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Advances in Metal Chemistry of Quinonoid Compounds: New Types of Interactions between Metals and Aromatics

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ABSTRACT

This Account presents an overview of current research activities that focus on novel types of interactions between cationic transition metal complexes and arene systems and on unprecedented quinonoid complexes which result from such interactions. When a negatively charged phenoxy group is present in a position para to the metal in a high oxidation state, intramolecular charge transfer occurs, giving the corresponding metallaquinones or quinone methide complexes. In addition, two types of interactions involving low-valent metal compounds have been observed: methylene arenium complexes which result from positive charge transfer to the aromatic ring and σ-bonded C−H and C−C agostic complexes of cationic metals. These σ-complexes are proposed as intermediates in metal-based bond activation processes.

Introduction

Quinonoid molecules constitute a large family of compounds that play important roles in biological systems and in industrial applications. Quinones are key compounds in photosynthesis and respiratory electron transport chains. They serve as hormones and pigments and are used as pharmaceuticals such as antibiotics and anti-cancer drugs. They are also extensively used as synthons in organic synthesis.[1] In the course of our studies of transition metal activation of strong, unstrained carbon−carbon bonds using aromatic PCP-type systems,[2] we have observed unexpected, facile dearomatization processes which led to the formation of unusual quinone methide complexes. The observed loss of aromaticity under mild conditions prompted us to investigate the driving forces causing it, as well as the more general phenomenon of quinonoid chemistry of transition metal complexes. These studies have provided insight regarding general phenomena involved upon interactions of transition metal complexes with aromatics, which are of primary importance as they lie at the basis of metal-promoted transformations of aromatic compounds and may lead to new synthetic methodology and to new materials.

In principle, one can differentiate between two possible forms of interactions: those involving metal coordination to the π-system of the aromatic ring, including intermediate cases of η^2 and η^4 coordination, and those in which the metal is directly attached to the aromatic ring via a σ-bond. The latter type is very relevant to activation of aromatic compounds by metal complexes, and also to various cross-coupling reactions involving aryl halides. Thus, it is of interest to determine the electronic factors that regulate the charge flow from the aromatic moiety to the metal and back, as well as the substituents effect on these processes.

Intramolecular Metal−Quinone Methide Complexes

We have found that Rh(I) and Ir(I) can selectively insert into a strong, unstrained C−C bond in PCP- and PCN-type ligand systems under very mild conditions.[3] The mechanism of the insertion step was proven to involve a concerted three-centered transition step, similar to the one reported for C−H bond activation (Scheme 1). There was no para-substituent effect on the rate of the bond activation process. Unexpectedly, in the case of the phenolic ligand **1d**, the resulting σ-aryl Rh(III) methyl complex **2d** was thermally unstable, giving after heating the quinone methide complex **3** (Scheme 2).[4]

Quinone methides (QMs)—a class of compounds in which one of the oxygen atoms of a quinone is replaced by a methylene (or a substituted methylene) group—are of much current interest.[5] For example, the biosynthesis of the natural polymers melanin and lignin involves *p*-QM intermediates.[6] Several antitumor drugs, including the clinically employed anthracylins and mitomycin C, are believed to generate a QM moiety as the active form.[7] Transient *p*-QM intermediates are often utilized in organic synthesis, including in the synthesis of natural products.[8] However, QMs, especially the simple ones (i.e., those not having substituents at the exocyclic methylene group), are very unstable and often unisolable in a pure form, as they rapidly polymerize upon concentration of their dilute solutions.[9] So far, no "simple" QM was isolated, except for cases in which the QM moiety is part of a fused aromatic system with little contribution from the QM form.[10] The driving force behind these rapid reactions with the medium or the self-condensation is aromatization to the zwitterionic compound, which is capable of reactions

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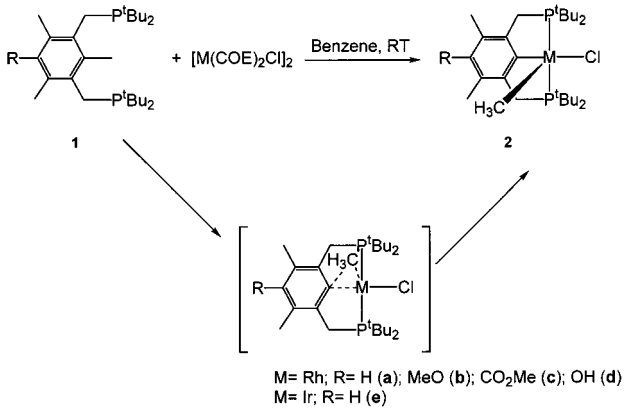
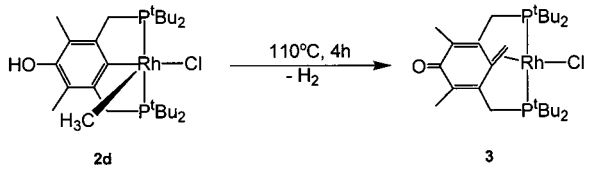
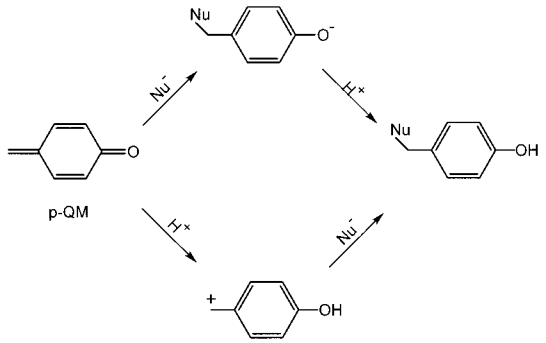
Scheme 1



