Nucleophilic Aromatic Addition Reactions of the Metallabenzenes and Metallapyridinium: Attacking Aromatic Metallacycles with Bis(diphenylphosphino)methane to Form Metallacyclohexadienes and Cyclic \( \eta^2 \)-Allene-Coordinated Complexes

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Abstract: The reactions of phosphonium-substituted metallabenzenes and metallapyridinium with bis(diphenylphosphino)methane (DPPM) were investigated. Treatment of [Os(CHC\((PPh_2)CH(CHC(PPh_3)CH)Cl_2(PPh_3)]Cl with DPPM produced osmabenzenes \([Os(CHC(PPh_2)CH(CHC(PPh_3)CH)]Cl_2(PPh_3)]Cl\) and [Os(CHC(PPh_2)CH(CHC(PPh_3)CH)]Cl\((PPh_3)CH_2Cl\) (2), [Os(CHC(PPh_2)CH(CHC(PPh_3)CH)]Cl\((PPh_3)CH_2Cl\) (3), and cyclic osmium \( \eta^2 \)-allene complex [Os(CH=C(PPh_3)CH=\((\eta^2-C=CH)]Cl_2([PPh_3]CH_2([PPh_3)]Cl) (4).\] When the analogue complex of osmabenzone 1, ruthenabenzone [Ru(CHC(PPh_3)CH(C(PPh_3))CH\((PPh_3)]Cl_2(PPh_3)]Cl, was used, the reaction produced ruthenacyclohexadiene \([Ru(CH=\(C\)PPh_3)CH=\((\eta^2-C=CH)]Cl_2(PPh_3)]Cl_2(PPh_3)]Cl\) (2) and \([Ru(CH=\(C\)PPh_3)CH=\((\eta^2-C=CH)]Cl_2(PPh_3)]Cl_2(PPh_3)]Cl\) (3), which could be viewed as a Jackson–Meisenheimer complex. Complex 6 is unstable in solution and can easily be converted to the cyclic ruthenium \( \eta^2 \)-allene complex \([Ru(CH=C(PPh_3)CH=\((\eta^2-C=CH)])([PPh_3]CH_2([PPh_3)]Cl_2(PPh_3)]BF_4 (11).\]

Keywords: metallabenzenes • metallacycles • metallapyridinium • nucleophilic addition • transition metals

Introduction

Transition-metal-containing metallalaaromatics have recently attracted considerable attention because they can display aromatic properties and mediate organometallic reactions.[1–4] Particularly, significant progress of the chemistry of metallabenzenes has been made.[1–4] Previous studies have led to the isolation and characterization of a remarkable number of stable metallabenzenes.[5] Very rich chemical properties of metallabenzenes have also been demonstrated. Unique characteristic chemical reactions, for example, electrophilic aromatic substitution (S_{E-Ar}) and nucleophilic aromatic substitution (S_{N-Ar}), provide strong chemical support for the aromaticity of the metallabenzenes ring. However, S_{E-Ar} and S_{N-Ar} reactions of metallabenzenes are only seen in a few reports,[5,6] partly due to the relatively more reactive metal center.

Agreement with the theoretical prediction about the stability of metallabenzenes by Thorn and Hoffmann,[7] most of the stable metallabenzenes are those with \( \pi \) donors ortho or para to the metal. In contrast, well-characterized metallabenzenes bearing electron-withdrawing groups have rarely been isolated.[8–10] The iridabenzenes and related iridanaphthalene reported by Paneque et al. represent the first examples of metallabenzenes with electron-withdrawing groups, namely CO_2Me.[11] We prepared a series of phosphonium-substituted metallabenzenes, including osmabenzenes and ruthenabenzenes.[12,13] The bicyclic species, which were described as tethered metallabenzenes by Roper, Wright, and co-workers, constitute an addition to the special class of

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metallaaromatics containing electron-withdrawing groups.\textsuperscript{[10]} It has been demonstrated that Paneque’s iridabenzenes could undergo nucleophilic attack at the para carbon atom of a metallacycle due to the electronic effects introduced by the electron-withdrawing groups.\textsuperscript{[8a,b]} In this regard, it is reasonable to assume that nucleophilic attack would also occur in our phosphonium-substituted metallaaromatics.

