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Coupling Reactions of an Allenylcarbene Complex with Alkynes and Styrene

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The allenylcarbene complex [$OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$] undergoes coupling reactions with $HC\equiv CSiMe_3$ and $PhC\equiv CC\equiv CPh$ to produce the fulvene complexes [$OsCl_2\{\eta^6\text{-}C_5H_2(Ph)(SiMe_3)(=CHPh)\}(PPh_3)$] and [$OsCl_2\{\eta^6\text{-}C_5H(Ph)_2(C\equiv CPh)(=CHPh)\}(PPh_3)$], respectively. A similar coupling reaction also occurs between [$OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$] and styrene.

Introduction

The [2+2+2] cyclotrimerization of alkynes to give six-membered aromatic rings is one of the most common reactions promoted by transition metal complexes and has been utilized in the synthesis of many useful natural products and novel organic materials.[1–3] In sharp contrast, examples of metal-mediated [2+2+1] cyclotrimerization of alkynes to give thermodynamically less stable isomeric fulvene derivatives are limited to only a few scattered reports.

The stoichiometric formation of fulvene metal complexes from formal [2+2+1] cyclotrimerizations of alkynes has been reported for the reaction of rhodium,[4] iridium,[5] and palladium[6] complexes with alkynes. Reported catalytic cyclotrimerization reactions of alkynes to give fulvenes include the titanium aryloxide/$LiC\equiv C$*t*Bu-catalyzed cyclotrimerization of *tert*-butylacetylene[7] and the [$(\eta^3\text{-}C_3H_5)PdCl]_2$/dppf-catalyzed cyclotrimerization of aliphatic alkynes.[8] Fulvene or fulvenyl intermediates may also be involved in the reactions of terminal alkynes with transition metal complexes to give complexes with ligands derived from the oligomerization of alkynes.[9–15]

There are several possible pathways that can lead to the formation of fulvenes from the [2+2+1] cyclotrimerization of alkynes; these are illustrated in Scheme 1. Fulvenes may be formed via a metallacyclopentadiene route, which involves oxidative coupling of two molecules of alkynes at the metal to give a metallacyclopentadiene intermediate, isomerization of another molecule of alkyne to a vinylidene ligand, and reductive cyclization to a fulvene product by coupling of the vinylidene ligand and the metallacyclopentadiene ring (Scheme 1, path a). Reactions of preformed iridiacyclopentadiene compounds with terminal alkynes have been shown to produce fulvene complexes.[5] In the reaction involving a base (Scheme 1, path b), for example the titanium aryloxide/$LiC\equiv C$*t*Bu-catalyzed cyclotrimerization of *tert*-butylacetylene, a metallacyclopentadiene-acetylide intermediate has been proposed. This intermediate undergoes reductive coupling followed by an insertion to give the fulvenyl complex, which reacts with alkyne to give fulvene and regenerate the metallacyclopentadiene-acetylide intermediate.[7] In principle, fulvenes could also be formed via metallacyclobutene intermediates (Scheme 1, path c). This reaction has been proposed for the formation of a fulvene complex from the reaction of $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene) with $HC\equiv C$*t*Bu in the presence of $AgPF_6$.[4] In this regard, it would be interesting to demonstrate that preformed metallacyclobutene complexes could react with alkynes to give fulvene complexes.

We have recently reported the synthesis of the η^2-allenylcarbene complex [$OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$] (**1**),[16,17] which can be regarded as an isomer of an osmacyclobutene, from the reaction of $PhC\equiv CH$ with the vinylidene complex [$OsCl_2(=C=CHPh)(PPh_3)_2$] or [$OsCl_2(PPh_3)_3$]. In this work, we will describe its coupling reactions with alkynes. Its reaction with styrene has also been investigated for comparison.

Results and Discussion

Coupling Reaction of [$OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$] (1) with Alkynes

Treatment of **1** with $HC\equiv CSiMe_3$ in dichloromethane produced the η^6-fulvene complex [$OsCl_2\{\eta^6\text{-}C_5H_2(Ph)(SiMe_3)(=CHPh)\}(PPh_3)$] (**2**), which was isolated as a green solid in 81% yield (Scheme 2). The NMR spectroscopic

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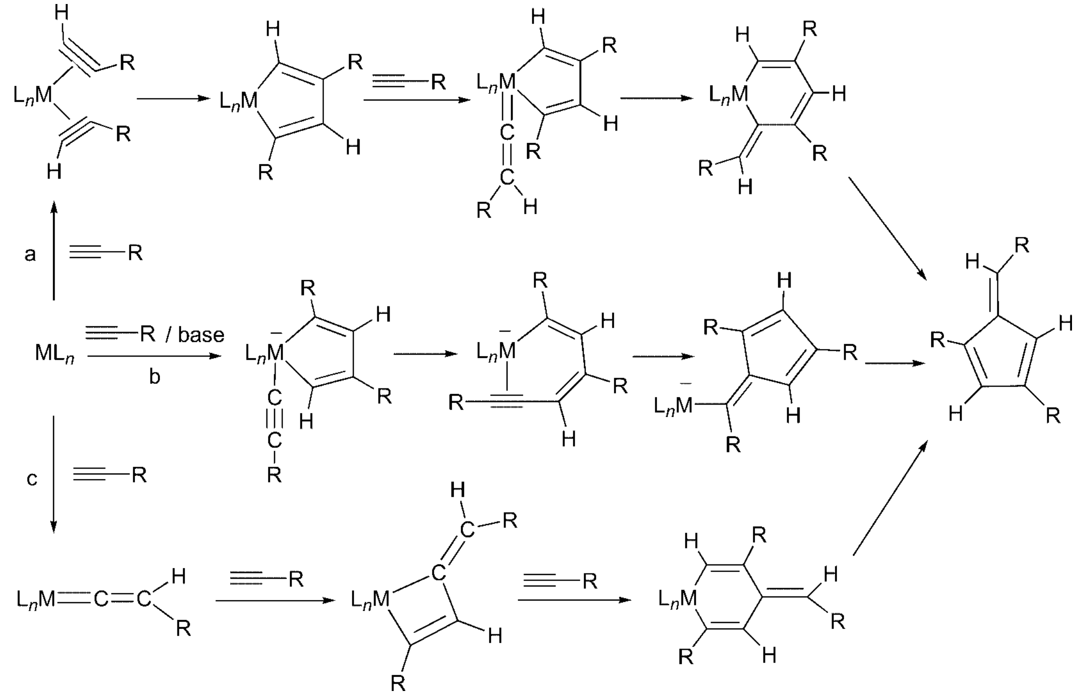
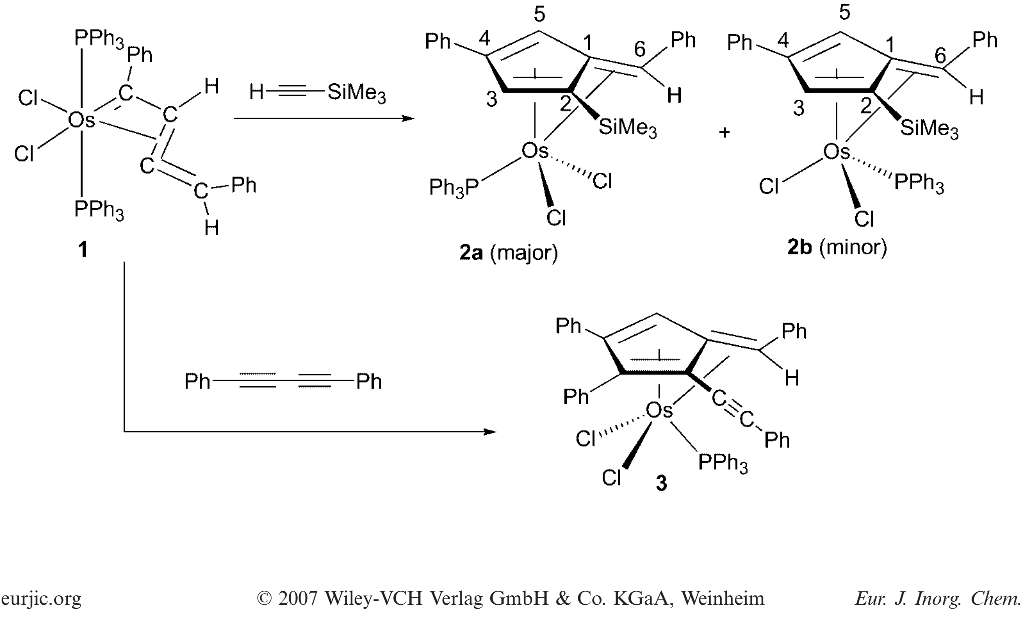


