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Osmabenzenes from Osmacycles Containing an η^2-Coordinated Olefin

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Abstract: Treatment of HC≡CC-(CH_3)(OH)CH=CH_2 with [$OsCl_2$-$(PPh_3)_3$] in dichloromethane yielded the η^2-olefin-coordinated osmacycle [Os{CH=C(PPh_3)C(=CH_2)-η^2-CH=CH_2}Cl_2(PPh_3)$_2$] (**9**). Transformations of osmacycle **9** by treatment with benzonitrile under various conditions have been investigated. Reaction of **9** with excess benzonitrile at room temperature afforded the dicationic osmacycle [Os{CH=C(PPh_3)C(=CH_2)-η^2-CH=CH_2}(PhCN)$_2$(PPh_3)$_2$]Cl_2 (**11**) by ligand substitution, which reacted further to the intramolecularly coordinated η^2-allene complex [Os{CH=C(PPh_3)C-(CH_3)=(η^2-C=CH_2)}(PhCN)$_2$(PPh_3)$_2$]Cl_2 (**12**). In contrast, heating a chloroform solution of **9** to the reflux temperature in the presence of excess benzonitrile generated osmabenzene [Os{CHC-(PPh_3)C(CH_3)CHCH}(PhCN)$_2$-(PPh_3)$_2$]Cl_2 (**14**). Complexes **11**, **12** and **14** are in fact isomers. In the absence of excess benzonitrile, the isolated dicationic **12** and **14** readily dissociate the benzonitrile ligands in solution to produce the neutral complex [Os{CH=C(PPh_3)C(CH_3)=(η^2-C=CH_2)}Cl_2-(PPh_3)$_2$] (**13**) and the monocationic osmabenzene [Os{CHC(PPh_3)C(CH_3)-CHCH}Cl(PhCN)(PPh_3)$_2$]BPh_4 (**15**), respectively. Mechanisms for the formation of osmabenzene **14** from **11** and **12** are proposed based on DFT calculations.

Keywords: benzonitrile · isomerization · metallacycles · osmabenzene · osmium

Introduction

Research on aromatic metallacycles has made rapid progress during the last decades.[1–2] In particular, metallabenzenes, as one class of six-membered metallacyclic aromatic compounds derived from formal replacement of one CH moiety in benzene by an isolobal transition-metal fragment, have attracted considerable attention in recent years.[3–4] Several approaches have been developed to construct stable metallabenzene rings. The common strategies previously employed include cyclisation reactions of alkynes with metalthiocarbonyl,[5] deprotonation of pentadienediyl iridium species (derived from the reactions of [$IrCl(PR_3)_3$] with potassium 3,5-dimethylpentadienide),[6] reactions of [L_nMCl] with lithiated 3-vinyl-1-cyclopropenes,[7] oxidation of iridium complexes derived from the coupling of alkynes and coupling of iridacyclopentadiene with alkenes,[8] protonation of *cis*-(alkynyl)(buta-1,3-dien-1-yl) iridium complexes,[9a] and reactions of terminal alkynes with metallacyclopentadienes followed by protonation.[9b] Although a number of stable metallabenzenes have been synthesized through these methods, exploring a general approach remains interesting and challenging.

We have recently developed a convenient route to prepare a series of new osmabenzenes and ruthenabenzenes from the reactions of [$MCl_2(PPh_3)_3$] (M = Os, Ru) with readily accessible HC≡CCH(OH)C≡CH,[10a–c] which contributes a valuable addition to previous synthetic methodologies. The reactions were initiated by coordination of the alkyne to the metal centre and nucleophilic attack of the dissociated PPh_3 at the coordinated alkyne. One of the key intermediates, [Os{CH=C(PPh_3)CH(OH)-η^2-C≡CH}Cl_2(PPh_3)$_2$] (**1**), was successfully isolated.[10b] In our investigation of the reactivity of the η^2-alkyne-coordinated alkyne alcohol complex **1**, we found that it can easily transform to the η^2-olefin-coordinated α,β-unsaturated ketone complex **2** under acidic conditions. Whereas complex **2** is very stable, the PMe_3-substituted analogue **3** slowly isomerises to osmaphenol **4** (Scheme 1).[10d]

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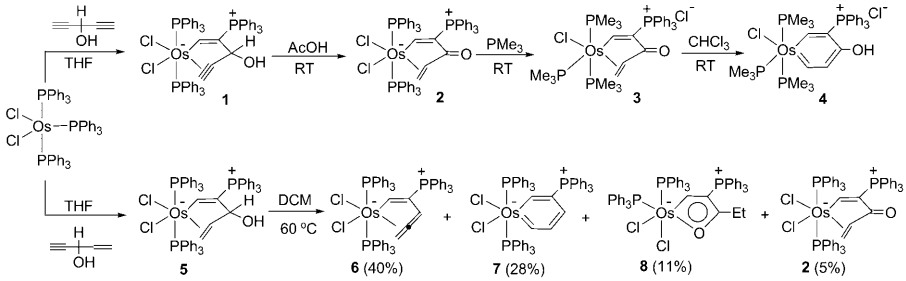


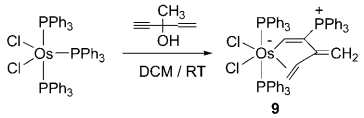
Scheme 1.

During the course of our further investigations on the construction of aromatic metallacycles through cycloaddition of unsaturated C_5 building blocks with simple transition-metal complexes bearing phosphine ligands, we extended the strategy using HC≡CCH(OH)CH=CH_2 as the building block. Similarly, the reaction of $[OsCl_2(PPh_3)_3]$ with HC≡CCH(OH)CH=CH_2 provided a convenient and efficient cyclometalation route to produce the η^2-olefin-coordinated allyl alcohol osmacycle **5**, which was found to afford four different conjugated osmacycles with the cyclic osmium η^2-allene complex **6** and osmabenzene **7** as the major products on heating (Scheme 1).[10e]

In our further efforts to extend the scope of the chemistry, we now have investigated the reaction of $[OsCl_2(PPh_3)_3]$ with commercially available HC≡CC(CH_3)(OH)CH=CH_2, which bears a methyl substituent on the central carbon, with the goal of developing a general route to synthesize metallabenzenes analogous to **7** with different substituents in the *para* position of the metallacycle backbone by an alteration of the unsaturated C_5 unit. The reaction led to the formation of the η^2-olefin-coordinated osmacycle [Os{CH=C(PPh_3)C(=CH_2)-η^2-CH=CH_2}Cl_2(PPh_3)$_2$] (**9**) with an exocyclic methylene group double-bonded to the ring carbon derived from dehydration, which is similar to **2** with the exocyclic methylene group instead of the oxo on the γ-C of the ring. In view of the fact that the PMe_3-substituted analogue of **2** can readily isomerise to osmaphenol **4**, it would be of interest to study the reactivity of **9** to see if related osmabenzenes can be similarly obtained. Herein we present the transformations of osmacycle **9** under various conditions. As expected, introduction of benzonitrile into the reaction systems led to the cyclic osmium η^2-allene complex [Os{CH=C(PPh_3)C(CH_3)=(η^2-C=CH_2)(PhCN)$_2$(PPh_3)$_2$}]Cl_2 (**12**) and osmabenzene [Os{CHC(PPh_3)C(CH_3)CHCH}(PhCN)$_2$(PPh_3)$_2$]Cl_2 (**14**) in high yields under different conditions. Moreover, osmacyclic η^2-allene complex **12** can isomerise to osmabenzene **14**. DFT calculations suggest the detailed mechanism for the formation of osmabenzene includes a hydrogen-transfer process in which benzonitrile acts as an activating ligand and the chloride counterion as a catalyst.