Scheme 2



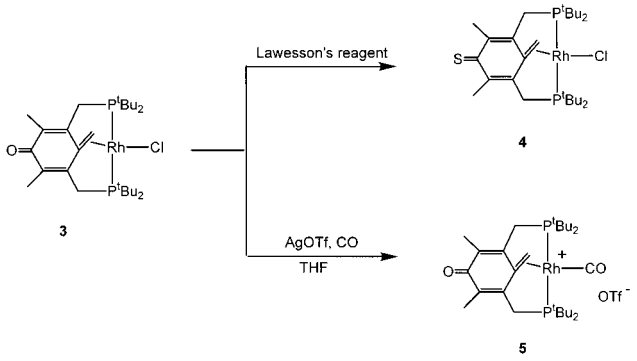
Scheme 3



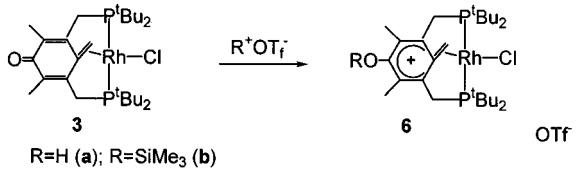
with both electrophiles and nucleophiles (Scheme 3). Therefore, the observed stability of **3** could only be attributed to the formation of a strong metal−olefin bond that remains stable even at the expense of the loss of aromaticity.

Complex **3** represents an example of a well-studied group of Rh(I) complexes of the general formula ClRh(Palkyl$_3$)$_2$(olefin). While these complexes are normally highly reactive in oxidative addition of many common reagents, such as dihydrogen, iodomethane, and hydrogen chloride,[11] the combination of the QM moiety with the diphosphine Rh(I) complex gave a product that did not react with any of the mentioned reagents, even under harsh conditions. The outstanding stability of the QM complex **3** permits the selective modification of both the metal center and the carbonyl part of the molecule, with no aromatization taking place (Scheme 4). For example, using Lawesson's reagent, it was possible to replace the carbonyl oxygen with sulfur. It is noteworthy that, in contrast to **4**, the organic thioquinone methides *are unknown*, as they undergo rapid oligomerization even when the methylene group is substituted with strong electron-withdrawing groups, such as CN.[12]

Scheme 4



Scheme 5



Positive Charge on the Ring: Methylene Arenium Metal Complexes

Exploring whether it is possible to re-aromatize the QM complex **3**, we reacted it with strong electrophiles (HOTf, Me_3SiOTf). Unexpectedly, aromatization did not take place, and the corresponding green methylene arenium complexes **6** were formed in quantitative yield (Scheme 5).[13] The crystal structure of **6a** demonstrated substantial averaging of the carbon−carbon bond distances inside the ring as compared to the corresponding bonds in the parent complex **3** (Figure 1). However, incomplete averaging indicated asymmetric positive charge distribution, with most of it being localized at the ortho- and para-carbon atoms. These findings led us to the suggestion that the methylene arenium compounds can alternatively be viewed as a discrete isolated resonance form of a benzyl cation, stabilized by coordination to a transition metal center. The structure of the benzyl cation can be described by two extreme resonance forms: the aromatic form with the positive charge at the methylene carbon atom, and the methylene arenium form, in which the positive charge is ring localized (Figure 2).[14] The former is by far more documented, especially when the methylene group is removed from the ring plane.[15] Complexes **6** represent unprecedented examples of the methylene arenium form of a benzyl cation stabilized by metal complexation. Table 1 presents a comparative analysis of the ^{13}C NMR signals of the CH_2 group in **6a** and in substituted benzyl cations.[15]

Further insight into the charge distribution came after we discovered a general approach toward the synthesis of the methylene arenium compounds. When the methyl rhodium complexes **2** (as well as the iridium complex **2e**)[3a] were reacted with a slight excess of triflic acid, hydrogen (not the expected methane!) was evolved, and the green methylene arenium complexes **6** were formed in quantitative yields (Scheme 6).[16] The proposed mechanism of this process, supported by kinetic studies, involves the forma-

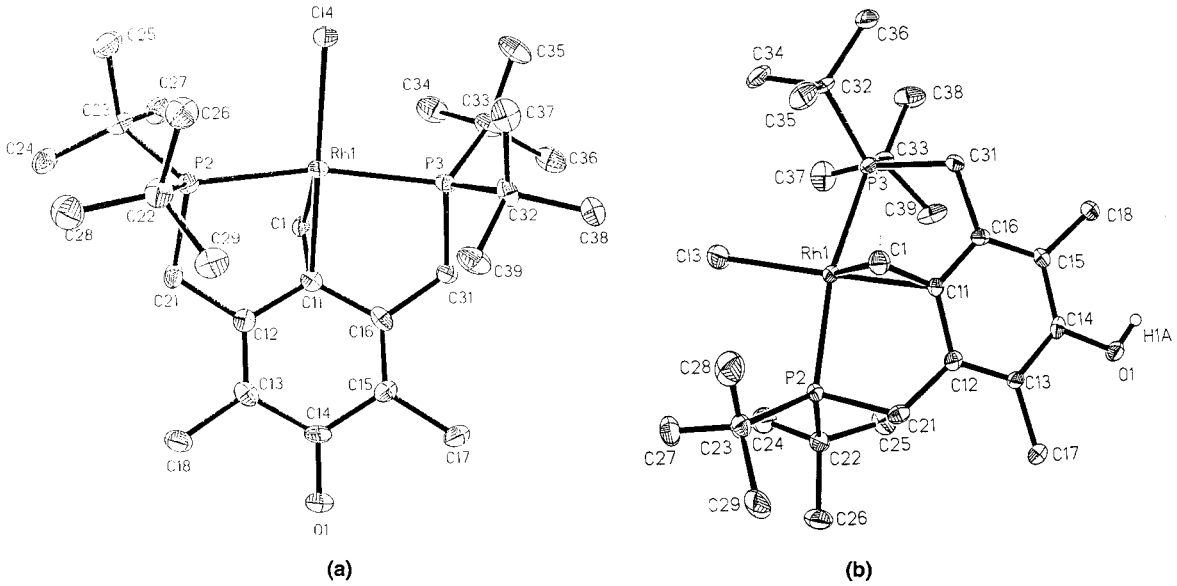


FIGURE 1. ORTEP drawing of (a) the QM complex **3** and (b) the methylene arenium complex **6a**.

