivalent phosphorus atoms coupled to each other with a relatively low coupling constant of $J = 16.1$ Hz. Its ^{1}H NMR spectrum exhibits, in addition to the signals from the dtbpp ligand, a doublet of doublets at $\delta = 2.76$, which corresponds to the exocyclic CH_2 group that has shifted upfield. A similar shift is observed for the ring protons, which resonate at $\delta = 6.58$ and 6.91. The latter signal is coupled to one phosphorus atom, and appears as doublet of doublets. The ^{13}C{^{1}H} NMR spectrum gives rise to a broad singlet at $\delta =$ 184.36, attributed to the quinonoid carbonyl group. The exocyclic carbon appears as a doublet at $\delta = 46.89$ [$J(P,C) =$ 33.3 Hz]. The IR spectrum of **11** shows a strong absorption at $\tilde{\nu} = 1587$ cm^{-1} (with a shoulder at 1608 cm^{-1}) that originates from the C=O stretching mode of the conjugated carbonyl.

Complex **11** is thermally stable in solution and in the solid state. A sample kept under nitrogen atmosphere for two months showed no substantial decomposition. A benzene solution of **11** (3 mg, 1 mL) slowly reacted with ambient dioxygen to yield the bisphosphine oxide (approximate halflife time 2 days). Remarkably, the s-QM moiety in complex **11** is stable towards alcohols, whereas the free s-QM has no measurable life time in such media. Moreover, no displacement of the s-QM from the complex was achieved by addition of a large excess of DBA or methyl acrylate to an ethanol solution of **11**, even upon heating for 1 h at 55 °C. The observation that the s-QM could not be released from the complex [(dtbpp)Pd(s-QM)] under conditions which allowed the displacement of BHT-QM from its dppe-Pd complex **4**, can be attributed to the steric hindrance introduced by the *tert*-butyl groups on the phosphorus atoms. These groups block the approach of a new ligand to the metal, which is a requirement for the associative ligand-substitution pathway. When a solution of **11** in methanol was kept under a CO atmosphere for 12 h; discoloration of the orange solution was observed, and the ^{31}P{^{1}H} NMR spectrum indicated the complete disappearance of the s-QM complex **11**. GC-MS analysis of the mixture revealed the presence of 4-methoxymethyl phenol, the product from the addition of MeOH to s-QM. When ethanol was used as the solvent, the ethoxy analogue was detected; this indicates that the s-QM release can be achieved by the use of an appropriate ligand and the released QM species is effectively trapped in protic media to give the 1,6-Michael-type addition products.

Conclusions

We have developed a general approach towards the synthesis of simple *p*-quinone methide metal complexes. These highly reactive organic transients are generated in the coordination sphere of the metal and are stabilized by coordination of the exocyclic double bond of the quinone methide moiety to an electron-rich palladium(0) center. This coordination results in a remarkable increase in stability and inertness towards alcohol and water. Under appropriate conditions, the QM moiety can be released and trapped. The generality and efficiency of the method was demonstrated by the generation, stabilization, full characterization, and controlled release of the biologically relevant quinone methide BHT-QM and of the simplest, and so far elusive, representative of the quinone methide family, 4-methylene-2,5-cyclohexadien-1-one.

Experimental Section

General procedures: All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier). All solvents were of reagent grade or better. Pentane, diethyl ether, benzene, and THF were distilled over sodium/benzophenone ketyl. Acetone was dried by filtration through neutral alumina. 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). Commercially available reagents were used as received. [(tmeda)PdMe$_2$] was prepared as previously reported.[26]

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker DPX250 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent h_1 ([D]chloroform 7.24 ppm, [D$_6$]acetone 2.04 ppm, [D$_6$]benzene 7.15 ppm) and all-*d* solvent peaks (chloroform 77.00 ppm, acetone 29.8 ppm, benzene 128.00 ppm), respectively. ^{31}P chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% phosphoric acid sample. All measurements were performed at 21 °C. Infrared spectra were recorded on a FT-IR Nicolet PROTÉGÉ 460 spectrophotometer. IR samples were prepared in the glovebox as films on NaCl plates. The elemental analyses were performed at the Hebrew University of Jerusalem (Israel).