Scheme 1.

data (in CD_2Cl_2) of the isolated solid suggest the presence of two isomers (**2a** and **2b**) in a ratio of 4.5:1 in solution (Scheme 2).

The structure of **2a** was determined by X-ray diffraction analysis of a single crystal grown from a CH_2Cl_2 solution of **2** layered with hexane. Selected bond lengths and angles are shown in Table 1. The structure shown in Figure 1 clearly reveals that coupling of HC≡CSiMe$_3$ with the allenylcarbene ligand has occurred to give the η^6-4,6-diphenyl-2-(trimethylsilyl)fulvene complex **2**.

The interaction of osmium and the exocyclic double bond in complex **2a** is indicated by the inclination of the C(1)–C(6) bond toward osmium, with an angle of 26.9° from the fulvene ring plane. The displacement of C(6) from the fulvene ring plane is 0.625 Å. However, this interaction is weak, as reflected by the rather long Os–C(6) separation [2.632(4) Å] and the relatively short exocyclic double bond [the C(1)–C(6) distance being 1.380(5) Å]. Three extreme canonical forms (see Scheme 3), namely an η^6-triene (**2**), an η^5-cyclopentadienido-σ-alkyl ("tucked-in", **2′**), and a zwit-



Scheme 2.

Table 1. Selected bond lengths [Å] and angles [°] for [$OsCl_2\{\eta^6$-$C_5H_2(Ph)(SiMe_3)(=CHPh=\}(PPh_3)]$ (**2a**).

Os(1)–C(1)	2.143(3)	Os(1)–C(2)	2.182(4)
Os(1)–C(3)	2.183(4)	Os(1)–C(4)	2.288(3)
Os(1)–C(5)	2.184(4)	Os(1)–C(6)	2.632(4)
Os(1)–Cl(1)	2.3920(9)	Os(1)–Cl(2)	2.3952(9)
Os(1)–P(1)	2.3547(9)	C(1)–C(2)	1.480(5)
C(2)–C(3)	1.421(5)	C(3)–C(4)	1.429(5)
C(4)–C(5)	1.417(5)	C(1)–C(5)	1.461(5)
C(1)–C(6)	1.380(5)	C(2)–Si(1)	1.882(4)
C(4)–C(11)	1.481(5)	C(6)–C(21)	1.449(5)
C(1)–Os(1)–P(1)	156.95(10)	C(4)–Os(1)–P(1)	95.76(9)
C(2)–Os(1)–P(1)	123.38(10)	C(5)–Os(1)–P(1)	127.21(10)
C(3)–Os(1)–P(1)	93.60(10)	C(6)–Os(1)–P(1)	170.78(9)
C(1)–Os(1)–Cl(1)	110.50(10)	C(4)–Os(1)–Cl(1)	155.96(10)
C(2)–Os(1)–Cl(1)	96.06(10)	C(5)–Os(1)–Cl(1)	148.68(10)
C(3)–Os(1)–Cl(1)	118.77(10)	C(6)–Os(1)–Cl(1)	87.50(10)
C(1)–Os(1)–Cl(2)	109.88(10)	C(4)–Os(1)–Cl(2)	115.23(10)
C(2)–Os(1)–Cl(2)	148.99(10)	C(5)–Os(1)–Cl(2)	94.71(11)
C(3)–Os(1)–Cl(2)	152.39(10)	C(6)–Os(1)–Cl(2)	88.80(10)
P(1)–Os(1)–Cl(1)	83.99(3)	P(1)–Os(1)–Cl(2)	87.55(3)
Cl(1)–Os(1)–Cl(2)	88.80(3)	C(1)–Os(1)–C(2)	40.00(13)
C(5)–C(1)–C(2)	107.9(3)	C(3)–C(2)–C(1)	104.3(3)
C(2)–C(3)–C(4)	112.6(3)	C(5)–C(4)–C(3)	106.4(3)
C(4)–C(5)–C(1)	108.7(3)	C(6)–C(1)–Os(1)	94.2(2)
C(6)–C(1)–C(2)	119.6(3)	C(6)–C(1)–C(5)	122.8(4)
C(1)–C(6)–C(21)	129.8(4)		