Recently, we reported the first \textit{S}_\text{Ar} reaction of metallabenzenes [Eq. (1)]\textsuperscript{,}[9] In light of the success that the osmaben-\begin{figure}[h]
\centering
\includegraphics[width=4cm]{image1.png}
\caption{Scheme 1. Reaction of osmabenzenes with DPPM: a) DPPM (1:1 molar ratio), CHCl$_3$, 60°C, 20 min; b) excess DPPM (1:3 molar ratio), CHCl$_3$, 60°C, 5 h; c) excess DPPM (1:2 molar ratio), CHCl$_3$, 60°C, 24 h.}
\end{figure}zene \textsuperscript{[4]} [\text{Os}^\text{CHC}(\text{PPh}_3)\text{CH}([\text{SCN}])\text{CH}((\text{NCS})_2\text{(PPh}_3)_2)] bearing a phosphonium substituent and a reactive thiocyanato group on the metallacycle could undergo intramolecular \textit{S}_\text{Ar} reaction, we studied the reactions of phosphonium-substituted metallaaromatics and metallaaromatic compounds with external nucleophile bis(diphenylphosphino)methane (DPPM), which may provide various binding modes besides being a nucleophilic reagent. However, the nucleophilic aromatic addition reactions of aromatic metallacycles were observed, rather than the expected \textit{S}_\text{Ar} reactions. During this study, we isolated interesting metallacyclopenta- and \textit{n}-allene-coordinated metallacycles. Thus, it gives new hope for the future development of our metallaaromatics in the synthesis of new metallacycles. The details of our findings are reported in this paper.

Results and Discussion

Reactions of osmabenzenes with DPPM: We presented that osmabenzenes \textsuperscript{[4]} [\text{Os}([\text{CHC(PPh}_3]_{\text{CH}}([\text{SCN}])_{\text{CH}}([\text{NCS}])_{\text{2}}][\text{(PPh}_3)_{\text{2}}]) could undergo an intramolecular \textit{S}_\text{Ar} reaction at ambient temperature and pressure to form a new fused metallaaromatic compound [Eq. (1)], which demonstrated that the nucleophilic reactivity of the metallacycle can be promoted when the electron density of the aromatic ring is significantly decreased in the presence of the transition-metal center and the electron-withdrawing phosphonium group.\textsuperscript{[4]} Since the phosphonium group can decrease the electron density of the metallacycle, we expect that osmabenzenes \textsuperscript{[4]} has two phosphonium groups positioned \textit{meta} to the metal center on the metallacycle, is more likely to facilitate the approach of a nucleophile.

To test this hypothesis, we initially studied the reactivity of \textsuperscript{1} with DPPM. However, \textsuperscript{1} is not reactive enough and does not undergo a \textit{S}_\text{Ar} reaction. Instead, it was consumed very slowly, as indicated by its poor NMR spectroscopy, when a solution of complex \textsuperscript{1} and DPPM (in 1:1 molar ratio) in CHCl$_3$ was stirred at room temperature. When the mixture was heated at 60°C for about 20 min, the reaction produced a green solution and the product could be isolated in high yield and identified as osmabenzenes \textsuperscript{2} (Scheme 1).

The structure of \textsuperscript{2} has been confirmed by an X-ray diffraction study. In agreement with the structure, the \textsuperscript{1}H NMR spectrum displays the two characteristic OsCH signals at $\delta = 17.3$ and 17.0 ppm. The \textsuperscript{13}C\textsuperscript{(1)}H NMR spectrum shows five signals at $\delta = 253.8$ (OsCH), 245.6 (OsCH), 150.4 (OsCHC(PPh$_3$)CH), 120.0 (C(PPh$_3$)), and 114.0 ppm (C(PPh$_3$)) for the carbon atoms of the metallacyclic ring. It clearly reveals that the two P atoms chelate to the metal center to result in a four-membered osmajacyle and the complex is only a simple diphasphene substitution product with displacement of two PPh$_3$ ligands of the metal center in complex \textsuperscript{1} (see Figure S1 in the Supporting Information).\textsuperscript{[12]}

To achieve the nucleophilic attack on a carbon atom of the metallacycle, we increased the proportion of DPPM in the reaction. When a mixture of \textsuperscript{1} and excess DPPM (in a 1:3 molar ratio) in CHCl$_3$ was heated at 60°C for 5 h, a yellow/brown solution containing predominantly \textsuperscript{2} along with small amounts of \textsuperscript{4} and some unidentified species was produced (Scheme 1). When the solution was left heating for 24 h, the reaction was cleaner. In this case, complex \textsuperscript{4} can be isolated as a yellow solid in 82% yield. The reaction of isolated \textsuperscript{2} with excess DPPM gave the same result.

As the unidentified species are in small amounts, it is difficult to characterize them. Fortunately, after recrystallization of the crude product from dichloromethane/n-hexane, a single crystal of \textsuperscript{3} was obtained, making it possible to determine its solid-state structure. As suggested by the structure (see Figure S2 in the Supporting Information),\textsuperscript{[11]} complex \textsuperscript{3} may be regarded as an intermediate of the transformation of \textsuperscript{2} to \textsuperscript{4}.