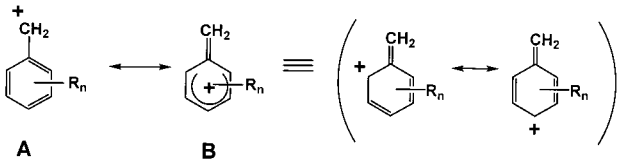


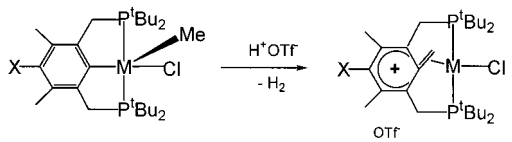
FIGURE 2. Resonance forms of the benzyl cation.

Table 1

Benzyl Cation	Methylene Carbon Atom ^{13}C NMR: δ (ppm)
$^+CR_2$, R= CH_3	+ 255
$^+CR_2$, R= adamantyl	+ 286.5
HO, P^tBu_2, Rh, Cl, P^tBu_2 (**6a**)	+ 44.15

Compare to + 41.95 in neutral **3**

Scheme 6



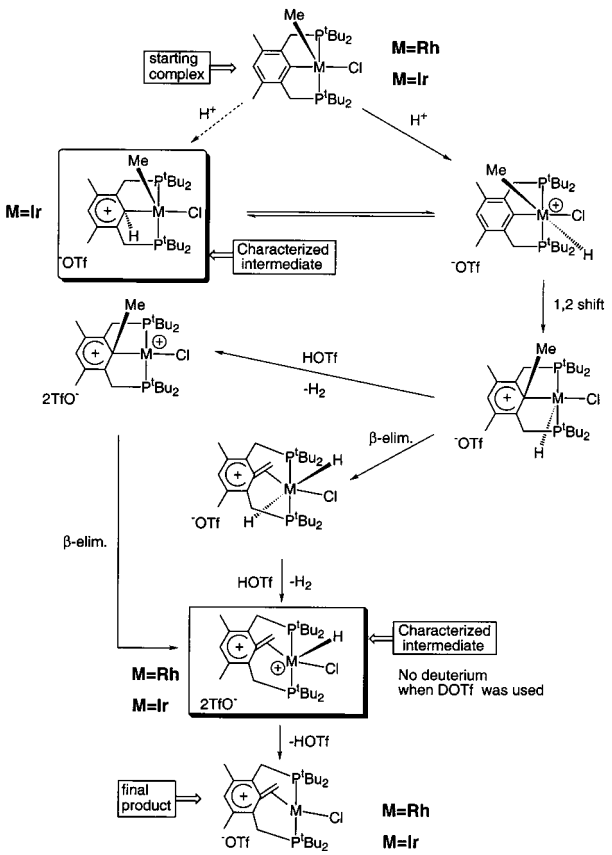
2

M = Rh; X= OH (**a**), H (**b**), CO_2Me (**c**)
M = Ir; X= H (**d**)

6

tion of the corresponding M(V) intermediate (by protonation trans to the apical methyl group), which then undergoes C−C reductive elimination, followed by β-hydrogen elimination and evolution of dihydrogen (Scheme 7). This procedure provided us with a series of methylene arenium complexes having different substituents in the position para to the ipso-carbon atom.

Scheme 7



^{13}C NMR is routinely utilized as a powerful technique to probe the positive charge distribution in carbocations in general and in benzyl cations, in particular.[17] It is expected that introducing electron-donating substituents into the position para to the methylene group should result in stabilization of ring-localized charge (i.e., meth-

Scheme 8

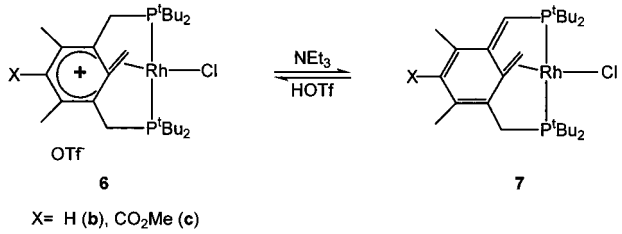


Table 2

methylene arenium complex	δ ^{13}C{^{1}H} NMR, ppm	
	=*C*H$_2$ carbon	ipso-carbon
6a (para OH)	44.15	74.06
6b (para H)	41.47	93.37
6c (para CO$_2$Me)	39.59	95.48

ylene arenium form), while electron-withdrawing groups would result in the charge being localized more at the methylene group. Table 2 presents ^{13}C NMR chemical shifts of the relevant carbon atoms in several methylene arenium Rh(I) complexes with different substituents in the para position. While, as expected, the signals of the quaternary ipso-carbon shift dramatically downfield upon going from the strong electron-donating OH group to the electron-withdrawing CO$_2$Me group (more than 21 ppm), the signals of the exocyclic methylene group shift slightly upfield (less than 5 ppm), indicating that its carbon atom does not directly participate in the positive charge delocalization, and that these compounds are best described as the methylene arenium form of a benzyl cation coordinated to a transition metal, regardless of the substituents.