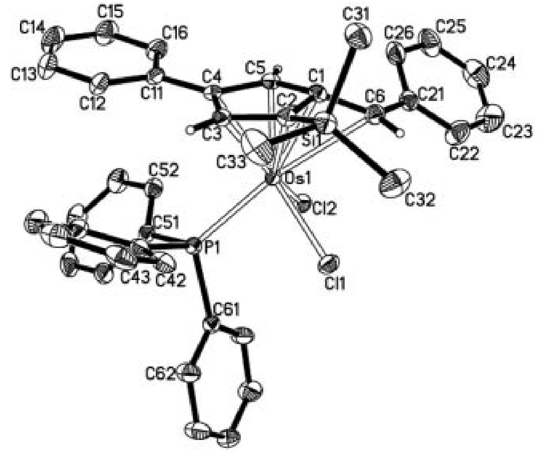


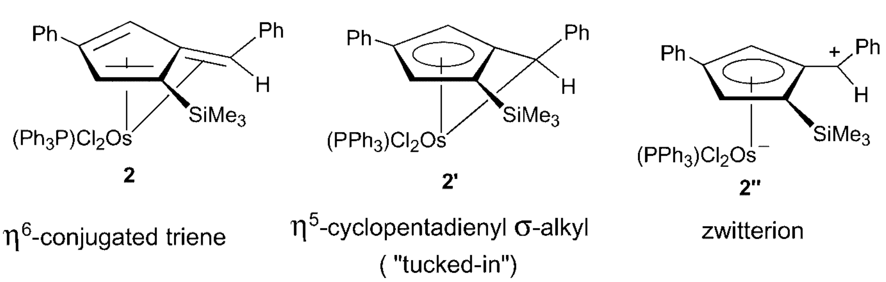
Figure 1. Molecular structure of [$OsCl_2\{\eta^6$-$C_5H_2(Ph)(SiMe_3)$-$(=CHPh)\}(PPh_3)]$ (**2a**).

terionic form (**2''**), can be considered for the fulvene complex.[18] The structural data of **2a** suggest that the fulvene ligand in **2a** can be regarded as being bound to the osmium in an η^6-triene fashion. As shown in Table 2, the Os–C-(exocyclic) bond lengths in the structurally characterized osmium fulvene complexes [$(\eta^5$-$C_5Me_5)Os\{\eta^6$-C_5Me_4-$(=CPh_2)\}](PF_6)$,[19] [$(\eta^5$-$C_5Me_5)Os\{\eta^6$-$C_5Me_4(=CH_2)\}]$-(BPh_4),[20] and [$(\eta^5$-$C_5Me_5)Os\{\eta^6$-$C_5Me_4(=CHC_6F_5)\}]$-(PF_6)[21] are significantly shorter and the exocyclic C–C bond lengths significantly longer than those in complex **2a**, which is indicative of a "tucked-in" bonding type in these complexes. As expected, the inclination angles in these complexes are also significantly larger (35.6–41.8°) than that in **2a** (26.9°).

The $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 at room temperature displays two singlets at δ = –0.3 (major) and –7.8 ppm (minor), thereby indicating the presence of two isomers in solution. In the ^1H NMR spectrum, the major isomer displays a singlet at δ = 6.51 ppm and two doublets at δ = 5.00 and 7.83 ppm for the three fulvene protons. The splitting of the signals at δ = 5.00 and 7.83 ppm is due to coupling with the ^{31}P nuclei, as suggested by $^1H\{^{31}P\}$ NMR experiments. The ^1H NMR spectrum of the minor isomer exhibits three singlets in the ^1H NMR spectrum at δ = 5.49, 6.31, and 6.80 ppm for the fulvene protons. Fulvene complexes such as [$Re(C_6F_5)\{(\eta^6$-$C_5Me_4(=CH_2)\}(CO)_2]$[18a,18b] and [$RuCl_2(py)\{(\eta^6$-$C_5Me_4(=CPh_2)\}]$[22] also exist as two isomers in solution. This isomerism has been attributed to the presence of conformational isomers due to restricted rotation about the metal-fulvene bond. A similar isomerism can be proposed for **2**. Scheme 4 shows three possible conformers of **2**. On the basis of steric reasons, one would expect the stability of these three conformers to be in the order **2a** > **2b** > **2c**.

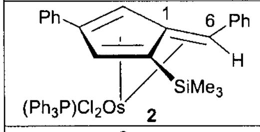
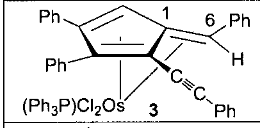
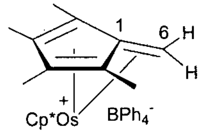
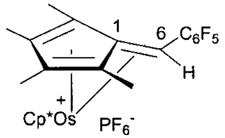
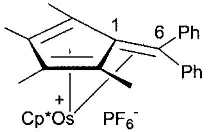
The two isomers observed in solution by NMR spectroscopy can be attributed to **2a** and **2b**. The major isomer can be assigned to the conformer revealed by the X-ray structure (**2a**), in which the exocyclic double bond is *trans* to PPh_3. In agreement with the structure, the ^1H NMR spectrum shows two signals at δ = 7.83 ($J_{P,H}$ = 5.8 Hz) and 5.00 ppm ($J_{P,H}$ = 4.0 Hz) assignable to C(6)H and C(5)H, respectively, and a singlet at δ = 6.51 ppm assignable to C(3)H. The minor isomer observed in solution may correspond to conformer **2b** in which the exocyclic double bond is *cis* to PPh_3. The three fulvene signals at δ = 5.49, 6.31, and 6.80 ppm observed for the minor isomer can be assigned to C(5)H, C(3)H, and C(6)H, respectively.

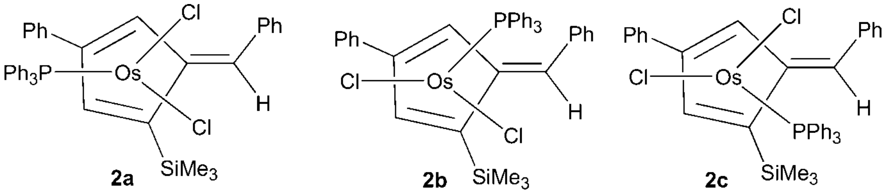
Scheme 5 shows a plausible mechanism for the formation of **2** from the coupling reaction. Complex **1** could rearrange



Scheme 3.