Synthesis of [4-(bromomethyl)-2,6-di-*tert*-butylphenoxy)]trimethylsilane (1)

Synthesis of the intermediate (2,6-di-tert-butyl-4-methylphenoxy)trimethylsilane: A solution containing 2,6-di-*tert*-butyl-4-methylphenol (5.2 g, 0.023 mol) and 1,1,1,3,3,3-hexamethyldisilazane (15 mL, 0.071 mol) in

DMF (35 mL) was refluxed under argon atmosphere for 20 h. The solution turned blue as the reflux started. Upon concentration by distillation under reduced pressure, a white precipitate was formed that was collected on a sinter, washed with DMF, and dried under vacuum to give the pure trimethylsilyl ether of 2,6-di-*tert*-butyl-4-methylphenol[15] (3.2 g, 47%), as identified by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): $\delta = 0.38$ (s, 9H; $SiMe_3$), 1.38 (s, 18H; *t*Bu), 2.24 (s, 3H; CH_3), 7.02 (s, 2H; Ar-H).

Synthesis of ***1*** *from the intermediate phenyl silyl ether*: *N*-Bromosuccinimide (400 mg, 2.2 mmol) and azobisisobutyronitrile (10 mg) were added to a CCl_4 solution (30 mL) of the intermediate phenyl silyl ether (500 mg, 1.7 mmol). The mixture was irradiated at close range with a 100 W lamp, which initiated the reflux. After 20–30 min the mixture was cooled and the floating imine was filtered off. The solvent was removed on a rotary evaporator and the residue was extracted with hexane. The dilute hexane solution (10 mL) was cooled to 4 °C for 6 h and the byproducts precipitated. From the concentrated supernatant liquid (≈4 mL) **1** crystallized (310 mg, 49%) and was isolated by decantation. ^{1}H NMR ($CDCl_3$): $\delta = 0.41$ (s, 9H; $SiMe_3$), 1.40 (s, 18H; *t*Bu), 4.49 (s, 2H; CH_2Br), 7.26 (s, 2H; Ar-H); ^{13}C {^{1}H} NMR ($CDCl_3$): $\delta = 3.97$ ($SiMe_3$), 31.12 (*t*Bu), 35.13 (*t*Bu), 35.27 (CH_2Br), 126.81 (Ar-H), 129.09 (Ar-C), 141.15 (Ar-C), 153.41 (Ar-O), the assignment was confirmed by a DEPT experiment; $C_{18}H_{31}BrOSi$: C 58.21, H 8.41; found C 58.30, H 8.16.

Synthesis of 2: A cold (−30 °C) solution of **1** (57 mg, 0.154 mmol) in acetone (2 mL) was added to a cold solution of [(tmeda)$PdMe_2$] (36 mg, 0.143 mmol) in acetone (2 mL). After standing for 15 min at −30 °C, the solvent was evaporated in vacuo, the residue was washed with pentane (4 mL), and **2** was extracted with diethyl ether (10 mL). Evaporation of the solvent gave pure **2** (67 mg, 79%). ^{1}H NMR ([D_6]acetone): $\delta = 0.37$ (s, 9H; $SiMe_3$), 1.39 (s, 18H; *t*Bu), 2.43 (s, 6H; NMe_2), 2.49 (s, 6H; NMe_2), 2.50 (t, J(H,H) = 5.5 Hz, 2H; NCH_2CH_2N), 2.79 (t, J(H,H) = 5.5 Hz, 2H; NCH_2CH_2N), 2.84 (s, 2H; CH_2Pd), 7.55 (s, 2H; Ar-H), the ^{1}H NMR of this complex in $CDCl_3$ is similar to the spectrum reported for [(tmeda)-($PhCH_2$)PdBr];[18] ^{13}C{^{1}H} NMR ([D_6]acetone): $\delta = 3.70$ ($SiMe_3$), 14.84 (CH_2Pd), 32.00 (*t*Bu), 35.49 (*t*Bu), 48.65 (NMe_2), 49.66 (NMe_2), 57.82 (NCH_2CH_2N), 63.79 (NCH_2CH_2N), 127.87 (Ar-H), 140.11 (Ar-C), 140.32 (Ar-C), 149.72 (Ar-O), the assignment was confirmed by a DEPT experiment.