The localization of the positive charge inside the ring is also evident from the reactivity of these complexes. For example, complex **5** cannot be converted into the methylene arenium complex by reacting it with 1 equiv of *p*-toluenesulfonic acid, the conjugated phenol being more acidic than the acid.[13] The rhodium complexes **6b**,**c** behave as very strong C−H acids and can be deprotonated with weak bases such as NEt$_3$ to give the xylylene complexes **7** (Scheme 8).[16] We have also prepared a stable difluoromethylene arenium complex by C−C activation of an aryl-CF$_3$ PCP ligand followed by fluoride abstraction with a Lewis acid.[18]

It is noteworthy that the methylene arenium form is clearly preferred over the benzylic Rh(III) form, in which the positive charge is localized at the metal center (Figure 3). This occurs at the expense of aromaticity in the latter form, even when electron-withdrawing substituents are present on the ring. Apparently, the localized positive charge in the M(III) benzylic species significantly reduces the stability of the arene resonance form. Table 3 demonstrates the differences in chemical shifts of key ^{1}H and ^{13}C NMR signals for three Rh and Ir methylene arenium complexes as well as the starting **1a**. The results suggest that the arenium character increases with an increase of the olefin complex stability as a result of higher back-bonding in the order of **8** < **6b** < **6d** (Figure 4).

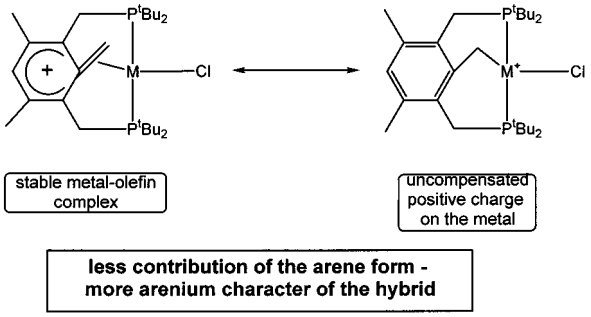


FIGURE 3. Methylene arenium complex limiting structures.

Table 3

NMR signal	DBPM ligand, ppm[a]	para H areniums, ppm			Δ (arenium−ligand), ppm		
		[RhCO]$^+$ [b]	Rh[c]	Ir[b]	[RhCO]$^+$	Rh	Ir
para H	6.80	7.98	8.60	9.20	1.18	1.8	2.4
para C	131.45	149.69	151.23	152.59	18.24	19.78	21.14
ortho C	136.30	150.42	160.80	169.28	14.12	24.50	32.98

[a] Solvent: C_6D_6. [b] Solvent: $CDCl_3$. [c] Solvent: CD_2Cl_2.

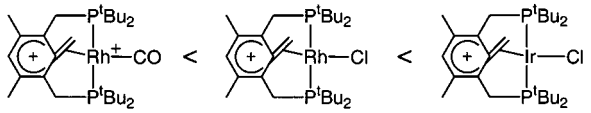
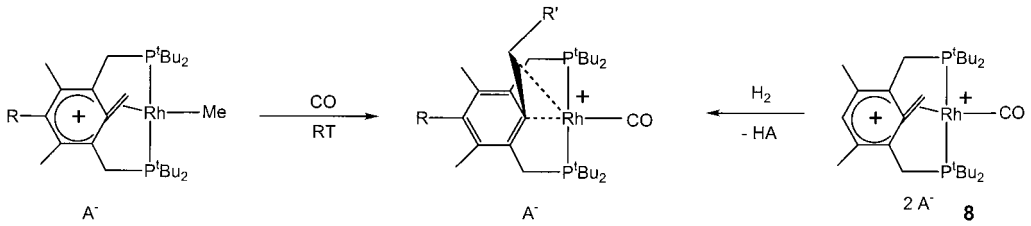


FIGURE 4. Methylene arenium complexes in order of increase of positive charge in the ring.

Positive Charge on the Metal: σ-Arenium vs Metal Agostic Complexes and Their Relevance to Bond Activation Processes in Aromatic Compounds

As it became evident that re-aromatization of the methylene arenium complexes did not take place upon varying the amount of the positive charge in the ring, we explored whether reactions at the metal center might lead to aromatization. Indeed, we found that the double bond in these complexes is susceptible to hydride[16] and alkyl migratory insertion[19] reactions in carbonyl Rh(I) complexes to give the corresponding alkyl aromatic compounds **9** (Scheme 9). Alternatively, the synthesis of **9** could be achieved as a result of C−C reductive elimination from the Rh(III) center facilitated by a carbon monoxide ligand (Scheme 10). The ^{13}C NMR spectra of complexes **9** showed no evidence of positive charge in the aromatic ring. Also, a very small *J*-coupling constant between the Rh atom and the ipso-carbon was observed. The alkyl carbon atom attached to the latter gave rise to a signal high upfield as compared with the signal of the methyl carbon in toluene derivatives (8.23 ppm in **9a**), and it showed small coupling constants due to interactions with the rhodium and phosphine nuclei. Complex **9b** was subjected to a single-crystal X-ray analysis, which clearly showed that compounds **9** are better represented as cationic alkyl aromatic metal complexes rather than σ-arenium complexes. This can be compared with a diamino pincer platinum complex for which an arenium structure was reported.[20] The ORTEP view of a cation of **9b** is shown in Figure 5.