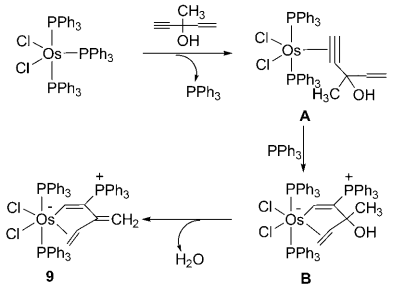
Results and Discussion

Synthesis of η^2-olefin-coordinated osmacycle 9: In contrast to the reaction of $[OsCl_2(PPh_3)_3]$ with HC≡CCH(OH)CH=CH_2 which led to the formation of the η^2-olefin-coordinated allyl alcohol osmacycle **5**, treatment of HC≡CC(CH_3)(OH)CH=CH_2 with $[OsCl_2(PPh_3)_3]$ in dichloromethane at room temperature for 5 h yielded a yellow precipitate, which was isolated by filtration and identified to be the η^2-olefin-coordinated osmacycle [Os{CH=C(PPh_3)C(=CH_2)-η^2-CH=CH_2}Cl_2(PPh_3)$_2$] (**9**) with an exocyclic methylene group double-bonded to the γ-C of the ring (Scheme 2). Complex **9** has poor solubility in common organic solvents except chloroform.



Scheme 2.

Again, as the case in our previously reported reactions,[10b,d,e] the reaction may involve similar nucleophilic attack of the phosphine on the coordinated alkyne to give the allyl alcohol intermediate **B** analogous to complex **5**. Apparently, dehydration occurred to form the exocyclic double bond in **9** (Scheme 3).



Scheme 3.

An X-ray single-crystal diffraction experiment has clarified the structure of **9**. As shown in Figure 1, the structure of **9** is similar to that of the η^2-olefin-coordinated α,β-unsaturated ketone complex **2** with the exocyclic methylene group instead of the oxo on the γ-C of the ring. The geometry of the osmium centre in **9** can be viewed as a distorted octahedron in which the six coordination sites are occupied by C1 and the C4–C5 double bond, two chloride atoms, and two phosphorus atoms of the phosphine ligands. The C3–C6

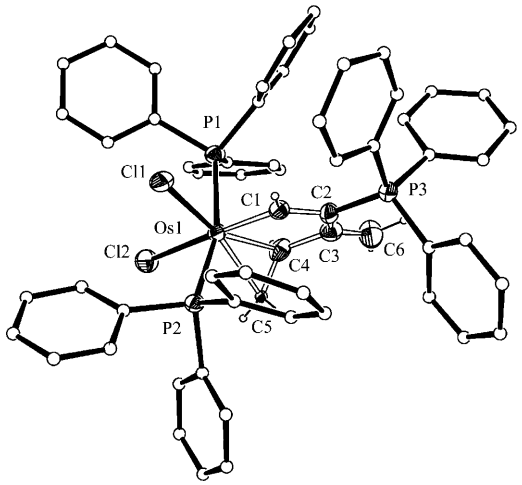
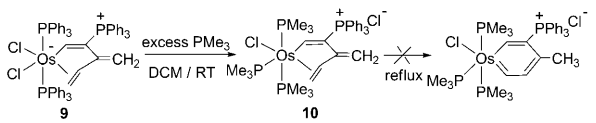


Figure 1. Molecular structure of complex **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 = 1.968(7), Os1–C4 = 2.167(8), Os1–C5 = 2.163(8), C1–C2 = 1.375(12), C2–C3 = 1.461(12), C3–C4 = 1.498(12), C4–C5 = 1.395(12), C3–C6 = 1.339(13); C1-Os1-C5 = 90.1(3), C1-Os1-C4 = 78.4(3), C4-Os1-C5 = 37.6(3), C2-C1-Os1 = 121.0(6), C1-C2-C3 = 116.7(7), C2-C3-C4 = 110.6(7), C3-C4-C5 = 117.1(8), C3-C4-Os1 = 112.5(6), C4-C5-Os1 = 71.3(4).

bond length of 1.339(13) Å is indicative of a C=C double bond, whereas the C4–C5 bond length of 1.395(12) Å is consistent with a coordinated C=C double bond.

Ligand substitution of osmacycle 9 with PMe_3: As mentioned above, the η^2-olefin-coordinated α,β-unsaturated ketone complex **2** is very stable, whereas the PMe_3-substituted analogue **3** can slowly isomerise to *p*-osmaphenol **4** in $CHCl_3$ (Scheme 1). The difference in the stability of **2** and **3** is presumably related to increased electrophilicity of the metal centre in the latter due to the replacement of one Cl and two PPh_3 ligands with three PMe_3, which consequently facilitates deprotonation of the coordinated olefin. It thus seems reasonable to expect that the similar PMe_3-substituted analogue of osmacycle **9** might convert to the related osmabenzene. Naturally, ligand substitution of complex **9** was carried out.

Treatment of **9** with excess PMe_3 (10 equiv) at room temperature produced complex **10** (Scheme 4). The structure of complex **10** is revealed by its NMR spectroscopy. The



Scheme 4.

$^{31}P\{^1H\}$ NMR spectrum showed one C*P*Ph_3 signal at δ = 10.4 ppm and three Os*P*Me_3 signals at $\delta = -44.8$, -45.0 and -54.8 ppm, respectively. In the ^1H NMR spectrum, characteristic signals were observed at $\delta = 10.1$ (OsC*H*), 5.2 (C(=CH_2)), 4.6 (C(=CH_2)), 3.5 (η^2-C*H*=CH_2), 2.4 (η^2-CH=CH_2) and 1.7 ppm (η^2-CH=CH_2), which were close to those of complex **9**. The $^{13}C\{^1H\}$ NMR spectrum showed five signals at $\delta = 220.9$ (Os*C*H), 159.1 (*C*(=CH_2)), 115.8 (*C*PPh_3), 108.1(C(=*C*H_2)), 51.7(η^2-*C*H=CH_2) and 30.5 ppm (η^2-CH=*C*H_2) for the carbons on the central structure.