Synthesis of 3: A solution of bis(diphenylphosphino)ethane (dppe; 35 mg, 0.088 mmol) in THF (1 mL) was added to a solution of **2** (52 mg, 0.088 mmol) in THF (2 mL) at −30 °C. After 30 min the solvent was removed in vacuo and the residue was washed with pentane (4 mL). Extraction of the residue with diethyl ether (7 mL) and evaporation of the solvent gave pure **3** (70 mg, 91%). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 30.12$ (d, J(P,P) = 40.6 Hz), 52.90 (d, J(P,P) = 40.6 Hz); ^{1}H NMR (C_6D_6): $\delta = 0.40$ (s, 9H; $SiMe_3$), 1.45 (s, 18H; *t*Bu), 1.50 (m overlapping with signal of *t*Bu, 2H; PCH_2CH_2P), 1.91 (dtd, J(P,H) = 27.0 Hz, J(H,H) = 8.4 Hz, J(P,H) = 5.2 Hz, 2H; PCH_2CH_2P), 3.94 (dd, J(P,H) = 10.5 Hz and 5.4 Hz, 2H; CH_2Pd), 6.97–7.10 (m, 12H; dppe), 7.31–7.40 (m, 4H; dppe), 7.75 (d, J(P,H) = 1.9 Hz, 2H; Ar-H), 7.91–7.99 (m, 4H; dppe).

Synthesis of 4 by the treatment of 3 with TBAF: Tetra-*n*-butylammonium fluoride trihydrate (TBAF, 1 equiv, 25 mg, 0.080 mmol) was added to a solution of **3** (70 mg, 0.080 mmol) in THF (2 mL). The mixture was kept at room temperature for 15 min, then the solvent was removed in vacuo. The residue was washed with pentane (4 mL) and **4** was extracted with diethyl ether (7 mL). Evaporation of the solvent gave pure **4** (53 mg, 91%). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 29.07$ (d, J(P,P) = 14.2 Hz), 37.49 (d, J(P,P) = 14.2 Hz); ^{1}H NMR (C_6D_6): $\delta = 1.61$ (s, 18H; *t*Bu), 1.83 (m, 2H; PCH_2CH_2P), 1.91 (m, 2H; PCH_2CH_2P), 3.40 (dd, J(P,H) = 7.1 Hz and 3.8 Hz, 2H; exocyclic CH_2), 6.93–7.55 (22H; Ar-H and QM-ring C-H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.53$ (dd, J(P,C) = 26.1, 16.3 Hz; PCH_2CH_2P), 26.60 (dd, J(P,C) = 26.5, 16.8 Hz; PCH_2CH_2P), 51.34 (d, 30.7 Hz, exocyclic CH_2), 82.28 (dd, J(P,C) = 12.5, 4.8 Hz, *C*=CH_2), 125–142 (Ar and QM ring), 183.96 (br d, J(P,C) = 3.7 Hz; C=O); the assignment was confirmed by a DEPT and a C-H correlation experiment; IR(neat): $\tilde{\nu} = 1598$ cm^{-1} (s); $C_{41}H_{46}OP_2Pd$: C 68.10, H 6.41; found C 68.55, H 7.05.

Synthesis of 4 by the treatment of 3 with AgOTf: Silver triflate (3 mg, 0.012 mmol) was added to a solution of **3** (10 mg, 0.011 mmol) in THF (2 mL) in the dark. The solid was filtered off and the solvent was removed in vacuo. The residue was washed with pentane (4 mL) and extracted with benzene (6 mL). ^{31}P and ^{1}H NMR analysis of the benzene extract showed two sets of signals corresponding to the triflate complex with the TMS protecting-group on the benzylic group (**5**) and the triflate complex with an unprotected phenol (**6**). The benzene solution was kept at room temperature and complete conversion of **5** to **6** was observed within 48 h (4 mg, ≈50%). Addition of equimolar *t*BuOK to a THF solution of **6** resulted in the clean formation of **4**, as observed by ^{31}P and ^{1}H NMR spectroscopy.