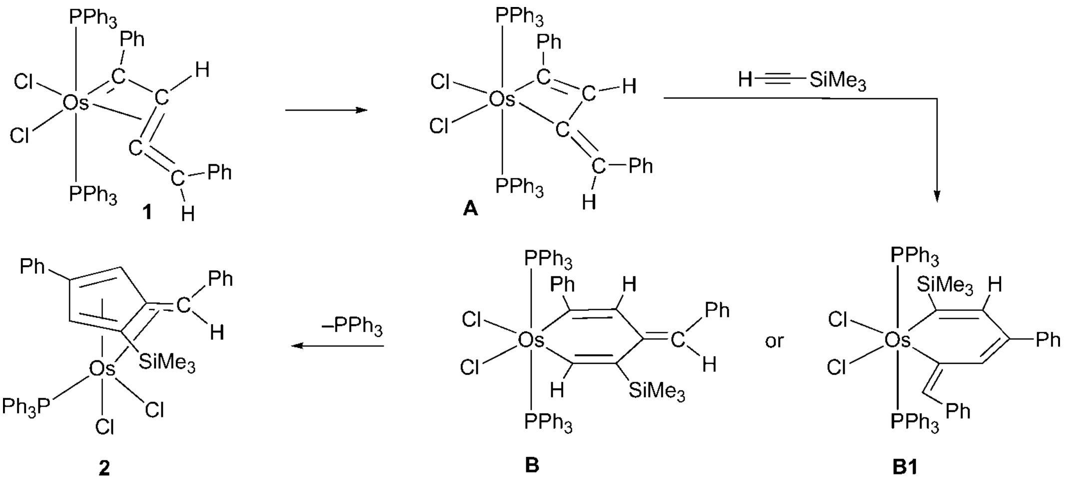
Table 2. Principal structural parameters of selected osmium fulvene complexes.

Compound	Os–C(1) [Å]	Os–C(6) [Å]	C(1)–C(6) [Å]	Inclination angle [°]	Ref.
	2.143(3)	2.632(4)	1.380(5)	26.9	this work
	2.097(4)	2.392(4)	1.424(6)	38.2	this work
	2.069(4)	2.224(5)	1.426(7)	41.8	[20]
	2.086(5)	2.401(6)	1.428(8)	35.6	[21]
	2.088(7)	2.387(9)	1.459(12)	38.4	[19]



Scheme 4.

to metallacyclobutene **A**, which undergoes cycloaddition with $HC\equiv CSiMe_3$ to give the metallacyclohexadiene intermediate **B** or **B1**. Complex **B** or **B1** could then undergo reductive elimination, followed by coordination of the fulvene to osmium and loss of one PPh_3 ligand to give **2**. A similar mechanism has been proposed previously.[4,9]



Scheme 5.

The reaction of **1** with PhC≡C–C≡CPh produced the analogous fulvene complex **3** (Scheme 1), although the reaction is slow in dichloromethane at room temperature. When a mixture of **1** and PhC≡C–C≡CPh in benzene was refluxed for 1 h, a brown solution containing **3** along with small amounts of unreacted **1** and an unidentified species with a ^{31}P chemical shift of $\delta = -16.0$ ppm was produced. Complex **3** was isolated in 43% yield from the reaction mixture. Attempts to isolate and identify the unknown species with a ^{31}P chemical shift of $\delta = -16.0$ ppm failed. The structure of **3** was also confirmed by a single-crystal X-ray diffraction study. A view of the molecular structure is shown in Figure 2 and selected bond lengths and angles are listed in Table 3.

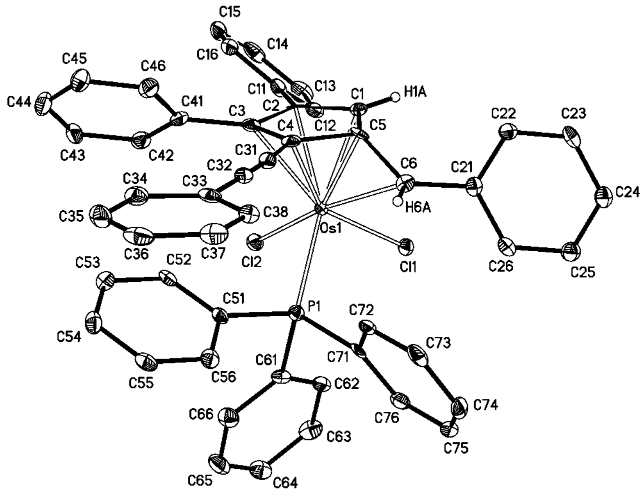


Figure 2. Molecular structure of $[OsCl_2\{\eta^6\text{-}C_5H(C{\equiv}CPh)(Ph)_2\text{-}(=CHPh)\}(PPh_3)]$ (**3**).

Like complex **2**, the fulvene ligand in **3** is also η^6-coordinated to osmium. However, the interaction between the exocyclic double bond and the osmium center is stronger for **3**. Thus, the Os–C(6) bond length is 2.392(4) Å and the exocyclic C–C double bond [C(5)–C(6)] bond length is 1.424(6) Å. For comparison, the Os–C(exocyclic) bond length is 2.632(4) Å and the exocyclic C–C bond length is 1.380(5) Å in complex **2a**. The inclination angle of **3** (38.2°) is also significantly larger than that of **2a** (26.9°). The structural features associated with the Os(η^6-fulvene) moiety in **3** are similar to those of the previously reported osmium fulvene complexes $[(\eta^5\text{-}C_5Me_5)Os\{\eta^6\text{-}C_5Me_4(=CPh_2)\}](PF_6)$,[19] $[(\eta^5\text{-}C_5Me_5)Os\{\eta^6\text{-}C_5Me_4(=CH_2)\}](BPh_4)$,[20] and $[(\eta^5\text{-}C_5Me_5)Os\{\eta^6\text{-}C_5Me_4(=CHC_6F_5)\}](PF_6)$[21] (see Table 2).

Consistent with the solid-state structure, the ^{1}H NMR spectrum displays two signals at $\delta = 6.00$ and 6.62 ppm assignable to the ring proton and the exocyclic =CH proton, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at $\delta = -8.0$ ppm (in CD_2Cl_2). It is interesting to note that two isomers are observed for **2** in solution but only one isomer is observed for **3**. Complex **3** can, in principle, also exhibit conformational isomerism in solution, and the exact reason why only one conformer is observed for **3** is not clear. The possibility that the fulvene ring is rotating very rapidly in **3** was excluded as additional ^{31}P signals were not observed for a CD_2Cl_2 solution of **3** at low temperature (220 K). Since in situ ^{31}P NMR spectroscopy showed a minor ^{31}P signal along with that of **3** (see above), we tentatively assume that another conformer of **3** may also be produced in the reaction, although we were not able to isolate or identify it. We note that two isomers have been observed for $[RuCl_2(py)\{(\eta^6\text{-}C_5Me_4(=CPh_2)\}]$ whereas only one isomer was observed for the closely related complex $[RuCl_2(dmso)\{(\eta^6\text{-}C_5Me_4(=CPh_2)\}]$.[22]

Table 3. Selected bond lengths [Å] and angles [°] for $[OsCl_2\{\eta^6\text{-}C_5H(C{\equiv}CPh)(Ph)_2(=CHPh)\}(PPh_3)]\cdot 3C_6D_6$ ($\mathbf{3}\cdot 3C_6D_6$).