Scheme 9



9: R=R'= H (**a**); R=R'= Me (**b**); A= BF_4; OTf

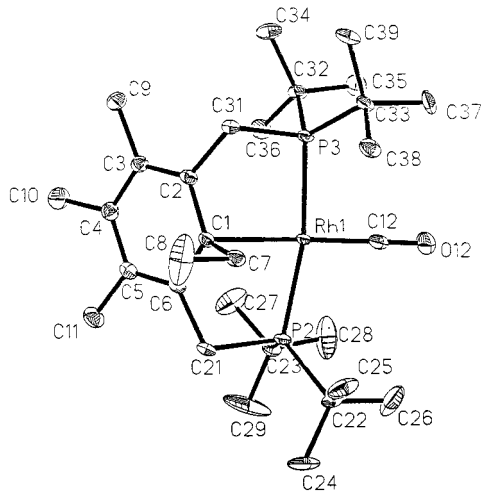
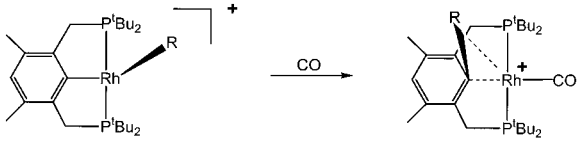


FIGURE 5. ORTEP drawing of the cationic complex **9b** exhibiting an "agostic" C−C bond.

Scheme 10



9: R=Me (**a**); CH_2Ph (**c**)

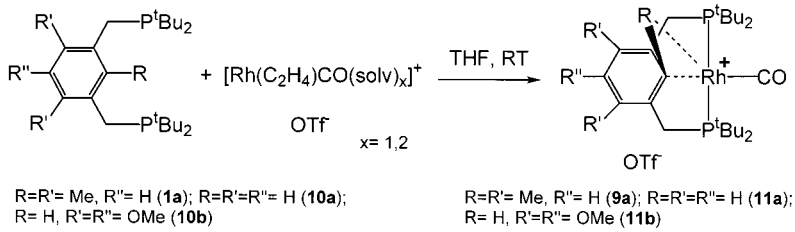
Unlike in the case of the methylene arenium complexes **6**, there is only negligible alternation in the carbon−carbon bond distances within the aromatic ring of **9b**. The Rh(1)−C(1)−C(7) bond angle of 90.25(16)° is substantially smaller than the tetrahedral angle, which speaks against the σ-arenium representation. The distance between the Rh atom and the ipso-carbon of 2.354(4) Å is extremely long for a single Rh−C bond, and even longer than a Rh−olefin bond (cf. 2.259(5) Å in **6b**). Importantly, the distance between the rhodium atom and C(7) of 2.817 Å is shorter than the sum of the van der Waals radii of the two atoms.

All this evidence speaks in favor of a stabilizing agostic interaction between the Rh and the single aryl−alkyl bond.[21] When **1a** was reacted with the $[Rh(C_2H_4)CO(solv)_x]^+$ (x = 1, 2), quantitative formation of **9a** took place, the C−C agostic complex being the thermodynamic sink of the whole system (Scheme 11). As we have demonstrated before, the [RhCl] fragment easily inserts into the C−C bond in **1**. Apparently, the substantially more electron poor $[RhCO]^+$ center cannot overcome the thermodynamic barrier to cleave the bond, and the agostically stabilized **9** could be viewed as the "arrested" transition state toward the carbon−carbon bond cleavage (Figure 6).

As the mechanism of metal insertion into a carbon−carbon bond was shown to be similar to that of insertion into a carbon−hydrogen bond, ligand **10a**, lacking a methyl substituent at the ipso-carbon, was reacted with $[Rh(C_2H_4)CO(solv)_x]^+$ (x = 1, 2). The C−H agostic complex **11a** was the only product of this reaction (Scheme 11).[22] Both the multinuclear NMR data and the single-crystal X-ray analysis indicated a strong interaction between the metal center and the C−H bond, while there was negligible contribution, if any, of the σ-arenium form. Further evidence to support our interpretation was obtained when we reacted the new ligand **10b**, bearing three methoxy substituents in the aromatic ring, with $[Rh(C_2H_4)CO(solv)_x]^+$ (x = 1, 2). The C−H agostic complex **11b** was isolated in quantitative yield. Complex **11b** showed ^1H and ^{13}C NMR data similar to those of **11a**. More importantly, a chemical shift comparison of key NMR signals of complexes **11a** and **11b** with the corresponding signals of their parent ligands demonstrated that there was practically no substituent effect between the two pairs. Had there been positive charge localized in the aromatic ring even to a minor extent, large differences between the two systems would have been expected. B3LYP/LANL2DZ density functional calculations on model compounds, performed by the group of J. M. L. Martin, fully confirmed that the agostic representation is the correct one. Interestingly, the agostic proton in **11a** is highly acidic, and it undergoes slow exchange with excess D_2O in THF. It can also be easily deprotonated by weak organic bases (NEt_3, collidine) to give **12a** (Scheme 12).

The observed reactivity of an aromatic C−H agostic complex is closely relevant to the mechanism of bond activation of aromatic compounds.[23] Although the insertion pathway a in Scheme 13 is well documented, there is little evidence in support of the generally accepted electrophilic pathway b, and no σ-arenium intermediate in C−H activation was reported. The kinetics and substituent directive effects of the latter pathway often do not follow the traditional pattern of electrophilic aromatic substitution in organic chemistry.[24] As the agostic complexes easily lose a proton upon interaction with weak bases, the agostic pathway c could be considered as an alternative to the electrophilic substitution (Scheme 13). We have shown that there is no need for substantial positive charge transfer from the metal to the aromatic ring in order to achieve "electrophilic-like" reactivity.

Scheme 11



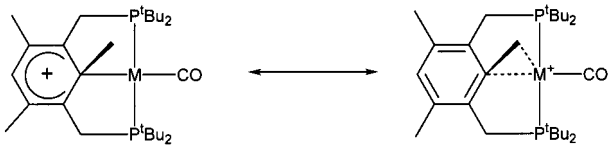
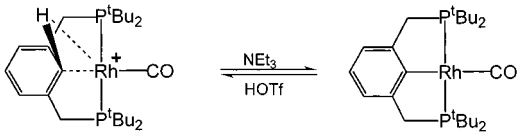


FIGURE 6. Stabilization of the arene form by an agostic C−C interaction.