Compound ***5***: ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 42.66$ (d, J(P,P) = 40.4 Hz), 52.95 (d, J(P,P) = 40.4 Hz); ^{1}H NMR (C_6D_6): $\delta = 0.25$ (s, 9H; $SiMe_3$), 1.25 (s, 18H; *t*Bu), 2.04 (m, 2H; PCH_2CH_2P), 2.25 (m, 2H; PCH_2CH_2P), 3.34 (m, 2H; CH_2Pd), 6.93 (d, J(P,H) = 5.2 Hz, 2H; Ar-H), 7.08–7.74 (m, dppe).

Compound ***6***: ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 40.19$ (d, J(P,P) = 40.0 Hz), 52.75 (d, J(P,P) = 40.0 Hz); ^{1}H NMR (C_6D_6): $\delta = 1.18$ (s, 18H; *t*Bu), 1.93 (m, 2H; PCH_2CH_2P), 2.16 (m, 2H; PCH_2CH_2P), 3.34 (d, J(P,H) = 9.3 Hz, 2H; CH_2Pd), 6.85 (d, J(P,H) = 4.5 Hz, 2H; Ar-H), 7.04–7.10 (m, 4H; dppe), 7.21–7.30 (m, 12H; dppe), 7.53 (dd, J(P,H) = 12.4 Hz, J(H,H) = 8.1 Hz, 4H; dppe).

X-ray crystal structure determination of 4: Orange crystals of **4**, suitable for a single crystal X-ray diffraction study, were obtained by slow diffusion at room temperature of pentane into a diethyl ether/pentane solution (≈3:1 v/v) of **4**.

Crystal data: $C_{41}H_{46}OP_2Pd$, orange prisms, $0.3 \times 0.3 \times 0.3$ mm^3, monoclinic, $P2(1)/n$ (No. 14), $a = 9.553(2)$, $b = 28.122(6)$, $c = 13.774(3)$ Å, $\beta = 107.52(3)°$, from 25 reflections, $T = 110$ K, $V = 3528.7(13)$ Å^3, $Z = 4$, $Fw = 723.12$, $\rho_{calcd} = 1.4361$ g cm^{-3}, $\mu = 0.648$ mm^{-1}.

Data collection and treatment: Rigaku AFC5R four-circle diffractometer, $Mo_{K\alpha}$, graphite monochromator ($\lambda = 0.71073$ Å), 14156 reflections collected, $1.45 \le \theta \le 27.50°$, $-12 \le h \le 7$, $0 \le k \le 36$, $-17 \le l \le 17$, ω-scan method, scan width = 1.4°, scan speed 12° min^{-1}, typical half-height peak width = 0.25°, 3 standards were collected 72 times each, with a 4% change in intensity, 8109 independent reflections ($R_{int} = 0.0560$).

Solution and refinement: Structure solved by direct methods (SHELXS-96). Full-matrix least-squares refinement based on F^2 (SHELXS-93). Idealized hydrogens were placed and refined in a riding mode, 412 parameters with 0 restraints, final $R_1 = 0.0290$ (based on F^2) for data with $I > 2\sigma I$, and $R_1 = 0.0336$ for all data based on all 8104 reflections, goodness-of-fit on $F^2 = 1.061$, largest electron density = 0.972 e Å^{-3}. Full details are described in the Supporting Information provided with ref. [13].

Displacement and trapping of BHT-QM: A solution of dibenzylideneacetone (DBA) (3 mg, 0.013 mmol) in C_6D_6 (1 mL) was added to a solution of **4** (7 mg, 0.010 mmol) in C_6D_6 (1 mL) at room temperature. Based on ^{31}P{^{1}H} NMR integration, ≈90% conversion of **4** to the known[16] [(dppe)Pd(DBA)] was observed within 10 min. Concomitant formation of free BHT-QM was detected by ^{1}H NMR spectroscopy. Excess MeOH (ca. 2 mL) was added and the volatiles were removed in vacuo. Extraction with pentane (4 mL) gave 2,6-di-*tert*-butyl-4-methoxymethylphenol, which was identified by means of GC-MS analysis and ^{1}H NMR spectroscopy. Yields are quantitative based on ^{1}H NMR integration.