Complex \textsuperscript{4} can be stored in the solid form in an inert atmosphere for at least one month without appreciable decomposition. The structure of \textsuperscript{4} can be readily deduced on the basis of NMR spectroscopy. The \textsuperscript{1}H NMR spectrum shows the signal of OsCH at $\delta = 11.7$ ppm, the signal of $\text{NCS} = \text{CH}(\text{PPh}_3)$ at $\delta = 3.4$ ppm, and the signal of C=PPh$_3$CH
at $\delta = 7.2$ ppm. In the $^{31}$P[1H] NMR spectrum, the signal of CPPh$_3$ appears at $\delta = 9.3$ ppm. And those signals of two DPPM chains are observed at $\delta = 43.8$ ((PPPh$_2$)$_2$CH) – (PPPh$_2$)CH, $-13.1$ ((PPPh$_2$)CH(PPPh$_2$)CH, $-5.8$ (OsPPPh$_2$CH(PPPh$_2$)), and $-28.2$ ppm (OsPPPh$_2$CH(PPPh$_2$)), respectively. In the $^{13}$C[1H] NMR spectrum, the signals of OsCH and CPPh$_3$ appear at $\delta = 207.2$ and 116.5 ppm, whereas the three carbon signals of the coordinated allene backbone appear at $\delta = 184.6$ ($\eta^2$-C=CH(PPPh$_2$)), 120.8 (OsCHC(PPPh$_2$)CH), and 18.6 ppm ($\eta^2$-C=CH(PPPh$_2$)), respectively.

The structure of 4 has also been determined by X-ray crystallography. A view of the complex cation is shown in Figure 1. The X-ray diffraction study confirmed that the complex contains a conjugated osmacycle with a terminal double bond of an allene coordinated to the metal atom. The metallacycle of 4 deviates significantly from planarity, as reflected by the sum of angles in the six-membered ring of 668.4°, which is significantly smaller than the ideal value of 720°. C5 lies 0.4135 A out of the plane of the five-membered ring (Os1/C1/C2/C3/C4). The dihedral angle between the Os1/C1/C2/C3/C4 plane and the Os/C4/C5 plane is 18.1°. As a consequence of its coordination to the metal center, the allene unit is strongly bent with a C3-C4-C5 angle of 152.2°.

Complex 4 is structurally related to our previously reported cyclic osmium $\eta^1$-allene complexes, which belong to the rare examples of metallacycles bearing an intramolecularly coordinated allene group. We have also demonstrated that a similar cyclic $\eta^1$-allene complex can isomerize to metalallabenzenne. Although the related metallabenzenne product of the S$_2$Ar reaction was not detected, we suppose that the nucleophilic attack of DPPM to osmabenzen 1 may occur and it may also be possible that the $\eta^1$-allene-coordinated osmacycle 4 is the isomer of the product of an S$_2$Ar reaction.

Reactions of ruthenabenzen with DPPM: To further study the nucleophilic attack of DPPM to a metallacycle, we also investigated the reactions of DPPM with the ruthenabenzen 5, that is, the analogue complex of osmabenzen 1, which is much more reactive as shown by our previous study. As indicated by an in situ NMR spectroscopic experiment, the reaction of ruthenabenzen 5 with DPPM (in 1:3 molar ratio) in CHCl$_3$ cleanly produced the ruthenacyclohexadiene complex 6 (Scheme 2). The reaction was essentially completed in approximately 2 h at room temperature.

Figure 1. Molecular structure for the cation of complex 4 (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–P1: 2.4057(15), Os1–P3: 2.3540(14), Os1–C11: 2.4319(15), Os1–Cl2: 2.5098(14), Os1–C1: 2.028(6), Os1–C4: 2.003(5), Os1–C5: 2.158(6), C1–C2: 1.364(7), C2–C3: 1.459(8), C3–C4: 1.348(7), C4–C5: 1.387(8), P4–C5: 1.779(6), P5–C2: 1.757(6); P1–Os1–P3: 176.11(6), Cl1–Os1–Cl2: 84.12(5), C1–Os1–C4: 72.5(2), C1–Os1–C5: 109.5(2), Os1–C1–C2: 122.2(4), C1–C2–C3: 111.1(5), C2–C3–C4: 108.8(5), C3–C4–C5: 152.2(6), C3–C4–Os1: 125.3(5), C4–C5–Os1: 64.6(3), C5–C4–Os1: 76.7(3).