Scheme 12



11a **12a**

Other examples of arene η^2 C−H agostic complexes have been reported.[25]

Charge Transfer through the Ring: Discovery of the First Metallaquinone

We were interested in preparing a metallaquinone molecule, i.e., a quinone molecule in which one of the oxygens is replaced by a metal. Despite the great importance of quinonoid compounds, especially in biology and materials science, such a compound was unknown prior to our studies. As a matter of fact, we are aware of only a single example of a stable quinonoid compound containing a heavier element (phosphorus)[26] instead of the oxygen. Whereas the excited state of quinones is biradical, we expected the metallaquinone to have a strong dipolar contribution to its excited state (Figure 7).

As none of the methods for the preparation of organic quinones was suitable for our purpose, a new synthetic pathway was designed (Scheme 14). Reaction of the phenolic PCP ligand **13** with the corresponding Ru(II) precursor, followed by addition of the strong π-acid carbon monoxide, gave the cyclometalated complex **14**. Deprotonation of **13** with a base gave the desired ruthenaquinone **15** in a quantitative yield.[27] Interestingly, the spectroscopic characteristics of **15** are solvent dependent. It is solvatochromic, being red-orange in the relatively nonpolar benzene and THF and yellow in methanol. While in benzene or THF solutions complex **15** exhibited NMR and IR signals indicative of a quinonoid system, and the IR spectrum confirmed that this structure is prevailing in the solid state as well, those signals were absent in methanol or acetone solutions. For example, the ^{13}C NMR spectra recorded in THF-d_8 show signals at 303.08 ppm (characteristic of the C═Ru carbon of carbene complexes[28]) and at 187.45 ppm (characteristic of the C═O carbon of quinones). In methanol or acetone these signals disappear, and new signals appear in the aromatic region. Likewise, the intense band of the carbonyl group at 1670 cm^{-1} in the IR spectrum of a benzene solution of **15** disappears upon dissolving **15** in methanol. The observed phenomena are a result of the presence of the neutral Ru(0) metallaquinone form of **15** in nonpolar solvents and its zwitterionic Ru(II) form in polar ones (Scheme 15). Remarkably, the metal oxidation state is influenced by the solvent. The zwitterionic **15b** was crystallized from acetone solution, and its structure was confirmed by a single-crystal X-ray analysis (Figure 8).

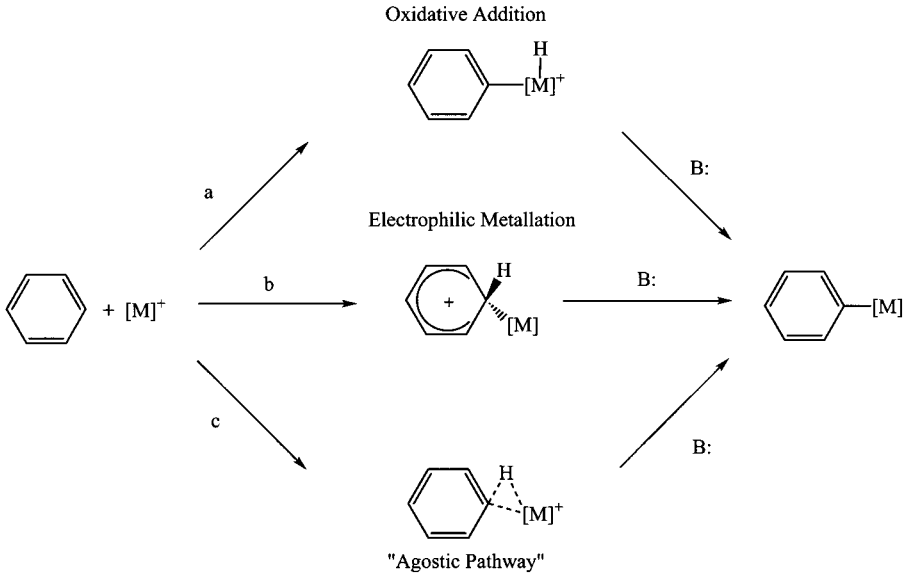
Again, as in the case of **11**, high-level calculations, performed by the group of J. M. L. Martin, have been extremely useful. DFT studies have demonstrated that the metallaquinone structure of **15** represents the minimum of energy for the system in the gas phase. Moreover, it was possible to theoretically predict the IR spectrum of **15**, which matched well the experimental data, including the first assignment of the Ru═C stretch, which appears at 1036 cm^{-1}. The electronic absorption in the visible range is assigned to an excitation from the Ru═C π HOMO into the ring π^* LUMO. Calculations show that distortion of the quinonic form to the zwitterionic form requires about 13 kcal/mol.

The isolation of the first metallaquinone, combined with its ability to reversibly transform into its zwitterionic form, might open new directions in the chemistry of the quinonoid compounds, with relevance to catalysis and materials science.