BHT-QM: ^{1}H NMR (C_6D_6): $\delta = 1.37$ (s, 18H; *t*Bu), 5.20 (s, 2H; CH_2), 6.77 (s, 2H; C-H).[5e]

2,6-Di-tert-butyl-4-methoxymethylphenol: ^{1}H NMR (C_6D_6): $\delta = 1.37$ (s, 18H; *t*Bu), 3.21 (s, 3H; OMe), 4.33 (s, 2H; CH_2O), 4.94 (s, 1H; OH), 7.31 (s, 2H; Ar-H); GC-MS (EI): m/z: 250 $[M]^+$, 235 $[M - CH_3]^+$, 219 $[M - OCH_3]^+$.[27, 28]

Reaction of 4 with air: A solution of **4** (≈5 mg) in C_6D_6 (1 mL) was exposed to air for 2 h at room temperature. ^{1}H and ^{31}P{^{1}H} NMR revealed the quantitative formation of bis(diphenylphosphinoxide)ethane (dppe-oxide).

Dppe-oxide: ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 31.17$ (s); ^{1}H NMR (C_6D_6): $\delta = 2.69$ (d, 4H; J(P,H) = 2.5 Hz, PCH_2CH_2P), 6.97 (m, 12H), 7.71 (m, 8H).[29]

Synthesis of 7: Thexyldimethylchlorosilane (6 mL, 30 mmol) was added to a solution of *p*-cresol (2.5 g, 23 mmol) and imidazole (3.9 g, 57 mmol) in DMF (10 mL). The solution was stirred at room temperature for 15 h. Hexane (20 mL) was added to create a two-phase system. The hexane phase was washed with water (10 mL) and dried with Na_2SO_4. The hexane was removed on a rotary evaporator at 30 °C to give the pure phenyl silyl ether (5.66 g, 98%). ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, 6H; $SiMe_2$), 0.95 (s, 6H; CMe_2), 0.95 (d, J(H,H) = 6.8 Hz, 6H; $(CH_3)_2CH$), 1.74 (sept, J(H,H) = 6.8 Hz, 1H; $(CH_3)_2CH$), 2.28 (s, 3H; Ar-CH_3), 6.72 (d, J(H,H) = 8.4 Hz, 2H; Ar-H), 7.02 (d, J(H,H) = 8.4 Hz, 2H; Ar-H); $C_{15}H_{26}OSi$: C 71.94, H 10.46; found C 70.80, H 10.25.

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N-Bromosuccinimide (370 mg, 2.0 mmol) and azobisisobutyronitrile (10 mg) were added to a solution of the phenyl silyl ether (410 mg, 1.6 mmol) in benzene (30 mL). The mixture was irradiated under a nitrogen atmosphere at close range with a 100 W lamp, which initiated reflux. After 20 min the mixture was cooled, the solvent was evaporated with a rotor evapotator at 30 °C until ≈7 mL remained, and the floating imine was filtered off. Based on integration of the ^{1}H NMR signals (with a program to suppress the benzene signal), the reaction mixture was found to contain 75% benzyl bromide **7** and 25% of the unreacted material. Upon removal of the solvent and exposure to air, liquid **7** hydrolized rapidly to result in a purple film. Therefore, the benzene solution of the benzyl bromide **7** (≈0.2 M) was degassed and introduced into the glovebox. Aliquots of this solution were concentrated under vacuum and dissolved in acetone immediately before use. ^{1}H NMR ($CDCl_3$): $\delta = 0.22$ (s, 6H; $SiMe_2$), 0.93 (d, J(H,H) = 6.9 Hz, 6H; $(CH_3)_2CH$), 0.94 (s, 6H; CMe_2), 1.72 (sept, J(H,H) = 6.9 Hz, 1H; $(CH_3)_2CH$), 4.48 (s, 2H; Ar-CH_2-Br), 6.77 (d, J(H,H) = 8.6 Hz, 2H; Ar-H), 7.25 (d, J(H,H) = 8.6 Hz, 2H; Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -2.44$ ($SiMe_2$), 18.54 (Me_2CH), 20.11 (Me_2C), 25.04 (Me_2C), 34.02 (CH_2Br), 34.11 (Me_2CH), 115.65 (Ar-C), 120.36 (Ar-H), 130.37 (Ar-H), 155.74 (Ar-O); the assignment was confirmed by DEPT and C-H correlation experiments.