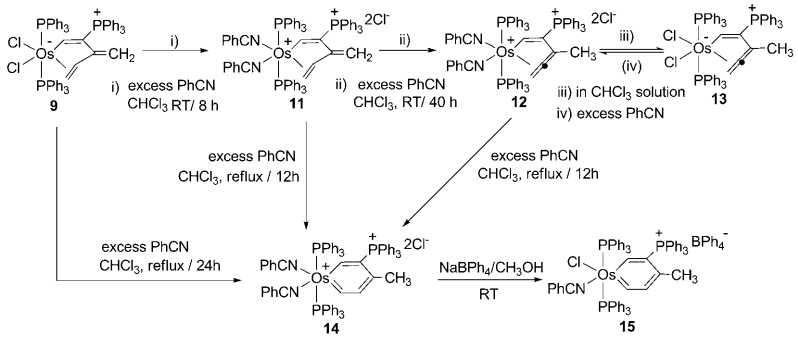
Although the structure of **10** is similar to that of **3**, which can isomerise to *p*-osmaphenol **4**, isomerisation of **10** to the expected osmabenzene was not observed, even under refluxing conditions. These contrasting results can probably be attributed to the different electronic nature of the exocyclic group of the γ-C on the ring in the two complexes. In comparison with the methylene group in complex **10**, the electron-withdrawing oxo group in complex **3** greatly decreases the electron density of the coordinated olefin, thus facilitating deprotonation of **3** to give osmaphenol **4**.

Cyclic osmium η^2-allene complex 12 from the reaction of osmacycle 9 with benzonitrile at room temperature: It is well known that the nitrile ligand is a π acceptor that can coordinate to an electron-rich metal centre and increase the electrophilicity of organometallic frames.[11] Hydride migration as a result of a decrease in electron density on the metallic centre by nitrile substitution has been reported.[12] Thus, in our case, it can be expected that the replacement of two chloride ligands in the neutral osmacycle **9** by nitrile ligands should greatly decrease the electron density on the metallic centre. As a consequence, hydrogen transfer on the metallacycle might be favourable and thus allow isomerisation of the osmacycle to the related osmabenzene. Hence, we investigated the reactions of osmacycle **9** with benzonitrile.

Treatment of complex **9** with excess benzonitrile in chloroform at room temperature for 8 h produced a yellow solution, from which the dicationic benzonitrile-substituted complex **11** could be isolated in 86% yield (Scheme 5).

The structure of the bis-benzonitrile coordinated complex **11** could be readily deduced from its NMR spectrum. The ^1H NMR spectrum showed the characteristic OsC*H* signal at $\delta = 9.9$ ppm. The signals of the coordinated olefin appeared at $\delta = 4.1$ (η^2-C*H*=CH_2), 3.1 (η^2-CH=CH_2) and 3.0 ppm (η^2-CH=CH_2), respectively, which shifted lower field compared with the corresponding signals of complex **9** at $\delta = 3.3$ (η^2-C*H*=CH_2), 2.8 (η^2-CH=CH_2) and 2.4 ppm (η^2-CH=CH_2). The results are attributed to the replacement of the chloride ligands with the benzonitrile molecules, which decrease the electron density of the metal centre and the coordinated double bond. In addition, the $^{31}P\{^1H\}$ NMR spectrum showed three signals at $\delta = 9.3$ (s, C*P*Ph_3), 1.4 (d, J(P,P) = 213.8 Hz, Os*P*Ph_3) and -9.2 ppm (d, J(P,P) = 213.8 Hz, Os*P*Ph_3), respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the existence of two coordinated benzonitrile substituents were confirmed by the signals at $\delta = 120.8$ (s, Ph*C*N), 119.7 ppm (s, Ph*C*N).

Although stable in the solid state, a solution of **11** in the mixture of chloroform and benzonitrile could isomerise almost quantitatively to osmacyclic species bearing the η^2-allene group [Os{CH=C(PPh_3)C(CH_3)=(η^2-C=CH_2)}-



Scheme 5.

$(PhCN)_2(PPh_3)_2]Cl_2$ (**12**) after stirring for 40 h at room temperature. Complex **12** can also be obtained from **9** by stirring the solution in a mixture of chloroform and benzonitrile for 48 h at room temperature.

NMR spectroscopy confirmed the structure of complex **12**. The ^{1}H NMR spectrum showed Os*CH* signal at $\delta =$ 11.7 ppm. The signal of η^2-C=*CH*$_2$ appeared at $\delta = 2.6$ ppm with a broad peak, and the *CH*$_3$ signal at $\delta = 1.7$ ppm. The ^{31}P{^{1}H} NMR spectrum displayed only two signals at $\delta = 9.0$ (*CP*Ph$_3$) and -10.1 ppm (Os*P*Ph$_3$), indicative of the symmetric structure. In the ^{13}C{^{1}H} NMR spectrum, the signals of Os*C*H, *C*PPh$_3$ appeared at $\delta = 204.4$ and 121.1 ppm, whereas the three carbon signals of the coordinated allene backbone appeared at $\delta = 183.1$ (η^2-*C*=CH$_2$), 123.1 (*C*(CH$_3$)) and 23.8 ppm (η^2-C=*C*H$_2$), respectively. Consistent with the structure, the ^{1}H and ^{13}C NMR data associated with the metallacycle were similar to those of complex **6**.[10e]

In this context, it should be mentioned that the isolated dicationic complex **12** is unstable in solution and it can readily dissociate the benzonitrile ligands and convert to the chloride-substituted neutral complex [Os{CH=C(PPh$_3$)C-(CH$_3$)=(η^2-C=CH$_2$)}Cl$_2$(PPh$_3$)$_2$] (**13**). As indicated by ^{31}P{^{1}H} NMR, the signals due to **13** are evident ($\approx$5%) approx. 20 min after dissolving **12** in $CDCl_3$. When the solution was stored for three days, the ^{31}P NMR spectrum showed signals of **12** and **13** in about a 1:5 ratio; however, the conversion was incomplete even after a week (the ^{13}C NMR data of **12** can be obtained in the presence of approx. 5 equiv of purposely added benzonitrile). As was also the case in our attempts to grow the single crystal of complex **12**, the yellow crystals blocks of **13** can be obtained instead by recrystallisation of complex **12** in a solution of chloroform layered with ether. Interestingly, addition of excess benzonitrile to the chloroform solution of complex **13** regenerated complex **12**.

The structure of **13** was established by X-ray diffraction (Figure 2). The geometry of the Os centre can be viewed as an octahedron with two PPh$_3$ ligands at the axial positions, and two chloride atoms, the vinyl carbon (C1), olefin double bond (C4=C5) at the equatorial coordination sites. The coplanarity of the six atoms Os1, C1, C2, C3, C4 and C5 is reflected by the small deviation (0.0287 Å) from the rms planes of the best fit. The allene unit deviates slightly from linearity with a C3-C4-C5 angle of 161.1(11)°.