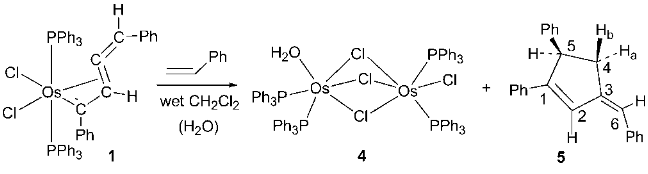
Os(1)–C(1)	2.199(4)	Os(1)–C(2)	2.276(4)
Os(1)–C(3)	2.287(4)	Os(1)–C(4)	2.188(4)
Os(1)–C(5)	2.097(4)	Os(1)–C(6)	2.392(4)
Os(1)–Cl(1)	2.3898(11)	Os(1)–Cl(2)	2.3840(11)
Os(1)–P(1)	2.3686(12)	C(1)–C(2)	1.398(6)
C(2)–C(3)	1.462(6)	C(3)–C(4)	1.437(6)
C(4)–C(5)	1.453(6)	C(1)–C(5)	1.445(6)
C(5)–C(6)	1.424(6)	C(2)–C(11)	1.483(6)
C(6)–C(21)	1.461(6)	C(3)–C(41)	1.486(6)
C(4)–C(31)	1.442(6)	C(31)–C(32)	1.190(6)
C(32)–C(33)	1.444(6)		
C(1)–Os(1)–P(1)	159.92(11)	C(4)–Os(1)–P(1)	102.79(12)
C(2)–Os(1)–P(1)	152.66(11)	C(5)–Os(1)–P(1)	120.96(12)
C(3)–Os(1)–P(1)	117.11(11)	C(6)–Os(1)–P(1)	95.15(11)
C(1)–Os(1)–Cl(1)	91.24(11)	C(4)–Os(1)–Cl(1)	146.74(12)
C(2)–Os(1)–Cl(1)	110.52(11)	C(5)–Os(1)–Cl(1)	107.24(12)
C(3)–Os(1)–Cl(1)	147.87(11)	C(6)–Os(1)–Cl(1)	85.47(11)
C(1)–Os(1)–Cl(2)	116.47(11)	C(4)–Os(1)–Cl(2)	124.62(12)
C(2)–Os(1)–Cl(2)	86.85(11)	C(5)–Os(1)–Cl(2)	150.61(12)
C(3)–Os(1)–Cl(2)	90.49(11)	C(6)–Os(1)–Cl(2)	170.55(11)
P(1)–Os(1)–Cl(1)	94.06(4)	P(1)–Os(1)–Cl(2)	83.30(4)
Cl(1)–Os(1)–Cl(2)	85.34(4)	C(5)–Os(1)–C(4)	39.58(16)
C(2)–C(1)–C(5)	109.5(4)	C(1)–C(2)–C(3)	108.6(4)
C(4)–C(3)–C(2)	106.8(4)	C(3)–C(4)–C(5)	108.6(4)
C(1)–C(5)–C(4)	106.5(4)	C(6)–C(5)–Os(1)	83.3(3)
C(6)–C(5)–C(1)	121.6(4)	C(6)–C(5)–C(4)	117.6(4)
C(5)–C(6)–C(21)	125.3(4)	C(4)–C(31)–C(32)	176.2(5)
C(31)–C(32)–C(33)	176.8(5)	C(3)–C(4)–C(31)	126.3(4)
C(31)–C(4)–C(5)	125.2(4)		

It is interesting to note that complexes **2a** and **3** adopt different conformations in the solid state. This difference could be related to the relative bulkiness of $SiMe_3$, Ph, and C≡CPh. One might expect that the steric effects of these groups are in the order $SiMe_3 >$ Ph > C≡CPh, therefore the bulky PPh_3 ligand tends to be in a position close to C≡CPh rather than Ph in **3**, but close to Ph rather than $SiMe_3$ in **2a**.

We also studied the reaction of **1** with $SiMe_3C{\equiv}C\text{–}C{\equiv}CSiMe_3$. However, the reaction produced many unidentified phosphorus-containing species which proved difficult to separate and identify.

Coupling Reaction of $[OsCl_2\{=CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(PPh_3)_2]$ (1) with Styrene

The easy formation of fulvene complexes from the reaction of $[OsCl_2\{=CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(PPh_3)_2]$ (**1**) with alkynes promoted us to investigate the reaction of **1** with styrene. Treatment of complex **1** with an excess of styrene in wet CH_2Cl_2 leads to the formation of the bimetallic complex $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(H_2O)(PPh_3)_2]$ (**4**) as the only phosphorus-containing product (Scheme 6).



Scheme 6.

Complex **4** was isolated as a light-brown solid in 75% yield and was characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. The $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6 displays four sets of doublets of equal intensity at δ = –6.5, –7.8 ($J_{P,P}$ = 11.4 Hz), –16.4, and –17.4 ppm ($J_{P,P}$ = 16.7 Hz), thereby indicating the presence of four inequivalent phosphorus nuclei. This pattern is closely analogous to that of the dinuclear complex $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os\{=C=CH[C(OH)Ph_2]\}(PPh_3)_2]$[23] and suggests the formation of a bimetallic complex of the type $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(L)(PPh_3)_2]$.

Definite proof of the structure came from a single-crystal X-ray structure analysis. Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution of **4** layered with hexane. Selected bond lengths and angles are given in Table 4 and a view of the molecular geometry of **4** is shown in Figure 3. The structure of **4** is similar to that of $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os\{=C=CH[C(OH)Ph_2]\}(PPh_3)_2]$,[23] with replacement of the vinylidene ligand in the latter complex by an aqua ligand, and deserves no further comments.

Table 4. Selected bond lengths [Å] and angles [°] for $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(H_2O)(PPh_3)_2]\cdot CH_2Cl_2$ (**4**·CH_2Cl_2).