Synthesis of 8: A cold solution (−30 °C) of **7** (1.5 mL, ≈0.3 mmol) in acetone (1 mL) was added to a cold solution of [(tmeda)$PdMe_2$] (47 mg, 0.186 mmol) in acetone (1 mL). After standing for 15 min at −30 °C, the solvent was evaporated in vacuo, the residue was washed with pentane (4 mL) and extracted with diethyl ether (7 mL). Evaporation of the ether gave **8** (36 mg, 35%). Extraction of the residue with benzene (4 mL) afforded 10 mg of the known[26] [(tmeda)$Pd(CH_3)Br$] complex (17%). ^{1}H NMR (C_6D_6): $\delta = 0.18$ (s, 6H; $SiMe_2$), 0.95 (s, 6H; CMe_2), 0.97 (d, J(H,H) = 6.8 Hz, 6H; $(CH_3)_2CH$), 1.42 (m, 2H; NCH_2CH_2N), 1.51 (m, 2H; NCH_2CH_2N), 1.73 (sept, J(H,H) = 6.8 Hz, 1H; $(CH_3)_2CH$), 1.79 (s, 6H; NMe_2), 2.24 (s, 6H; NMe_2), 3.36 (s, 2H; CH_2Pd), 6.77 (d, J(H,H) = 8.5 Hz, 2H; Ar-H), 7.83 (d, J(H,H) = 8.5 Hz, 2H; Ar-H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = -2.30$ ($SiMe_2$), 14.87 (CH_2Pd), 18.81 (Me_2CH), 20.42 (Me_2C), 25.27 (Me_2C), 34.53 (Me_2CH), 48.53 (br, NMe_2), 49.29 (br, NMe_2), 56.94 (br, NCH_2CH_2N), 62.70 (br, NCH_2CH_2N), 120.16 (Ar-H), 130.94 (Ar-H), 141.32 (Ar-C), 152.21 (Ar-O); The assignment was confirmed by a DEPT experiment.

Synthesis of 9: A cold (−30 °C) solution of dppe (7 mg, 0.018 mmol) in THF (1 mL) was added to a cold solution of **8** (10 mg, 0.018 mmol) in THF (1 mL). After standing at −30 °C for 15 min, the solvent was removed under vacuum. The residue was washed with pentane (4 mL), and extracted into diethyl ether (12 mL) with the assistance of mechanical shaking. Removal of the solvent in vacuo gave **9** (13 mg, 86%). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 32.21$ (d, J(P,P) = 40.2 Hz), 54.63 (d, J(P,P) = 40.2 Hz); ^{1}H NMR (C_6D_6): $\delta = 0.13$ (s, 6H; $SiMe_2$), 0.95 (s, 6H; CMe_2), 0.97 (d, J(H,H) = 6.9 Hz, 6H; $(CH_3)_2CH$), 1.52 (m, 2H; PCH_2CH_2P), 1.70 (sept, J(H,H) = 6.9 Hz, 1H; $(CH_3)_2CH$), 1.87 (m, 2H; PCH_2CH_2P), 3.93 (dd, J(P,H) = 10.6, 5.0 Hz, 2H; CH_2Pd), 6.56 (d, J(H,H) = 8.4 Hz, 2H; Ar-H), 6.96–7.03 (m, 12H; dppe), 7.38 (dd, J(H,H) = 8.4 Hz, weakly coupled to ^{31}P, 2H; Ar-H), 7.27–7.36 (m, 4H; dppe), 7.86–7.94 (m, 4H; dppe).

Reaction of 9 with *n*Bu_4NF: A cold (−30 °C) solution of **9** (13 mg, 0.016 mmol) in THF (2 mL) and a cold solution of TBAF (5 mg, 0.016 mmol) in THF (1 mL) were mixed and kept at −30 °C for 25 min. The solvent was evaporated under vacuum and the residue was extracted with diethyl ether (8 mL). The solution was analyzed by means of ^{31}P{^{1}H}, ^{1}H, and ^{1}H{^{31}P} NMR spectroscopy, which revealed that it contained 43% [$(dppe)_2Pd$] and 57% of a new complex, the characteristic NMR signals of which are: ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 38.62$ (d, J(P,P) = 24.6 Hz), 56.42 (d, J(P,P) = 24.6 Hz); ^{1}H NMR (C_6D_6): $\delta = 1.21$ (dd, J(P,H) = 8.0, 4.0 Hz, 2H; benzylic position), 1.69 (m, 2H; PCH_2CH_2P), 1.87 (m, 2H; PCH_2CH_2P).