The solid-state structure of **13** is also fully supported by the solution NMR spectroscopic data. The ^{1}H NMR spectrum showed an Os*CH* signal at $\delta =$ 12.2 ppm, and the signal attributed to η^2-C=*CH*$_2$ at $\delta =$

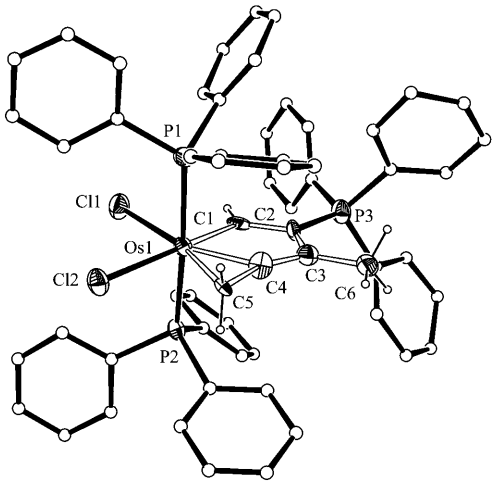


Figure 2. Molecular structure of complex **13**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 = 2.031(10), Os1–C4 = 2.069(10), Os1–C5 = 2.158(10), C1–C2 = 1.381(13), C2–C3 = 1.459(14), C3–C4 = 1.332(14), C4–C5 = 1.352(13), C3–C6 = 1.550(13); C1-Os1-C5 = 110.7(4), C1-Os1-C4 = 73.6(4), C4-Os1-C5 = 37.2(4), C2-C1-Os1 = 119.9(8), C1-C2-C3 = 113.9(9), C2-C3-C4 = 109.2(9), C3-C4-C5 = 161.1(11), C4-C5-Os1 = 67.8(6), C3-C4-Os1 = 123.4(8), C4-C5-Os1 = 67.8(6).

2.3 ppm. The ^{31}P{^{1}H} NMR displayed two singlets at $\delta = 6.7$ (*CP*Ph$_3$) and -10.8 ppm (Os*P*Ph$_3$).

In the absence of excess benzonitrile, the replacement of benzonitrile ligands in complex **12** by chloride ligands can be due to the relatively weaker coordination ability of benzonitrile compared to chloride. Moreover, neutral species **13** with a π-donating ligand (Cl^-) is more stable than the dicationic complex of **12** with a π-acceptor ligand (PhCN). The X-ray structural analysis and NMR characterisation of **13** further confirmed the structure of complex **12**. However, it should be noted that neutral species **9** could not isomerise to **13** under various conditions without benzonitrile.

As an interesting class of coordinated allene complexes, metallacycles bearing an intramolecularly coordinated allene group have only been reported rarely.[13–14] Complexes **12** and **13** represent rare examples of cyclic osmium η^2-allene complexes, which may be comparable with allenylcarbene complexes [Os{=CPh-η^2-CH=C=CH(Ph)}Cl$_2$(PPh$_3$)$_2$] reported by Jia et al,[13a] [CpRu{(=C(Fc)-η^2-CH=C=

CH(Fc)}(PPh_3)]PF_6 reported by Kirchner et al.[14c] and our previously reported complex **6**.[10e]

Osmabenzene 14 from heating osmacycle 9 in benzonitrile: In our further effort to encourage the isomerisation of the η^2-olefin-coordinated osmacycle **9** to osmabenzene, we found that treatment of **9** and excess benzonitrile under reflux in chloroform for 24 h led to the formation of osmabenzene **14** in a high yield (Scheme 5).

Complex **14** was identified as a monophosphonium-substituted osmabenzene on the basis of NMR data. In particular, the ^{1}H NMR spectrum showed two characteristic OsC*H* signals at $\delta = 17.7$ (OsC*H*CH) and 16.1 ppm (OsC*H*C(PPh_3)), which were comparable with those of our reported osmabenzenes.[10d,e] The signal attributed to the exocyclic methyl group was observed at $\delta = 1.1$ ppm, and that of OsCHC*H* appeared at $\delta = 6.5$ ppm. In the ^{31}P{^{1}H} NMR spectrum, two singlets were at $\delta = 20.4$ (C*P*Ph_3) and -3.0 ppm (Os*P*Ph_3). In the ^{13}C{^{1}H} NMR spectrum, the signals at $\delta = 122.4$ and 121.3 ppm were attributed to the two benzonitrile ligands on the metal centre. In addition, the five carbon signals of the metallacycle appeared at $\delta = 257.3$ (Os*C*HCH), 230.3 (Os*C*HC(PPh_3)), 153.5 (*C*(CH_3)), 132.0 (OsCH*C*H) and 110.8 ppm (*C*PPh_3), respectively.

Similar to complex **12**, the benzonitrile ligands of osmabenzene **14** can readily dissociate from the metal centre in solution. The lability of the benzonitrile ligand on these complexes offers an opportunity to construct the related derivatives by substitution reactions. Treatment of **14** with sodium tetraphenylboron in methanol led to the formation of osmabenzene **15** (Scheme 5).

Figure 3 shows a view of the cation geometry of complex **15**. The coordination around the osmium atom can be rationalised as an octahedron with the phosphorous atoms of PPh_3 ligands occupying *trans* positions (P1-Os1-P2 = 172.9 (1)), whereas one chloride atom and one benzonitrile ligand are *cis* each other (Cl1-Os1-N1 = 91.2(2)) in the same perpendicular plane with the six-membered osmabenzene ring. The structural characterization of **15** further confirmed the formulation of complex **14**.

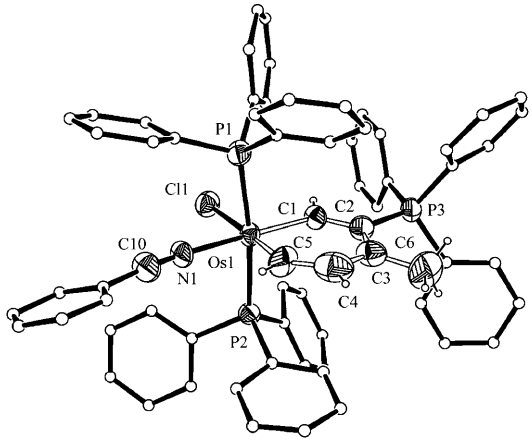


Figure 3. Molecular structure of the complex cation of **15**. Thermal ellipsoids are drawn at the 50% probability level. Counteranion and hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond length [Å] and angles [°]: Os1–C1 = 2.009(8), Os1–C5 = 1.961(9), Os1–N1 = 2.076(7), C1–C2 = 1.349(12), C2–C3 = 1.438(12), C3–C4 = 1.351(15), C3–C6 = 1.514(14), C10–N1 = 1.125(12); C1-Os1-C5 = 90.8(5), N1-Os1-C5 = 86.5(4), C2-C1-Os1 = 128.7(7), C1-C2-C3 = 121.0(8), C2-C3-C4 = 123.3(11), C3-C4-C5 = 131.8(13), C2-C3-C6 = 122.0(9), C4-C5-Os1 = 123.7(11), N1-C10-C11 = 174.5(13), C10-N1-Os1 = 173.0(9), P1-Os1-P2 = 172.9 (1), Cl1-Os1-N1 = 91.2(2).