Os(1)–P(1)	2.337(3)	Os(2)–P(3)	2.278(3)
Os(1)–P(2)	2.335(3)	Os(2)–P(4)	2.287(3)
Os(1)–Cl(1)	2.439(2)	Os(2)–Cl(1)	2.392(3)
Os(1)–Cl(2)	2.463(3)	Os(2)–Cl(2)	2.523(3)
Os(1)–Cl(3)	2.403(3)	Os(2)–Cl(3)	2.540(2)
Os(1)–O(1)	2.294(9)	Os(2)–Cl(4)	2.401(3)
P(2)–Os(1)–P(1)	99.51(10)	P(3)–Os(2)–P(4)	98.21(10)
P(1)–Os(1)–Cl(1)	168.96(10)	Cl(1)–Os(2)–Cl(4)	161.17(8)
P(2)–Os(1)–Cl(2)	168.35(9)	P(3)–Os(2)–Cl(2)	170.58(9)
O(1)–Os(1)–Cl(3)	165.29(18)	P(4)–Os(2)–Cl(3)	164.24(9)
P(1)–Os(1)–Cl(3)	93.65(10)	P(3)–Os(2)–Cl(1)	93.34(9)
P(2)–Os(1)–Cl(3)	100.64(10)	P(4)–Os(2)–Cl(1)	94.19(10)
P(2)–Os(1)–Cl(1)	90.13(9)	P(3)–Os(2)–Cl(4)	96.76(10)
Cl(3)–Os(1)–Cl(1)	79.18(9)	P(4)–Os(2)–Cl(4)	100.03(10)
P(1)–Os(1)–Cl(2)	91.70(9)	P(4)–Os(2)–Cl(2)	87.51(9)
Cl(3)–Os(1)–Cl(2)	81.66(9)	Cl(1)–Os(2)–Cl(2)	79.03(8)
Cl(1)–Os(1)–Cl(2)	79.03(8)	Cl(4)–Os(2)–Cl(2)	89.56(10)
O(1)–Os(1)–P(1)	92.64(17)	P(3)–Os(2)–Cl(3)	95.59(9)
O(1)–Os(1)–P(2)	91.41(19)	Cl(1)–Os(2)–Cl(3)	77.40(8)
O(1)–Os(1)–Cl(1)	92.49(17)	Cl(4)–Os(2)–Cl(3)	85.80(9)
O(1)–Os(1)–Cl(2)	84.88(19)	Cl(2)–Os(2)–Cl(3)	77.85(8)
Os(2)–Cl(1)–Os(1)	87.48(8)	Os(1)–Cl(2)–Os(2)	84.10(8)
Os(1)–Cl(3)–Os(2)	84.97(8)		

Obviously, the hydrocarbon ligand of **1** has been eliminated from the metal center in the reaction. The ^1H NMR spectrum of the reaction mixture shows the formation of several organic products, among which compound **5** is the most dominant (ca. 78%). A sample of compound **5** could be isolated as an oil by column chromatography on silica gel using hexane as the eluent, and its structure was readily deduced from spectroscopic data. Thus, the FAB mass spectrum shows an ion peak at *m*/*z* 308.1, indicating that it is composed of a molecule of styrene and the original allenylcarbene unit of **1**. The ^1H NMR spectrum (C_6D_6) shows two multiplets at δ = 2.98 and 3.29 ppm, which could be assigned to the two diastereotopic C*H*$_2$ ring protons $C(4)H_a$ and $C(4)H_b$, respectively (see Scheme 6 for labelling). The ^1H and ^1H-^1H COSY NMR spectra clearly indicate that the CH_2 group is adjacent to a CH group, which has its ^1H NMR signal at δ = 4.16 ppm and is assignable to the signal of C(5)H. The presence of the stereogenic center at C5 is responsible for the different environments around $C(4)H_a$ and $C(4)H_b$. The coupling constant between $C(4)H_a$ and $C(4)H_b$ is 17.3 Hz, while the coupling constants between C(5)H and C(4)Hs are 3.7 and 8.3 Hz for $C(4)H_a$ and $C(4)H_b$, respectively, consistent with the assignment that the latter is formally *trans* to C(5)H. In the ^1H NMR spectrum, the signal of the C(2)H ring proton appears at δ = 6.32 ppm and the signal of the exocyclic C*H*Ph proton [C(6)H] appears as a triplet at δ = 7.51 ppm due to coupling with the protons of the CH_2 group.

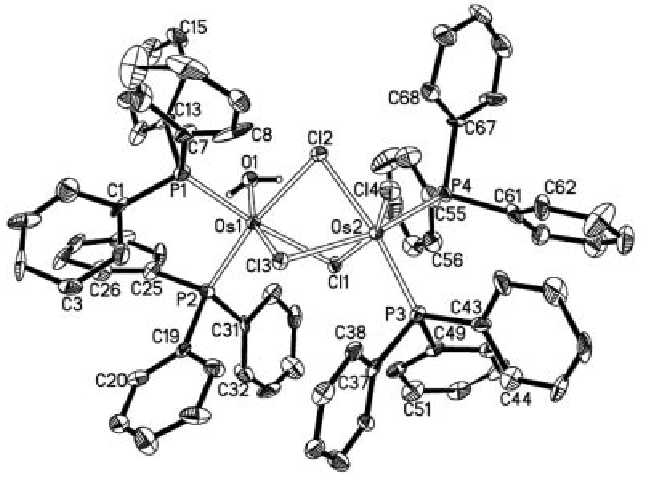
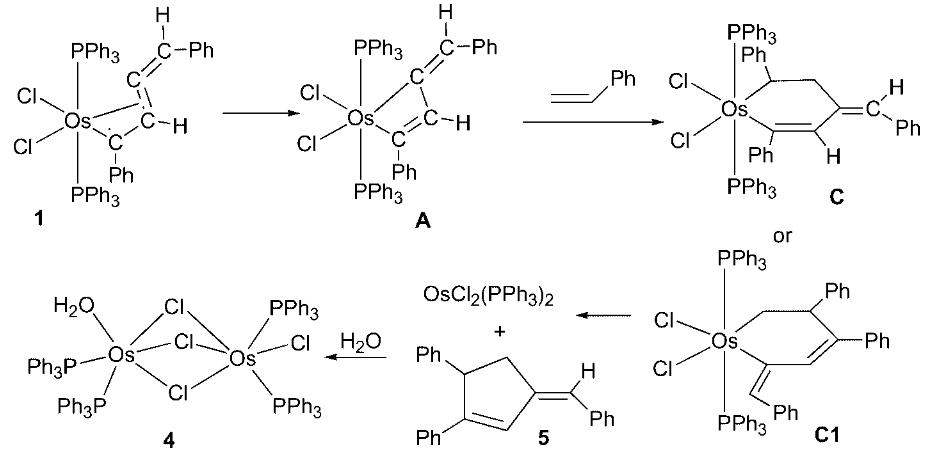


Figure 3. Molecular structure of $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(H_2O)(PPh_3)_2]$ (**4**).