Charge Transfer through the Ring: Intermolecular Metal−Quinone Methide Complexes

Having discovered the factors that determine the charge transfer from and through the aromatic ring to the metal in the PCP bis-chelating system, we decided to pick up the challenge and design a system that would generate a "simple" quinone methide metal complex, in which the p-QM moiety is *not part of the PCP ligand system*. Such a complex would potentially allow for stabilization of a QM molecule to the extent that it could be handled in protic media and be released in a controlled fashion. As a model compound we chose the QM derived from 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT). BHT 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

Scheme 13



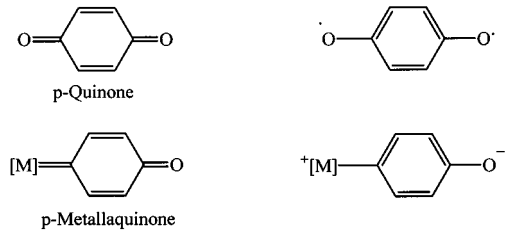
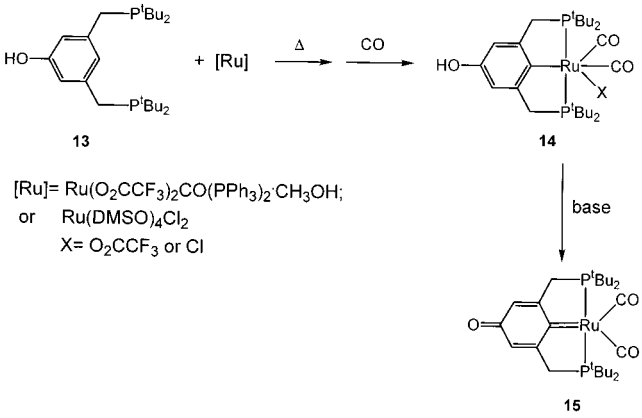


FIGURE 7. Quinone and metallaquinone.

Scheme 14



Scheme 15

compound and the toxicological effects of its metabolites, primarily the quinone methide derivative, BHT-QM, are of great interest.[29] Yet, studying the reactivity of QMs in biotic systems is seriously obstructed by the high instability of these compounds and their incompatibility with protic media.

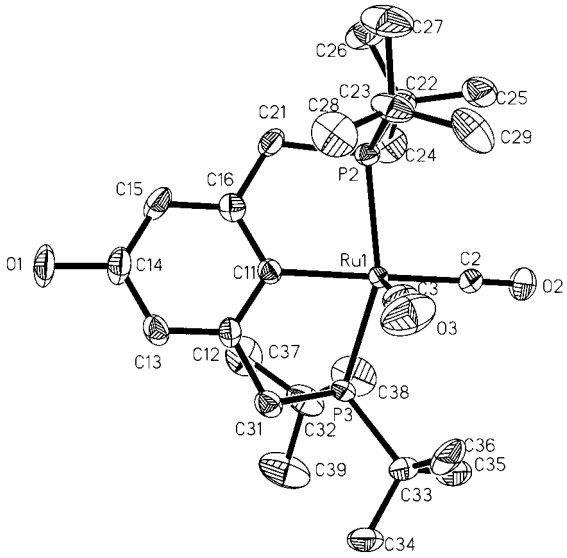
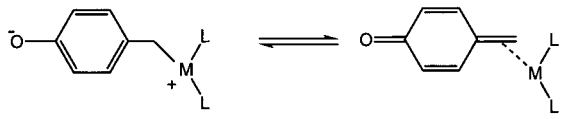


FIGURE 8. ORTEP drawing of the zwitterionic complex **15b**.

Scheme 16



Based on our previously described observations, we sought to prepare a cationic metal−benzyl complex with an oxy group in the para position. Electron transfer from the oxygen to the metal via the aromatic ring would result in formation of the QM complex (Scheme 16). Electron-rich palladium complexes were chosen as metal precursors since the resulting Pd(0) complexes were expected to have strong back-bonding interactions with the electron-poor QM moiety in the final product. Scheme 17 demonstrates the successful implementation of our hypothesis. The final BHT-QM complex **16** was formed in a quantitative yield upon removal of the protecting trimethylsilyl group.[30] The X-ray crystal structure of **16** (Figure 9) shows

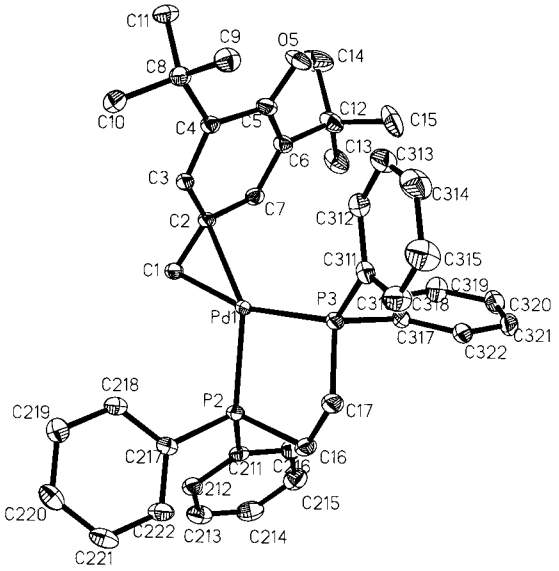
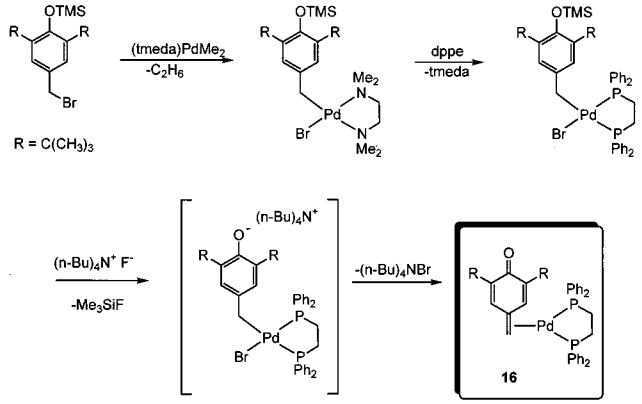


FIGURE 9. ORTEP drawing of the QM complex **16**.