It is interesting to note that complexes **11**, **12** and **14** are actually isomers. Thus, refluxing isolated **11** or **12** in a mixture of chloroform and benzonitrile also led to the formation of the tautomeric osmabenzene **14** in a high yield (Scheme 5). To the best of our knowledge, isomerisations of allene complexes to metallabenzenes have not been reported. However, the equivalent conversions starting from neutral species **9** were impossible to achieve, even under refluxing conditions in common organic solvents other than nitrile. We therefore concluded that benzonitrile plays a key role in the reactions.

Density functional theory (DFT) calculations: In order to better understand the important role of benzonitrile for the transformation of complexes **11** and **12** to osmabenzene **14**, DFT calculations were performed to elucidate the mechanism for the formation of osmabenzene **14′** from complexes **11′** and **12′**, where **14′**, **11′** and **12′** are model complexes of **14**, **11** and **12** in which PH_3 and HCN are used as models for the PPh_3 and PhCN ligands, respectively.

Figure 4 shows the relative free energy profiles for the transformation of complex **11′** to osmabenzene **14′**. As shown in Figure 4, the formation of osmabenzene **14′** from complex **11′** is both kinetically and thermodynamically feasible at room temperature with an effective barrier of 29.5 kcal mol^{-1} and an exothermicity of 5.4 kcal mol^{-1}. From reactant **11′**, the reaction proceeds to an agostic intermediate **LM1** via the first transition state (**TS1**). The geometric feature of **LM1** clearly suggests that one α-H is activated, which may be abstracted by the Cl^- counterion. The barrier (**TS2**) for the reaction from **LM1** to **LM2** is 11.2 kcal mol^{-1}, and the reaction is exothermic by 7.8 kcal mol^{-1}. We note that a formal Os–C is formed in **LM2** so that the ring is closed. The formation of osmabenzene **14′** is completed once molecular HCl gives away its proton via **TS3**. Hence, all in all, the Cl^- counterion plays a catalytic role in the transformation of **11′** to **14′**.

The reaction from **11′** to **LM2** can be formally viewed as an electrophilic substitution. In the first stage, the positively charged metal centre acts as the electrophile, and in the second stage, the Cl^- counterion subtracts the agostic H. The role of excess benzonitrile is thus clear. Whereas π-donating ligands (Cl^-) as in **9** tend to reduce the electrophilicity of the metal centre, substitution of chloride with the benzonitrile will increase the electrophicility of the metal. Our calculations actually show that starting from chloride, ligands will increase **TS1** by about 5.7 kcal mol^{-1} in the potential energy profile.

Figure 5 shows the relative free energy profiles for the transformation to osmabenzene **14′** from allene complex **12′**.

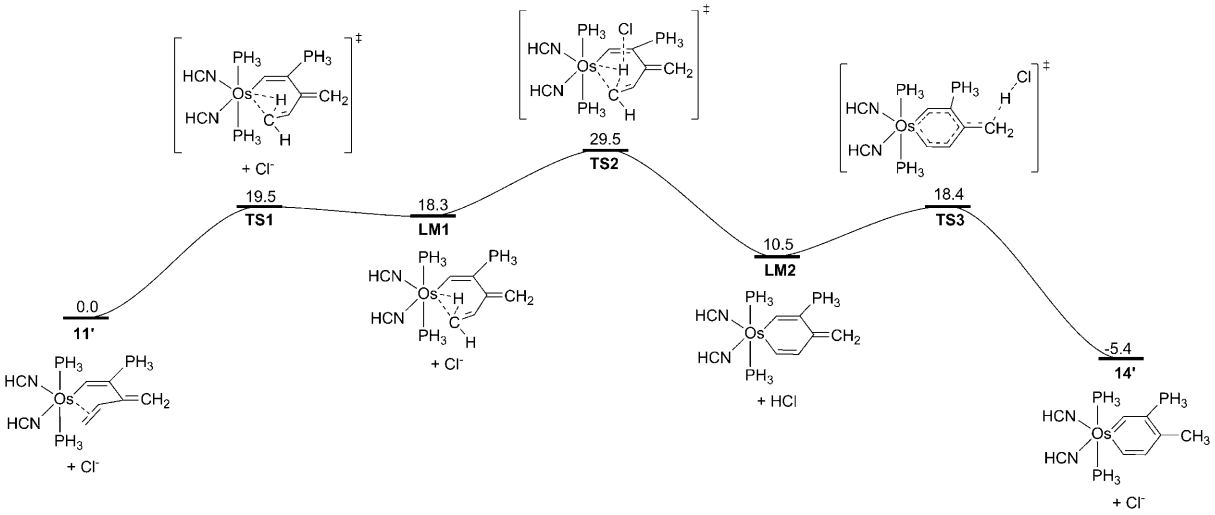


Figure 4. Energy profile for the formation of **14′** from **11′**. The calculated relative free energies are given in kcal mol^{-1}.

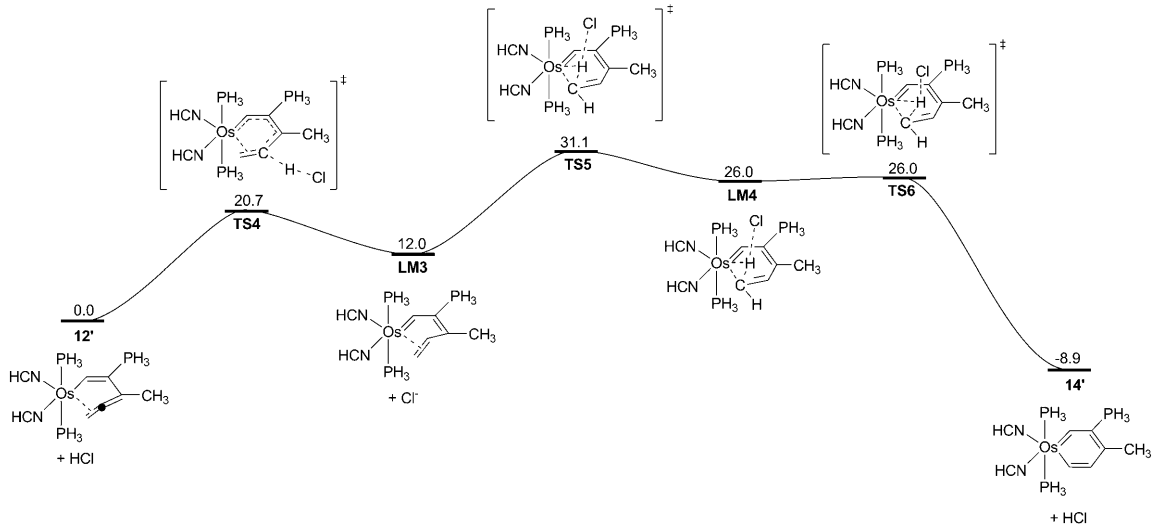


Figure 5. Energy profile for the formation of **14′** from **12′**. The calculated relative free energies are given in kcal mol^{-1}.