Synthesis of 10: A cold (−30 °C) solution of **8** (36 mg, 0.065 mmol) in THF (1 mL) was mixed with a cold solution of bis(di-*tert*-butylphosphino)propane (dtbpp) (24 mg, 0.066 mmol) in THF (1 mL), and was kept for 20 min at −30 °C. The solution was dried under vacuum, washed with diethyl ether (4 mL), and extracted with benzene (6 mL). Removal of the solvent gave **10** (26 mg, 52%). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 30.30$ (d, J(P,P) = 49.4 Hz), 49.55 (d, J(P,P) = 49.4 Hz); ^{1}H NMR (C_6D_6): $\delta = 0.21$ (s, 6H; $SiMe_2$), 0.95 (s, 6H; CMe_2), 0.96 (d, J(H,H) = 6.9 Hz, 6H; $(CH_3)_2CH$), 1.18 (d, J(P,H) = 12.6 Hz, 18H; *t*Bu), 1.20 (d, J(P,H) = 13.0 Hz, 18H; *t*Bu), 1.70 (sept, J(H,H) = 6.9 Hz, 1H; $(CH_3)_2CH$), 3.95 (br d, J(P,H) = 8.1 Hz, 2H; CH_2Pd), 6.81 (d, J(H,H) = 8.6 Hz, 2H; Ar-H), 7.81 (br d, J(H,H) = 8.2 Hz, 2H; Ar-H).

Synthesis of 11: A cold (−30 °C) solution of *n*$Bu_4NF \cdot 3H_2O$ (7 mg, 0.022 mmol) in THF (1 mL) was added to a cold solution of **10** (17 mg, 0.022 mmol) in THF (1 mL). The mixture was kept for at −30 °C 15 min. The solution was evaporate under vacuum and washed with pentane (4 mL). Extraction of the residue with diethyl ether (7 mL) and removal of the solvent afforded spectroscopically pure **11** (12 mg, 100%). ^{31}P{^{1}H} NMR (THF): $\delta = 38.63$ (d, J(P,P) = 16.1 Hz), 52.29 (d, J(P,P) = 16.1 Hz); ^{1}H NMR (C_6D_6): $\delta = 0.85$ (d, J(P,H) = 12.7 Hz, 18H; *t*Bu), 0.92 (d, J(P,H) = 12.6 Hz, 18H; *t*Bu), 1.50 (m, coupled to ^{31}P, 4H; dtbpp), 2.76 (dd, J(P,H) = 6.0, 4.0 Hz, 2H; exocyclic CH_2), 6.58 (d, J(H,H) = 9.2 Hz, 2H; QM ring), 6.91 (dd, J(P,H) = 2.5 Hz, J(H,H) = 9.2 Hz, 2H; QM ring); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 21.57$ (dd, J(P,C) = 9.5, 1.5 Hz; $PCH_2CH_2CH_2P$), 21.79 (dd, J(P,C) = 8.6, 3.3 Hz; $PCH_2CH_2CH_2P$), 23.70 (dd, J(P,C) = 5.2 Hz, 4.4 Hz; $PCH_2CH_2CH_2P$), 29.73 (d, J(P,C) = 7.6 Hz, *t*Bu), 29.98 (d, J(P,C) = 6.2 Hz; *t*Bu), 35.68 (d, J(P,C) = 6.7 Hz, *t*Bu), 36.29 (dd, J(P,C) = 7.0, 1.5 Hz; *t*Bu), 46.89 (d, 33.3 Hz, exocyclic CH_2), 125.10 (s, QM ring), 143.50 (s, QM ring), 184.36 (s, C=O); the assignment was confirmed by a DEPT and a C-H correlation experiment; IR(film): $\tilde{\nu} = 1587$ (s), 1608 cm^{-1} (m).

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