Complex 6 was isolated as a reddish-brown solid. Its structure has been established by X-ray diffraction. As shown in Figure 2, Ru1, C1, C2, C3, and C4 are almost coplanar, which is reflected by the deviation (0.0363 Å) from the RMS planes of the best fit, whereas C5 lies 0.5209 Å out of the ring. The dihedral angle between the Ru1/C1/C2/C3/C4 plane and the Ru1/C4/C5 plane is 31.4°. The nonplanarity of the metallacycle is presumably due to the steric effects of the substituent DPPM. The nonplanar structure of 6 is similar to the six-membered ring of the iridacyclohexadiene [Ir(CH=C(Me)CH=C(Me)CH)O–C(=O)–C(CH$_2$)$_3$], which has been described as a half-boat conformation by Blecke. The bond length of Ru1–C1 (1.977(8) Å) is within the range of those observed for typical Ru–C(vinyl) single bonds (1.932–2.141 Å). The Ru1–C5 length (2.261(8) Å), which is appreciably longer than the bond length of Ru1–C1 (1.977(8) Å), is expected for Ru–C(sp$^3$) single bonds (1.954–2.418 Å). The original delocalization in the metallacycle has been destroyed, as reflected by the marked short-long C–C distance alternations. The C1–C2 (1.382(11) Å) and C3–C4 (1.345(11) Å) bonds are apprecia-
Figure 2. Molecular structure for the cation of 6 (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–P3: 2.333(2), Ru1–P1: 2.429(2), Ru1–P2: 2.374(2), Ru1–Cl1: 2.538(2), Ru1–C1: 1.977(8), Ru1–C5: 2.261(8), C1–C2: 1.382(11), C2–C3: 1.436(10), C3–C4: 1.345(11), C4–C5: 1.501(12), P4–C5: 1.803(7), P5–C2: 1.791(9), P6–C4: 1.826(9), P3–Ru1–P5: 171.13(8), C1–Ru1–C5: 89.8(3), Ru1–C1–C2: 128.9(3), C2–C1–C2: 123.5(8), C2–C1–C4: 128.7(8), C3–C4–C5: 124.1(8), C4–C5–Ru1: 115.0(5).

Solution NMR spectroscopic data and elemental analysis of 6 are consistent with its solid-state structure. Six sets of resonances and reciprocal coupling lead to the quite complicated 31P{1H} NMR spectrum of 6. The signals of CPh3 appear at δ = 22.0 and 17.7 ppm and those of RuPPh2CH2PPh2 appear at δ = −14.5 and −17.9 ppm, whereas the other two phosphorus signals of the RuPPh2CH2PPh2CH chain are observed at δ = 48.5 and 25.5 ppm, respectively. The 1H NMR spectrum has three characteristic CH signals at δ = 13.4 (RuCH(sp3)), 6.4 (RuCH(CPPh3)), and 4.8 ppm (RuCH(sp3)). The 13C{1H} NMR spectrum displays the carbon signals of the metallacycle at δ = 251.8 (RuC(sp3)), 112.3 (C(PPh3)), 151.7 (RuCH(CPPh3)CH), 107.7 (C(PPh3)), and 13.2 ppm (RuC(sp3)), respectively.

Metallacyclohexadienes and their reaction chemistry are currently of considerable interest. The interconversions between metallacyclohexadienes and metallabenzenes have been explored during the last decade. Paneque et al. demonstrated that the nucleophilic attack of OH- or MeO- to iridaaromatics allows the formation of Jackson–Meisenheimer complexes [Eq. (2)].

In our reaction, ruthenacyclohexadiene 6 could also be viewed as a Jackson–Meisenheimer complex and provides another piece of evidence for the aromatic nature of metallabenzenes, which could undergo the nucleophilic aromatic addition reaction. It is also worth noting that 6 could be described as the first example of isolated ruthenacyclohexadiene. The earlier reported complex [Ru(C4H2(CO)Me-2)(CO)Me-4(CHCO)Me-5](CO)(PPh3)] is now generally recognized as a metallabenzo furan considering its delocalization within the ruthenacyclic system.

Solid samples of complex 6 can be stored in air at ambient temperature for at least two weeks without appreciable decomposition. However, 6 is unstable in solution and can easily convert to the cyclic ruthenium η2-allene complexes. As indicated by in situ NMR spectroscopy, when a solution of 6 in CHCl3 was stirred at room temperature for four days, 6 was completely consumed to give a 1:1 mixture of 7 and 8 (Scheme 2). When the mixture of 7 and 8 was refluxed for a further 30 min, the mixture would entirely convert to 8 as the final product. A similar result was obtained when a stirred solution of 6 in CHCl3 was left standing for one week.

The poor solubility of 7 in the solvent mixture helps the separation of 7 and 8. Crystals suitable for X-ray diffraction were grown from a CHCl3 solution of 8 layered with n-hexane. Definite proof of the structure came from a single-crystal X-ray structure analysis. Obviously, 8 is the analogue complex of the cyclic osmium η2-allene complex 4. As shown in Figure 3, Ru1, C1, C2, C3, and C4 are coplanar, which is reflected by the deviation (0.0039 Å) from the RMS planes of the best fit, whereas C5 deviates out of the plane.
ring. The dihedral angle between the five-membered ring (Ru1/C1/C2/C3/C4) and the three-membered ring made up of Ru1, C4, and C5 is 19.7°. Similar to complex 4, the allene unit of 8 also deviates from linearity, as reflected by the C3-C4-C5 angle of 151.8°. The angle is close to the allenylcarbone complex \([\text{Ru}=\text{C}(\text{Rc})-\eta^1\text{C}=\text{C}=(\text{Rh})]\) (Cp)-\((\text{PPh}_3)\text{PF}_6\) (138.6°),

while much smaller than our previously reported osmium complex \([\text{Os}(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=(\text{Ph})\text{(Cp)Cl}]\text{PF}_6\) (171.0°).\cite{9d}

Scheme 3. Proposed mechanism for the reaction of metallabenzenes with DPPM.