Interestingly, we find that molecular HCl acts as catalyst in this reaction. Our calculations suggest that HCl can be generated locally (e.g. HCl together with **LM2** in Figure 4). Experimentally, the existence of molecular HCl is conceivable due to the employment of solvent $CHCl_3$, which would decompose on exposure to light to produce HCl. With catalysis by HCl, the calculated apparent activation energy for the transformation from complex **12′** to **14′** is about 31.1 kcal mol^{-1} (**TS5**). Such a barrier is comparable to that in Figure 4, and is surmountable under the experimental condition.

There is another interesting difference between mechanisms shown in Figure 4 and Figure 5. Whereas structures with Cl^- associated to agostic H could be computationally located as in **TS5** and **LM4**, the analogous complexes are not found in **TS1** and **LM1**. Such an association stabilises **LM4** by approximately 4 kcal mol^{-1}. This phenomenon should be attributed to the stronger acidity for **TS5** and **LM4**, which lead to a barrierless process (**TS6**) and finally to the osmabenzene complex **14′**.

Our calculations demonstrate that i) transformations from complexes **11′** and **12′** to **14′** are both feasible; higher acidity would favour osmabenzene formation via the allene complex. ii) As the rate determining step involves an electrophilic substitution step, replacement of the chloride ligands by benzonitrile will increase the electrophilicity of the metal centre, which enhances the whole transformation reaction. iii) The Cl^- counterion acts as a base that catalyses the hydrogen-transfer process, and the additional role of excess benzonitrile is to provide a more polar environment, which facilitates Cl^- transfer within the reaction system. We also notice that in previous theoretical investigations on other or-

ganometallic processes, it has been proposed that coordination of nitriles could reduce the active barrier,[12a] and roles played by Cl^- similar to those we propose here have already been postulated for the reaction of CH_4 with $[(bpym)PtCl_2]$[15] and for the cycloisomerisations of bromoallenyl ketones with $[Au(PH_3)Cl]$.[16]

Conclusions

Reaction of $HC{\equiv}CC(CH_3)(OH)CH{=}CH_2$ with $[OsCl_2(PPh_3)_3]$ yielded the η^2-olefin-coordinated osmacycle $[Os\{CH{=}C(PPh_3)C(=CH_2)\text{-}\eta^2\text{-}CH{=}CH_2\}Cl_2(PPh_3)_2]$ (**9**). Transformations of osmacycle **9** under different conditions have been investigated. Whereas the reaction of **9** with PMe_3 under various conditions led to simple ligand substitution only, reaction of **9** with excess benzonitrile at room temperature initially afforded the dicationic osmacycle $[Os\{CH{=}C(PPh_3)C(=CH_2)\text{-}\eta^2\text{-}CH{=}CH_2\}(PhCN)_2(PPh_3)_2]Cl_2$ (**11**) and then produced the intramolecularly coordinated η^2-allene complex $[Os\{CH{=}C(PPh_3)C(CH_3){=}(\eta^2\text{-}C{=}CH_2)\}(PhCN)_2(PPh_3)_2]Cl_2$ (**12**). Heating a chloroform solution of **9** in the presence of excess benzonitrile at the reflux temperature generated osmabenzene $[Os\{CHC(PPh_3)C(CH_3)CHCH\}(PhCN)_2(PPh_3)_2]Cl_2$ (**14**), which could be also obtained from heating isolated **11** or **12** in the mixture of chloroform and benzonitrile at the reflux temperature. Complexes **11**, **12** and **14** are in fact isomers. We have demonstrated for the first time that certain transition-metal allene complexes can isomerise to metallabenzenes. DFT calculations of the transformations of model complexes **11′** and **12′** to osmabenzene complex **14′** show that the hydrogen-transfer process between them could be readily implemented by catalysis using a Cl^- counterion after replacement of the chloride ligands by benzonitrile. To date, we have successfully implemented the conversions of various osmacycles containing an η^2-coordinated olefin to osmabenzenes, which encourages us to develop a general method for the formation of metallabenzenes from such metallacycles.

Experimental Section

General procedures: All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The starting materials $HC{\equiv}C(CH_3)(OH)CH{=}CH_2$ and benzonitrile were purchased from Sigma—Aldrich, and $[OsCl_2(PPh_3)_3]$ was synthesised by literature procedures.[17] Solvents were distilled under nitrogen from sodium benzophenone (ether, *n*-hexane) and calcium hydride (dichloromethane, chloroform). All NMR spectra were recorded with a Bruker AV300 (^1H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.5 MHz) spectrometer. ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analysis data were obtained on a Thermo Quest Italia SPA EA 1110 instrument.

$[Os\{CH{=}C(PPh_3)C(=CH_2)\text{-}\eta^2\text{-}CH{=}CH_2\}Cl_2(PPh_3)_2]$ (9): $HC{\equiv}CC(CH_3)(OH)CH{=}CH_2$ (113 μL, 1.05 mmol) was added to a solution of $[OsCl_2(PPh_3)_3]$ (1.00 g, 0.96 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 5 h to give a brown-yellow suspension. The yellow solid was collected by filtration, washed with CH_2Cl_2 (2×2 mL), and then dried in vacuo. Yield: 0.59 g (53%); ^1H NMR (300.1 MHz, $CDCl_3$): $\delta=$ 11.0 (d, $J(P,H)=18.8$ Hz, 1 H; Os*CH*), 4.5 (s, 1H; C(=C*H*$_2$)), 4.0 (s, 1H; C(=C*H*$_2$)), 3.3 (m, 1H; η^2-C*H*=CH$_2$), 2.8 (m, 1H; η^2-CH=C*H*$_2$), 2.4 (m, 1H; η^2-CH=C*H*$_2$), 6.6–7.9 ppm (m, 45H; PPh_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta=6.2$ (dd, $J(P,P)=6.0$, 5.7 Hz, C*P*Ph$_3$), −1.4 (dd, $J(P,P)=254.9$, 6.0 Hz, Os*P*Ph$_3$), −12.1 ppm (dd, $J(P,P)=254.9$, 5.7 Hz, Os*P*Ph$_3$); elemental analysis calcd (%) for $C_{60}H_{51}P_3Cl_2Os$: C 63.99, H 4.56; found: C 63.98; H 5.00.