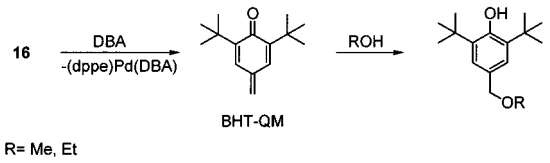
Scheme 17



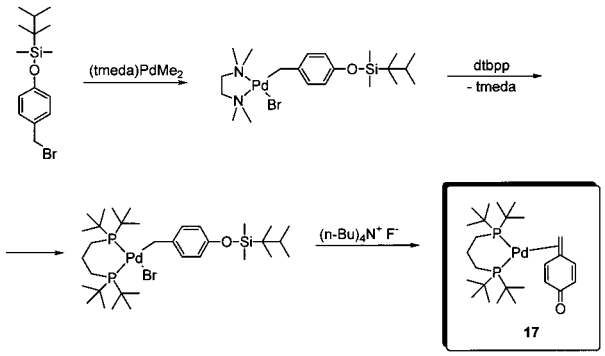
the expected alternation of the carbon−carbon bond distances in the quinonoid ring. The coordinated double bond is longer than in free alkenes due to the substantial back-bonding from Pd(0).

Similar to **3**, complex **15** is thermally stable and can be stored under a nitrogen atmosphere for months. In a clear indication of its stability toward QM dissociation from Pd, complex **16** is also stable toward gentle heating (55 °C) in benzene or even in wet methanol. Free BHT-QM would have reacted immediately with the media were there any dissociative equilibria between the P_2Pd fragment and the QM. Also, no reaction takes place when hard nitrogen donor ligands other than water (pyridine, acetonitrile) are present in solution; i.e., complex **16** is compatible with biotic media. However, controlled release of BHT-QM can be achieved by reaction of **16** with the electron-deficient alkene dibenzylideneacetone (DBA) or with diphenylacetylene (DPA), resulting in 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 substitution experiments were performed in methanol as a solvent, immediate trapping

Scheme 18



Scheme 19



of the free QM took place with formation of the 1,6-Michael-type adduct, 2,6-di-*tert*-butyl-4-methoxymethylphenol (Scheme 18). These data demonstrated, for the first time, that controlled release of free QM from the metal into solution, where it is effectively trapped by nucleophiles, could be achieved.

To demonstrate the general applicability of our approach toward generation of a simple p-QM at a palladium center, we attempted the synthesis of the simplest (i.e., unsubstituted) *p*-quinone methide (s-QM). Its isolation can be regarded as the ultimate goal of a study dealing with stabilization of quinone methides, as it reacts immediately upon formation and has never been characterized.[31] To generate the s-QM metal complex, we used the same strategy that was applied for the preparation of **16** with slight modifications. Scheme 19 presents the successful synthesis of the s-QM Pd(0) complex **17**, showing that the concept is general and practically any simple p-QM can be generated at the metal center.[32]As with **16**, complex **17** is thermally stable in solution and in the solid state. A sample kept under nitrogen atmosphere for 2 months showed no substantial decomposition. The s-QM moiety in complex **17** is stable toward alcohols, whereas the free s-QM has no measurable lifetime in such media. 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 **17**, 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 **16** is 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, required for the associative ligand substitution pathway. Displacement of s-QM from the Pd center in **17** can, however, be achieved by keeping its methanol solution under a CO atmosphere for 12 h. The GC−MS analysis of the mixture revealed the presence of the product of addition of MeOH

to s-QM, 4-methoxymethyl phenol. When ethanol is used as solvent, the ethoxy analogue is detected, showing that the s-QM release can be achieved by using an appropriate ligand, and the released QM species is being effectively trapped in protic media, resulting in the 1,6-Michael-type addition products. A few other QM complexes have been recently reported, although release of the QM moiety was not observed.[33]

Summary and Outlook

In this Account we presented the story of novel types of interactions between transition metals and aromatics. When a late transition metal center in a high oxidation state is coordinated to a *p*-phenoxy or *p*-oxybenzyl group, intramolecular charge transfer takes place, resulting in the formation of metallaquinones or quinone methide complexes. This results in a two-electron reduction of the metal. When no electron-donating group is present and the metal complexes are positively charged, the positive charge can be "stuck" between the metal and the aromatic ring. Two extreme situations can be observed. One involves the transfer of positive charge from the metal to the aromatic ring with metal stabilization from the outside, as is the case with methylene arenium complexes. The other involves a positively charged metal center stabilized by η^2 C−H or C−C agostic bonds with the aromatic moiety. The newly discovered C−H and C−C agostic interactions with the metal in the aromatic compounds provide unique information about the mechanism by which metal complexes insert into these bonds, as these agostic complexes can be viewed as arrested transition states for the insertion step. In addition, the observed acidity of the C−H agostic compounds provides an alternative route toward the activation of aromatic compounds by electron-poor late transition metal complexes.

With regard to the metal chemistry of the quinonoid compounds, one can see two major ways to explore the reported phenomena. One lies in the area of charge transfer through expanded conjugated systems. For example, would the formation of a metallaquinone take place when more than one aromatic ring is present in the system? If the answer is yes, then these new compounds can be good candidates for materials that require low-energy charge transfer through the long chain of conjugated bonds. The media-dependent reversible transformations between the quinonoid and zwitterionic forms demonstrate that the energy levels of these two forms are close, which could be applied to NLO materials or molecular switches.

Possible applications of metal−quinone methide complexes might be in the biological studies of active quinone methide forms. As most biologically active quinone methides are not isolable and/or are incompatible with biotic media, their metal complexes might serve as a supply of quinone methides. The ability of these metal complexes to release the quinone methide molecule in a controlled way could be relevant to drug delivery in biological systems. Various controlled release approaches are currently under investigation.

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