Scheme 7 shows a plausible mechanism for the formation of **4** and **5** from the reaction of **1** with styrene. Complex **1** can rearrange to metallacyclobutene **A**, which can undergo cycloaddition with styrene to give the metallacyclic intermediate **C** or **C1**. Subsequent reductive elimination of **C** or **C1** would give **5** and the transient $OsCl_2(PPh_3)_2$ fragment, which reacts with water in solution to give **4**. Although we have no direct evidence for intermediates **C** and **C1**, they are closely related to intermediates **B** and **B1**.

The allenylcarbene complex **1** was originally derived from the coupling of two molecules of phenylacetylene. Thus, the net transformation involving formation of **1** and the coupling of **1** with styrene represenst a rare example of a [2+2+1] co-cyclotrimerization of alkynes and alkenes.



Scheme 7.

While many examples of [2+2+2] co-cyclotrimerization of alkynes and alkenes to give cyclohexadienes are known,[24] the related [2+2+1] co-cyclotrimerization of alkynes and alkenes, to the best of our knowledge, is still unknown.

In summary, we have demonstrated that the allenylcarbene complex [OsCl$_2${=CPh(η^2-CH=C=CHPh)}(PPh$_3$)$_2$] (**1**), which is originally derived from the coupling of two molecules of phenylacetylene at osmium, can undergo coupling reactions with alkynes to give fulvene complexes. The reactions reported here support a previously proposed mechanism that [2+2+1] cyclotrimerization of alkynes could occur via metallacyclobutene intermediates. We have also shown that complex **1** can undergo a similar coupling reaction with styrene. This result is interesting as it represents a rare example of metal-mediated [2+2+1] co-cyclotrimerization of alkynes and alkenes.

Experimental Section

All manipulations were carried out under nitrogen using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, thf), sodium (benzene), or calcium hydride (CH$_2$Cl$_2$). [Os{=CPh(η^2-CH=C=CHPh)}(PPh$_3$)$_2$][16] was prepared according to the literature method. All other reagents were used as received from Aldrich Chemical Co. USA.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^{1}H and ^{13}C NMR shifts are quoted relative to TMS, and ^{31}P chemical shifts relative to 85% H$_3$PO$_4$. Mass spectra were recorded with a Finnigan TSQ7000 spectrometer.

[OsCl$_2${η^6-C$_5$H$_2$(Ph)(SiMe$_3$)(=CHPh)}(PPh$_3$)] (2): HC≡CSiMe$_3$ (0.43 mL, 3.0 mmol) was added to a solution of [OsCl$_2$(=CPh-CH=C=CPh)(PPh$_3$)$_2$] (0.50 g, 0.50 mmol) in CH$_2$Cl$_2$ (50 mL) and the reaction mixture was stirred at room temperature for 72 h to give a brown solution. The volume of the mixture was reduced to about 1 mL, then diethyl ether (20 mL) was added slowly with stirring and the mixture was filtered to remove a small amount of dark brown precipitate. The filtrate was evacuated to dryness under vacuum and the residue was extracted with 1 mL of benzene to give a brown solution. Addition of hexane (30 mL) to the benzene extract produced a green precipitate, which was collected by filtration, washed with hexane (2 × 30 mL), and dried under vacuum overnight. The ^{31}P{^{1}H} and ^{1}H NMR spectra indicate the presence of two isomers in a ratio of about 1:4.5. Yield: 0.34 g (81%). FAB-MS (NBA): *m/z* 826 [M$^+$]. C$_{39}$H$_{37}$Cl$_2$OsP$_2$Si: calcd. C 56.72, H 4.52; found C 56.68, H 4.61.

2a (PPh$_3$ is *trans* to the exocyclic double bond): ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, see Scheme 1 for labels): δ = 0.45 (s, 9 H, SiMe$_3$), 5.00 [d, $J_{P,H}$ = 4.0 Hz, 1 H, C(5)-H], 6.51 [s, 1 H, C(3)-H], 7.06–7.65 (m, C$_6$H$_5$, PPh$_3$, mixed with those of **2b**), 7.83 [d, $J_{P,H}$ = 5.8 Hz, 1 H, C(6)-H] ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ = 0.5 (s, SiMe$_3$), 73.3 (s, C-3), 82.00 (s, C-5), 83.4 (d, $J_{P,C}$ = 2.6 Hz, C-2), 98.1 (s, C-1), 108.1 (s, C-4), 108.5 (d, $J_{P,C}$ = 16.4 Hz, C-6), 127.6–135.9 (m, C$_6$H$_5$, PPh$_3$, mixed with those of **2b**) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = –0.3 (s) ppm.

2b (PPh$_3$ is *cis* to the exocyclic double bond): ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ = 0.50 (s, 9 H, SiMe$_3$), 5.49 [s, 1 H, C(5)-H], 6.31 [s, 1 H, C(3)-H], 6.80 [s, 1 H, C(6)-H], 7.06–7.65 (m, C$_6$H$_5$, PPh$_3$, mixed with those of **2a**) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ = –0.1 (s, SiMe$_3$), 79.2 (s, C-5), 82.6 (s, C-6), 94.5 (s, C-4), 97.5 (s, C-1), 100.4 (d, $J_{P,C}$ = 10.3 Hz, C-2), 111.5 (d, $J_{P,C}$ = 8.9 Hz, C-3), 127.9–137.1 (m, C$_6$H$_5$, PPh$_3$, mixed with those of **2a**) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = –7.8 (s) ppm.