$[Os\{CH{=}C(PPh_3)C(=CH_2)\text{-}\eta^2\text{-}CH{=}CH_2\}Cl(PMe_3)_3]Cl$ (10): A solution of PMe_3 in THF (1.0 M, 4.4 mL, 4.4 mmol) was added to a suspension of **9** (0.50 g, 0.44 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for about 12 h to give a light brownish solution. The volume of the solution was reduced to approximately 1 mL in vacuo. Addition of diethyl ether (10 mL) to the solution gave a white precipitate, which was collected by filtration. Subsequent recrystallisation of the crude product from dichloromethane/hexane yielded colourless crystals. Yield: 0.37 g (82%); ^1H NMR (300.1 MHz, $CDCl_3$): $\delta=10.1$ (d, $J(P,H)=27.0$ Hz, 1H; Os*CH*), 5.2 (s, 1H; C(=C*H*$_2$)), 4.6 (s, 1H; C(=C*H*$_2$)), 3.5 (br, 1H; η^2-C*H*=CH$_2$), 2.4 (br, 1H; η^2-CH=C*H*$_2$), 1.7 (br, 1H; η^2-CH=C*H*$_2$), 7.3–7.8 (m, 15H; PPh_3), 1.1–1.6 ppm (m, 27H; PMe_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta=10.4$ (dt, $J(P,P)=24.3$, 4.3 Hz, C*P*Ph$_3$), −44.8 (m, Os*P*Me$_3$), −45.0 (m, Os*P*Me$_3$), −54.8 ppm (dt, $J(P,P)=24.3$, 20.7 Hz, Os*P*Me$_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta=220.9$ (dtd, $J(P,C)=77.0$, 9.1, 4.5 Hz, Os*C*H), 159.1 (dd, $J(P,C)=22.3$, 5.8 Hz, *C*(=CH$_2$)), 115.8 (d, $J(P,C)=68.0$ Hz, *C*(PPh$_3$)), 108.1(s, C(=*C*H$_2$)), 51.7(d, $J(P,C)=11.3$ Hz, η^2-*C*H=CH$_2$), 30.5 (s, η^2-CH=*C*H$_2$), 120.1–134.4 (m, PPh_3), 15.0–17.3 ppm (m, PMe_3); elemental analysis calcd (%) for $C_{33}H_{48}P_4Cl_2Os$: C 47.77, H 5.83; found: C 47.71, H 5.47.

$[Os\{CH{=}C(PPh_3)C(=CH_2)\text{-}\eta^2\text{-}CH{=}CH_2\}(C_6H_5CN)_2(PPh_3)_2]Cl_2$ (11): A mixture of C_6H_5CN (0.90 mL, 8.8 mmol) and **9** (0.50 g, 0.44 mmol) in chloroform (10 mL) was stirred for 8 h at room temperature to give a brown solution. The volume of the solution was reduced to approximately 1 mL in vacuo. Addition of ether/*n*-hexane (1:1, 5 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with ether/*n*-hexane (1:1, 5×2 mL), and dried in vacuo. Yield: 0.51 g (86%); ^1H NMR (300.1 MHz, $CDCl_3$): $\delta=9.9$ (d, $J(P,H)=18.0$ Hz, 1 H; Os*CH*), 5.0 (s, 1H; C(=C*H*$_2$)), 4.3 (s, 1H; C(=C*H*$_2$)), 4.1 (m, 1H; η^2-C*H*=CH$_2$), 3.1 (m, 1H; η^2-CH=C*H*$_2$), 3.0 (m, 1H; η^2-CH=C*H*$_2$), 6.2–8.0 ppm (m, 55H; Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta=9.3$ (s, C*P*Ph$_3$), 1.4 (d, $J(P,P)=213.8$ Hz, Os*P*Ph$_3$), −9.2 ppm (d, $J(P,P)=213.8$ Hz, Os*P*Ph$_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta=203.1$ (br, Os*C*H), 155.8 (d, $J(P,C)=19.6$ Hz, *C*(=CH$_2$)), 120.8 (s, Ph*C*N), 119.7 (s, Ph*C*N), 112.6 (d, $J(P,C)=76.0$ Hz, *C*(PPh$_3$)), 107.5 (s, C(=*C*H$_2$)), 71.2 (d, $J(P,C)=13.1$ Hz, η^2-*C*H=CH$_2$), 52.7 (d, $J(P,C)=6.5$ Hz, η^2-CH=*C*H$_2$), 127.9–135.0 ppm (m, Ph); elemental analysis calcd (%) for $C_{74}H_{61}N_2P_3Cl_2Os$: C 66.71, H 4.61, N 2.10; found: C 66.70, H 4.79, N 2.69.

$[Os\{CH{=}C(PPh_3)C(CH_3){=}(\eta^2\text{-}C{=}CH_2)\}(C_6H_5CN)_2(PPh_3)_2]Cl_2$ (12): The mixture of C_6H_5CN (1.4 mL, 14 mmol) and **9** (0.50 g, 0.44 mmol) in chloroform (10 mL) was stirred for 48 h at room temperature to give a brown solution. The volume of the solution was reduced to approximately 1 mL in vacuo. Addition of ether/*n*-hexane (1:1, 5 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with ether/*n*-hexane (1:1, 5×2 mL) and dried in vacuo. Yield: 0.50 g (85%). ^1H NMR (300.1 MHz, $CDCl_3$): $\delta=11.7$ (d, $J(P,H)=18.0$ Hz, 1 H; Os*CH*), 2.6 (br, 2H; η^2-C=C*H*$_2$), 1.7 (s, 3H; C(*CH*$_3$)), 6.9–8.0 ppm (m, 55H; Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta=9.0$ (t, $J(P,P)=3.6$ Hz, C*P*Ph$_3$), −10.1 ppm (d, $J(P,P)=3.6$ Hz, Os*P*Ph$_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, collected in the presence of approx. 5 equiv of purposely added benzonitrile): $\delta=204.4$ (br, Os*C*H), 183.1 (d, $J(P,C)=21.6$ Hz, η^2-*C*=CH$_2$), 123.1 (d, $J(P,C)=25.6$ Hz, *C*(CH$_3$)), 121.2 (s, Ph*C*N), 120.0 (s, Ph*C*N), 121.1 (d, $J(P,C)=71.4$ Hz, *C*(PPh$_3$)), 23.8 (s, η^2-C=*C*H$_2$), 19.3 (s, C(*C*H$_3$)), 126.8–133.7 ppm (m, Ph); elemental analysis calcd (%) for $C_{74}H_{61}N_2P_3Cl_2Os$: C 66.71, H 4.61, N 2.10; found: C 66.82, H 4.74, N 2.13.

$[Os\{CH{=}C(PPh_3)C(CH_3){=}(\eta^2\text{-}C{=}CH_2)\}Cl_2(PPh_3)_2]$ (13): The solution of **12** (100 mg, 0.075 mmol) in chloroform (1 mL) was layered with ether (2 mL) in a glass tube for a week to give yellow crystals. Yield: 52 mg (62%); ^1H NMR (300.1 MHz, $CDCl_3$): $\delta=12.2$ (d, $J(P,H)=15.0$ Hz, 1 H; Os*CH*), 2.3 (br, 2H; η^2-C=C*H*$_2$), 1.3 (s, 3H; C(*CH*$_3$)=), 6.8–7.8 ppm (m,

45H; PPh_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 6.7$ (s, C*P*Ph_3), −10.8 ppm (s, Os*P*Ph_3); elemental analysis calcd (%) for $C_{60}H_{51}P_3Cl_2Os$: C 63.99, H 4.56; found: C 63.57, H 4.98.