- **Proposed mechanism for the reaction of metallabenzenes with DPPM**: Scheme 3 shows a proposed mechanism for the formation of metallacyclohexadiene and \(\eta^2\)-allene-coordinated metallacycles in the reaction of metallabenzenes with DPPM. The \(\text{PPh}_3\) ligand in metallabenzenes I could initially be displaced by DPPM to give the intermediates II, in which the bidentate ligand could undergo chelation with the metal center to give metallabenzenes III. Coordination of another DPPM with only one P atom to III gives IV, leaving the other P atom free, providing the possibility to undergo nucleophilic attack. Then, the intramolecular nucleophilic addition of the DPPM to the aromatic metallacycle affords the metallacyclohexadienes V. Although not common, a few nucleophilic attacks between bidentate phosphines and unsaturated hydrocarbyl ligands are known. For example, the nucleophilic attack of DPPM at C6 of the phosphido-bridged diiron allenyl complex \([\text{Fe}_2(\text{CO})_6\mu-\text{PPh}_3]\mu-\eta^2\text{C}^{'-}\text{C}^{'-}\text{C}((\text{H}))\text{C}=\text{C}=\text{C}_6\text{C}_6\text{H}_6\text{H}_2\]) and the nucleophilic attack of DPPM at the Rh end of the bridged alkyne of the complex \([\text{RhIrCH}(\text{CH})_(\text{CO})(\mu-\text{C}_6\text{H}_6)(\text{dppm}) ][\text{CF}_3\text{SO}_3\text{]}\)\cite{10c} \(\text{Jackson–Meisenheimer complexes V convert to } \eta^2\text{-allene-coordinated metallacycles VI, rather than the expected metallabenzenes. Complexes VI could form by the cleavage of the C4–P bond of V, which may be driven by the ring strain of the DPPM-tethered metallacycle. Complexes VI can rearrange to give the more stable complexes VII.}

A sequence of intermediates in the transformation of I to VII, except II, have been isolated from the reaction of DPPM with osmabenzenec 1 or with ruthenenbenzenec 5. Ready conversion of metallabenzenes I to \(\eta^2\)-allene-coordinated metallacycles VII is interesting, especially in view of the isolation and single-crystal X-ray structure determination of the Jackson–Meisenheimer complex V, which is derived from metallabenzenec IV by the intramolecular nucleophilic addition reaction of DPPM to the aromatic metallacycle.

We have recently demonstrated the transformation of \(\eta^2\)-allene-coordinated metallacycle to metallabenzenec (Scheme 4, path b).\cite{9b} In connection with our study on the transformation of I into VII, which represents the first example of the conversion of metallabenzenec to an allene-coordinated complex (Scheme 4, path a), our results show that the interconversion between metallabenzenes and allene-coordinated complexes could now be viable.

**Reactions of osmapyridinium with DPPM**: The reaction of metallapyridinium 9, a new member of metallaaromatics,\cite{9b} with DPPM has also been investigated for comparison.

Due to the high stability of 9, the reaction of osmapyridinium 9 with DPPM was performed in 1,2-dichloroethane at 80°C (Scheme 5). Complex 10 could be isolated as a yellow solid in 81% yield by heating the solution at 80°C for 8 h. The structure of 10 is revealed by NMR spectroscopy. Complex 10 exhibits the signal of \(\text{PPh}_3\) at \(\delta = 21.1\) ppm and that of \(\text{OsPPh}_3\text{CH}_2\text{PPh}_3\) at \(\delta = -56.0\) and \(-70.3\) ppm in the \(^{31}\text{P}[	ext{H}]\) NMR spectrum. Consistent with the presence of the aromatic metallacycle, the \(^{13}\text{C}[	ext{H}]\) NMR spectrum shows four signals at \(\delta = 231.2\) (OsCH), 177.9 (OsNH(CCH)),

\[\text{Scheme 4. Interconversion of metallabenzenec and a } \eta^2\text{-allene-coordinated metallacycle.}\]
was identified by in situ NMR spectroscopy. Conversion of 7004