[Os{CHC(PPh$_3$)C(CH$_3$)CHCH}(C$_6$H$_5$CN)$_2$(PPh$_3$)$_2$]Cl$_2$ (14): *Method A*: A mixture of C_6H_5CN (1.4 mL, 14 mmol) and [Os{CH=C-(PPh_3)C(=CH_2)-η^2-CH=CH_2}Cl_2(PPh_3)$_2$] (**9**; 0.50 g, 0.44 mmol) in chloroform (10 mL) was heated at the reflux temperature for 24 h to give a dark green solution. The volume of the solution was reduced to approximately 1 mL in vacuo. Addition of ether/*n*-hexane (1:1, 5 mL) to the solution gave a green precipitate, which was collected by filtration, washed with ether/*n*-hexane (1:1, 5×2 mL) and dried in vacuo. Yield: 0.47 g (79%).

Method B: A mixture of C_6H_5CN (0.78 mL, 7.8 mmol) and **11** (0.50 g, 0.38 mmol) or **12** (0.50 g, 0.38 mmol) in chloroform (10 mL) was refluxed for 12 h to give a dark green solution. The volume of the solution was reduced to approximately 1 mL in vacuo. Addition of ether/*n*-hexane (1:1, 5 mL) to the solution gave a green precipitate, which was collected by filtration, washed with ether/*n*-hexane (1:1, 5×2 mL) and dried in vacuo. Yield: 0.42 g (83%; from complex **11**); yield: 0.44 g (87%; from complex **12**). ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 17.7$ (d, J(H,H) = 9.0 Hz, 1 H; OsC*H*CH), 16.1 (d, J(P,H) = 27.0 Hz, 1H; OsC*H*C(PPh$_3$)), 6.5 (d, J-(H,H) = 9.0 Hz, 1H; OsCHC*H*), 1.1 (s, 3H; CH_3), 6.6–7.9 ppm (m, 55H; Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 20.4$ (s, C*P*Ph_3), −3.0 ppm (s, Os*P*Ph_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 257.3$ (d, J(P,C) = 9.1 Hz, Os*C*HCH), 230.3 (dd, J(P,C) = 9.8, 7.5 Hz, Os*C*HC(PPh$_3$)), 153.5 (d, J-(P,C) = 17.4 Hz, *C*(CH_3)), 132.0 (s, OsCH*C*H), 122.4 (s, Ph*C*N), 121.3 (s, Ph*C*N), 110.8 (d, J(P,C) = 74.7 Hz, *C*(PPh$_3$)), 27.3 (s, CH_3), 128.0–135.4 ppm (m, Ph); elemental analysis calcd (%) for $C_{74}H_{61}N_2P_3Cl_2Os$: C 66.71, H 4.61, N 2.10; found: C 67.29, H 4.30, N 2.06.

[Os{CHC(PPh$_3$)C(CH$_3$)CHCH}Cl(C$_6$H$_5$CN)(PPh$_3$)$_2$]BPh$_4$ (15): A solution of $NaBPh_4$ (0.34 g, 1.0 mmol) in CH_3OH (1 mL) was added dropwise to a solution of **14** (0.30 g, 0.23 mmol) in CH_3OH (10 mL), which led to the precipitation of a green solid that was collected by filtration, washed with CH_3OH (5×3 mL) and dried in vacuo. Yield: 0.31 g (90%); ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 15.8$ (d, J(H,H) = 8.7 Hz, 1 H; OsC*H*CH), 14.8 (d, J(P,H) = 25.8 Hz, 1H; OsC*H*C(PPh$_3$)), 7.5 (d, J-(H,H) = 8.7 Hz, 1 H; OsCHC*H*), 1.4 (s, 3H; CH_3), 6.3–7.8 ppm (m, 50H; Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 22.7$ (s, C*P*Ph_3), 14.2 ppm (s, Os*P*Ph_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$,): $\delta = 257.6$ (br, Os*C*HCH), 231.9 (br, Os*C*HC(PPh$_3$)), 112.6 (d, J(P,C) = 77.5 Hz, *C*(PPh$_3$)), 112.4 (s, Ph*C*N),161.8 (d, J(P,C) = 17.8 Hz, *C*(CH_3)), 28.1 (s, CH_3), 128.0–136.1 (m, PPh_3 and PhCN), 163.2–165.1 ppm (m, BPh_4); elemental analysis calcd (%) for $C_{91}H_{76}NBP_3ClOs$: C 72.24, H 5.06, N 0.93; found: C 71.97, H 5.09, N 1.06.

X-ray crystal structure determination of 9, 13 and 15: Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or $CHCl_3$ solutions layered with ether or *n*-hexane for complexes **9**, **13** and **15**. Selected crystals were mounted on top of a glass fibre and transferred into a cold stream of nitrogen. The data was collected on an Oxford Gemini S Ultra CCD Area Detector or a Bruker Apex CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Multi-scan or empirical absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full-matrix least-squares on F^2 with the Bruker SHELXTL-97 program package. Non-H atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Details of crystal data, data collection, and refinements are summarised in Table 1. CCDC-699564 (**9**), 699565 (**13**) and 699566 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: Quantum chemical calculations were performed by means of hybrid density functional theory at the B3LYP level.[18] Full geometry optimisations and analytical frequency calculations were performed with basis sets of 6–31G**[19] for main group elements and Hay's small-core ECP (effective core potential, Lanl2dz[20] as denoted in Gaussian 03) for Os atoms. Solvent effects were considered by using the conductor-like polarisable continuum model (CPCM)[21] with CH_3CN as the model solvent. Free energies G at 298 K were reported.

All the calculations were carried out with the Gaussian 03 program suite.[22]

Table 1. Crystal data and structure refinement for **9**, **13** and **15.**

Complex	**9**	**13**·1.5 H_2O	**15**·0.5 H_2O
formula	$C_{60}H_{51}Cl_2OsP_3$	$C_{60}H_{51}Cl_2OsP_3$ ·1.5 H_2O	$C_{67}H_{56}ClNOsP_3$ $B(C_6H_5)_4$·0.5 H_2O
M_r	1126.02	1153.04	1521.91
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1$	$P2_1/n$	$\bar{P}1$
a [Å]	11.393(2)	10.0191(3)	12.671(6)
b [Å]	20.226(4)	24.6752(9)	14.042(7)
c [Å]	13.789(3)	22.3716(7)	21.791(10)
α [°]	90	90	92.785(9)
β [°]	111.760(3)	98.039(3)	101.743(9)
γ [°]	90	90	95.906(9)
V [Å^3]	2951.2(10)	5476.4(3)	3766(3)
Z	2	4	2
ρ_{calcd} [g cm^{3-}]	1.267	1.398	1.342
μ [mm^{-1}]	2.366	2.553	1.840
F(000)	1132	2324	1554
crystal size [mm]	0.20×0.16×0.08	0.22×0.20×0.17	0.28×0.17×0.06
reflns collected	20678	26755	27707
indep reflns	10158	9536	13185
data/restraints/ params	10158/1/595	9536/90/622	13185/192/862
GOF on F^2	1.018	1.017	1.028
$R(F)/wR$ $[I > 2\sigma(I)]$	0.0444, 0.1265	0.0615, 0.1243	0.0721, 0.1910
$R(F^2)/wR(F^2)$ (all)	0.0474, 0.1280	0.1368, 0.1343	0.0915, 0.2015

Acknowledgements

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