Figure 4. Molecular structure for the cation of complex 11

156.0 (C(Ph)), and 120.4 ppm (C(PPh₃)). In addition, the signals at δ=18.6 (OsCH) and 14.0 ppm (OsNPh) assigning to the protons of the metallacycle appear in the 1H NMR spectrum. The structure of 10 has also been confirmed by X-ray diffraction and it can be described as a derivative of 9, in which both P atoms of diphosphene chelate to the metal center (see Figure S3 in the Supporting Information).[12]

When the mixture of 9 and DPPM in 1,2-dichloroethane was kept at 80°C for several days, a mixture of 10 and 11 was identified by in situ NMR spectroscopy. Conversion of complex 10 to 11 seems to be promoted by PPh₃. It is found that the desired complex 11 cannot be obtained from the refluxing 1,2-dichloroethane solution of the pure sample 10. When a solution of the isolated complex 10 in 1,2-dichloroethane was heated at 80°C in the presence of purposely added PPh₃, the reaction was completed after four days to give 11 as the dominant product.

The structure of 11 has been clarified by an X-ray single-crystal diffraction experiment. As shown in Figure 4, the structure of 11 is similar to those of the cyclic η²-allene complexes 4 and 8. The cyclic osmium η²-allene-imine complex 11 is also structurally similar to the Fischer carbene complexes [M-[CH(Fe)N(C(H₂)₃)CH=([η²-C=C-CH₃)](CO)₃] (M=W, Cr, Mo), which contain the bidentate allene-aminocar- bile ligand.[20] As discussed above, the metallasalenes of 4 and 8 deviate significantly from planarity. However, the closely related intramolecularly coordinated η²-allene complex 11 adopts a nearly planar structure. The maximum deviation from the least-squares plane through Os1, N1, and C2–C5 is 0.028 Å for C5. We suspected that the steric and electronic effects might play important roles in the planarity.

In contrast to the reaction of metallabenzenes with DPPM, treatment of metallapyridinium 9 with one equivalent of DPPM yielded the cyclic η²-allene complex 11. The difference in the amount of DPPM required is probably related to the electron-deficient metallacycle of metallapyridinium 9, which facilitates the attack of the nucleophile. The reaction may also involve a Jackson–Meisenheimer intermediate relevant to the proposed mechanism in Scheme 3. Complex 11 may be formed through the conversion of the nondetectable Jackson–Meisenheimer intermediate, which is produced by the intramolecular nucleophilic addition reaction of DPPM with metallapyridinium 9.

**Conclusion**

We have demonstrated the nucleophilic aromatic addition reactions of the phosphonium-substituted metallabenzenes with bidentate DPPM. The process involves the nucleophilic attack of an aromatic metallacycle by the nucleophile DPPM, followed by the cleavage of the C–P bond. This was supported by the isolation and characterization of the intermediates, especially the Jackson–Meisenheimer complex. A similar reaction also occurred in our phosphonium-substituted metallapyridinium to give the cyclic osmium η²-allene-imine complex. The reactions are potentially useful as they provide a simple and efficient method for the synthesis of allene-coordinated metallasalanenes with different metals and substituents, through the intramolecular nucleophilic addition reaction, from the metallaaromatics.

**Experimental Section**

General comments: Unless otherwise stated, all manipulations were carried out at room temperature under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzenophene (n-hexane, diethyl ether), or calcium hydride (CH₂Cl₂, CHCl₃, CH₂(CH₂)CH₂Cl). The starting materials [Os(CHC(PPh₃)CH(C(PPh₃)CHCl)][PPh₃]Cl (1), [Ru(CHC(PPh₃)CHC(PPh₃)CHCl][PPh₃]Cl] (2), [Os[NHC(CH₂)C(Ph)(C(PPh₃)CHCl)][PPh₃]BF₄] (9) were synthesized by literature procedures[9,16,17] NMR spectroscopic experiments were performed on a Bruker AV-300 spectrometer (1H: 300.1, 13C: 75.5, 31P: 121.5 MHz) or a Bruker AV-400 spectrometer (1H: 400.1, 13C: 100.6, 31P: 162.0 MHz). 1H and 13C NMR spectroscopic chemical shifts are relative to TMS, and 31P NMR spectroscopic chemical shifts are relative to 85% H₃PO₄. Elemental analyses data were obtained on a Thermo Quest Italia S.P.A. EA 1110 instrument. 

**Figure 4. Molecular structure for the cation of complex 11 (ellipsoids at the 50% probability level). Counteraion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–P3: 2.423(2), Os1–P1: 2.361(2), Os1–C11: 2.445(2), Os1–C12: 2.425(2), Os1–N1: 2.055(7), Os1–C4: 2.007(8), Os1–C5: 2.184(8), N1–C2: 1.299(11), C2–C3: 1.443(12), C3–C4: 1.350(12), C4–C5: 1.388(12), C6–C7: 1.488(12), P2–C5: 1.803(9), P1–Os1–P3: 172.46(8), C11–Os1–C12: 89.01(7), N1–Os1–C4: 70.9(3), N1–Os1–C5: 109.2(3), Os1–N1–C2: 123.4(6), N1–C2–C3: 112.1(8), C2–C3–C4: 108.2(8), C3–C4–C5: 156.8(9), C3–C4–Os1: 125.4(6), C4–C5–Os1: 63.9(5), C5–C4–Os1: 77.7(5).**
and DPPM (53.8 mg, 0.14 mmol) in CHCl₃ (10 mL) was heated at 60°C for about 20 min to give a green solution. The volume of the mixture was reduced to approximately 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a green solid, which was collected by filtration, washed with diethyl ether (3 x 5 mL) and dried under vacuum. Yield: 0.16 g, 90%. [39] [H] NMR (CDCl₃, 162.0 MHz): δ = 20.4 (dd, J = 31.3, 7.3 Hz, C²PPP), 19.8 (d, J = 8.4 Hz, C¹PPP), -31.9 (d, J = 13.1 Hz, Os[PPPPP]), -55.4 (dd, J = 30.9, 13.1 Hz, OsPPP); [H] NMR plus HMQC (CDCl₃, 300.1 MHz): δ = 17.3 (t, J = 15.6 Hz, 1H, OsH(C); 17.0 (d, J = 19.2 Hz, 1H, OsCH); 8.0-6.3 (m, 52H; Ppp, Pph, OsCH(PPh₃)CH(PPh₃), 7.9 (brs, 1H; OsCHCl(PPh₂)CH), obscured by the phenyl signals and confirmed by 1H-13CHSQC), 8.7 (brs, 1H; OsCHCl(PPh₂)CH), 4.7 ppm (dt, J = 11.0, J = 13.2 Hz, 1H, (PPh₃)CH₂(PPh₃)). [30] [H] NMR (CDCl₃, 75.5 MHz): δ = 253.8 (m, OsCH); 245.6 (brs; OsCH), 190.4 (t, J = 22.7 Hz; OsCH(PPPPP)), 136.7-119.9 (m; Ppp, Pph, PpH), 120.0 (dd, J = 76.1, 13.2 Hz; C²PPP), 114.0 (dd, J = 76.1, 15.3 Hz; C¹PPP), 41.1 (dd, J = 21.2, 33.4 Hz; C¹PPP(CH₃)), 49.61 ppm (m; PpH(CH₃)), 48.13 ppm (d, J = 10.6 Hz; Os(CH₂)₅). elemental analysis (%) for C₃₆H₄₆Cl₆Os: C 66.49, H 4.37; found: C 66.21, H 4.83.

**[RuCH=CHPPh₂C(CH=CHPPh₂C)C(PC)(PP)(PC)(PPh₃)BF₄]** (10) A mixture of [Ru(CH₂)₅C≡C]₂Cl₂ (1.0 mmol) and DPPM (115.0 mg, 0.30 mmol) in CH₂Cl₂ (15 mL) was heated at 80°C for about 8 h to give a reddish-brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (3 x 5 mL) and dried under vacuum. Yield: 80.0 mg, 30%; [39] [H] NMR (CDCl₃, 121.5 MHz): δ = 39.7 (dd, J = 54.2, 20.0, 6.8 Hz; (PPh₃)CH(PPh₃), CH(PPh₃), 31.5 (dd, J = 295.3, 54.2, 22.5 Hz; (PPh₃)CH(PPh₃), CH(PPh₃), 6.8 (s, PP), 4.7 (dd, J = 40.5, 22.5 Hz; Ru(PPh₃)), 16.6 ppm (dd, J = 293.5, 40.5, 20.0 0.0 Hz; Ru(PPh₃)), H NMR plus HMQC (CDCl₃, 400.1 MHz): δ = 10.7 (t, J = 18.4 Hz, 1H; RuCH), 8.5-6.6 (m; 56H; Pph, Pph, RuCH(PPh₃)CH(PPh₃), 5.9, 5.3, 4.4, 3.6 (m, 4H; (PPh₃)CH(PPh₃)CH(PPh₃), CH(PPh₃)CH(PPh₃), 5.4 ppm (m, p=CH(PPh₃)); [30] [H] NMR plus DEPT-135 and HMQC (CDCl₃, 100.6 MHz): δ = 2910 (br; RuCH), 2028.0 (m, δ = 2910 (br; RuCH), 1351.9-119.3 (m; PpH, Pph, 125.1 (d, J = 24.1 Hz; RuCH(PPh₃)CH), 124.3 (d, J = 88.5 Hz; RuCH(PPh₃)CH), 40.4 (d, J = 70.2, 722 Hz; CH=P=CH(PPh₃)), 42.3, 24.8 ppm (m; (PPh₃)CH(PPh₃)CH(PPh₃)); elemental analysis (%) for C₁₈₂H₁₈₀Cl₆Ru: C 67.36, H 4.80; found: C 67.49, H 4.94.

**[RuCH=CHPPh₂C(CH=CHPPh₂C)C(PC)(PP)(PC)(PPh₃)BF₄]** (6): A mixture of [Ru(CH₂)₅C≡C]₂Cl₂ (1.0 mmol) and DPPM (173.0 mg, 0.45 mmol) in CHCl₃ (10 mL) was stirred at room temperature for about 1 week to give a yellowish-brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (3 x 2 mL) and dried under vacuum. Yield: 0.14 g, 77%; [39] [H] NMR (CDCl₃, 121.5 MHz): δ = 38.7 (dd, J = 55.9, 16.8, 17.9 Hz; (PPh₃)CH(PPh₃), CH(PPh₃), 24.4 (dd, J = 355.5, 29.8, 16.5 Hz; Ru(PPh₃)), 19.0 (dd, J = 355.4, 56.7, 14.3 Hz; (PPh₃)CH(PPh₃), CH(PPh₃), 5.6 (s, C₁PPP), -27.5 ppm (d, J = 29.9, 14.3 Hz; Ru(PPh₃)CH(PPh₃), H NMR plus HMQC (CDCl₃, 500.2 MHz): δ = 11.5 (d; J = 15.3 Hz, 1H; RuCH), 6.7 (brs, 1H; RuCH(PPh₃)CH), obscured by the phenyl signals and confirmed by 1H-13CHSQC), 8.3-6.5 (m; 56H; Pph, Pph, RuCH(PPh₃)CH(PPh₃), 5.9 (m, (PPh₃)CH(PPh₃)CH(PPh₃), 4.0 (brs, 2H; CH(CH₃)PPh₃), 3.3 (dd, J = 16.8, 5.1 Hz; 1H; CH=CH(PPh₃)CH(PPh₃), 3.5 ppm (m, 1H; (PPh₃)CH=P=CH(PPh₃), CH(PPh₃); elemental analysis (%) for C₁₈₂H₁₈₀Cl₆Ru: C 66.44, H 4.89; found: C 66.67, H 4.96.

**[OsH₂(PC)(CH₂)₂(PPh₂)CH(PPh₃)BF₄]** (8): A mixture of [OsH₂(PC)(CH₂)₂(PPh₂)CH(PPh₃)BF₄] (δ = 0.20 g, 0.15 mmol) and DPPM (173.0 mg, 0.45 mmol) in CHCl₃ (10 mL) was stirred at room temperature for about 1 week to give a yellowish-brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (3 x 2 mL) and dried under vacuum. Yield: 0.14 g, 81%; [39] [H] NMR (CDCl₃, 162.0 MHz): δ = 211.1 (s, C₁PPP), -56.0 (d, J = 48.9 Hz; (PPh₃)CH(PPh₃), -70.3 ppm (d, J = 48.9 Hz; (PPh₃)CH(PPh₃), 1H NMR (CDCl₃, 400.1 MHz): δ = 18.6 (m, 1H; OsCH), 14.0 (s, 1H; OsH), 7.9-6.8 (m, 40H; Pph, Pph, Ph), 5.6 (m, 1H; (PPh₃)CH(PPh₃), CH(PPh₃), 4.9 (m, 1H; (PPh₃)CH(PPh₃), 3.2 ppm (3H, CH₃); 1H NMR plus HMQC (CDCl₃, 100.6 MHz): δ = 2312 (brs; OsCH), 177.9 (d, J = 12.6 Hz; OsNCH₃), 156.0 (d, J = 17.6 Hz; OsP=C), 138.2-126.5 (m; Pph, Pph, Ph), 120.4 (d, J = 86.4 Hz; C(PPh₃), 47.6 (d, J = 34.2, 29.2 Hz; C(PPh₃)), 27.0 ppm (d, J = 48.5 Hz; CH); elemental analysis (%) for C₁₈₂H₁₈₀N₂Ba₄Os: C 56.36, H 4.12, N 1.22; found: C 56.52, H 4.31, N 1.16.

Nucleophilic Aromatic Addition Reactions
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Nucleophilic Aromatic Addition Reactions


Recent examples of other metallaaromatics except metallabenzenes:

Recent examples of other metallaaromatics except metallabenzenes:

Recent examples of other metallaaromatics except metallabenzenes:


Jackson-Meisenheimer complexes, also referred to as anionic σ complexes or Meisenheimer complexes, are key intermediates in the S₅Ar mechanism of aromatic nucleophilic substitution reactions. They are formed by the covalent addition of nucleophiles to a ring carbon atom of aromatic or heteroaromatic substrates bearing electron-withdrawing substituents and have been characterized as stable or transient species. For details, see: F. Terrier, Chem. Rev. 1982, 82, 77 –152.

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