[OsCl$_2${η^6-C$_5$H(C≡CPh)(Ph)$_2$(=CHPh)}(PPh$_3$)] (3): A mixture of [Os{=CPh(η^2-CH=C=CHPh)Cl$_2$(PPh$_3$)$_2$] (0.20 g, 0.20 mmol) and PhC≡C–C≡CPh (0.20 g, 0.99 mmol) in benzene (15 mL) was refluxed for 1 h. Unreacted [OsCl$_2${=CPh(CH=C=CPh)(PPh$_3$)$_2$] was then removed by filtration and residue was washed with benzene (2 × 5 mL). The solvent was removed from the brown filtrate under vacuum and the residue dissolved in CH$_2$Cl$_2$ (2 mL). Addition of diethyl ether (8 mL) to the residue gave a greenish brown precipitate, which was collected by filtration, washed with diethyl ether (3 × 2 mL), and dried under vacuum. The residue was recrystallized from benzene to give a red precipitate, which was collected by filtration, washed with benzene (2 mL) and diethyl ether (2 × 3 mL), and dried under vacuum. Yield: 80 mg (43%). C$_{50}$H$_{37}$Cl$_2$OsP·0.25CH$_2$Cl$_2$: calcd. C 63.45, H 3.97; found C 63.70, H 4.20. ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ = 6.00 (d, $J_{P,H}$ = 2.1 Hz, 1 H, =CH), 6.62 (d, $J_{P,H}$ = 5.1 Hz, 1 H, =C*H*Ph), 6.30–7.74 (m, 35 H, C$_6$H$_5$, PPh$_3$) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = –8.0 (s) ppm.

[(PPh$_3$)$_2$ClOs(μ-Cl)$_3$Os(H$_2$O)(PPh$_3$)$_2$] (4) and 5: Styrene (0.18 mL, 1.6 mmol) was added to a solution of [OsCl$_2${=CPh-

Table 5. Crystallographic details for complexes **2a**, **3**, and **4**.

	2a	**3**·3C_6D_6	**4**·CH_2Cl_2
Empirical formula	$C_{39}H_{37}Cl_2OsPSi$	$C_{50}H_{37}Cl_2OsP{\cdot}3C_6D_6$	$C_{72}H_{62}Cl_4OOs_2P_4{\cdot}CH_2Cl_2$
Formula weight	825.85	1164.19	1674.22
Temperature [K]	293(2)	100(2)	293(2)
Radiation (Mo-K_α) [Å]	0.71073	0.71073	0.71073
Crystal system	tetragonal	triclinic	triclinic
Space group	$P4_2/n$	$P\bar{1}$	$P\bar{1}$ (no. 2)
a [Å]	26.474(3)	12.6406(9)	14.162(5)
b [Å]	26.474(3)	14.4993(10)	14.612(5)
c [Å]	9.9105(15)	14.6828(10)	20.423(7)
α [°]	90	86.7760(10)	77.944(8)
β [°]	90	89.6520(10)	76.462(9)
V [$Å^3$]	6945.8(15)	2622(3)	3870(2)
Z	8	2	2
d_{calcd}, [$g\,cm^{-3}$]	1.579	1.475	1.437
Absorption coefficient [mm^{-1}]	3.933	2.607	3.608
F(000)	3280	1176	1648
Crystal size [mm]	0.35 × 0.30 × 0.30	0.20 × 0.15 × 0.05	0.12 × 0.04 × 0.04
θ range [°]	2.18 to 27.55	1.39 to 25.00	1.54 to 25.00
Reflections collected	45630	25255	18978
Independent reflections	7989 (R_{int} = 0.0488)	9174(R_{int} = 0.0499)	12237 (R_{int} = 0.0937)
Data / restraints / parameters	7989 / 0 / 409	9174 / 0 / 649	12237 / 62 / 780
Goodness-of-fit on F^2	0.930	0.992	0.943
Final R [$I > 2\sigma(I)$]	R_1 = 0.0287 wR_2 = 0.0631	R_1 = 0.0379 wR_2 = 0.0654	R_1 = 0.0770 wR_2 = 0.1186
Largest diff. peak and hole [$e\,Å^{-3}$]	1.177 and –0.747	1.137 and –1.506	1.542 and –1.062

(CH=C=CPh)$(PPh_3)_2$] (0.32 g, 0.32 mmol) in CH_2Cl_2 (20 mL) and the reaction mixture was stirred at room temperature for 24 h to give a light-brown solution. The volume of the reaction solution was reduced to about 1 mL and hexane (30 mL) was then added slowly with stirring to produce a light-brown precipitate. The mixture was further stirred for 10 min and then filtered. The solid was collected by filtration, washed with diethyl ether (2 × 15 mL) and hexane (15 mL), and dried under vacuum to give **4**. Yield: 0.19 g (75%). $C_{72}H_{62}Cl_4P_4Os_2$: calcd. C 54.41, H 3.93; found C 54.52, H 4.12. FAB-MS (NBA): m/z 1570.8 $[M - H_2O]^+$. ^1H NMR (300.13 MHz, C_6D_6): δ = 7.00–7.16 (m, 22 H), 7.26–7.35 (m, 26 H), 7.80–8.03 (m, 12 H), (PPh_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = –6.5 (d), –7.8 (d), ($J_{P,P}$ = 11.4 Hz), –16.4 (d), –17.4 (d) ($J_{P,P}$ = 16.7 Hz) ppm. The filtrate and the washing solution obtained above were collected together and the solvent was pumped off. The residue was extracted with 1 mL of benzene and loaded onto a silica gel column. The column was eluted with hexane to give the organic compound **5** along with a small amount of other unidentified organic species as a yellow solution, which was evaporated to dryness on a rotary evaporator and dried under vacuum to give a yellow oil. FAB-MS (NBA): m/z 308.1 [M^+]. ^1H NMR (300.13 MHz, C_6D_6, see Scheme 6 for labels): δ = 2.98 [m, $^2J_{C(4)\text{-}H_a,C(4)\text{-}H_b}$ = 17.3, $^3J_{C(4)\text{-}H_a,C(5)\text{-}H}$ = 3.7, $^4J_{C(4)\text{-}H_a,C(6)\text{-}H} \approx$ 1.8, $^4J_{C(4)\text{-}H_a,C(2)\text{-}H} \approx$ 0.9 Hz, 1 H, C(4)-H_a], 3.29 [m, $^2J_{C(4)\text{-}H_a,C(4)\text{-}H_b}$ = 17.3, $^3J_{C(4)\text{-}H,C(5)\text{-}H}$ = 8.3, $^4J_{C(4)\text{-}H_b,C(6)\text{-}H} \approx$ 2.0, $^4J_{C(4)\text{-}H_b,C(2)\text{-}H} \approx$ 0.9 Hz, 1 H, C(4)-H_b], 4.16 [ddd, $^3J_{C(4)\text{-}H_b,C(5)\text{-}H}$ = 8.3, $^3J_{C(4)\text{-}H_a,C(5)\text{-}H}$ = 3.7, $^4J_{C(2)\text{-}H,C(5)\text{-}H}$ = 2.5 Hz, 1 H, C(5)-H], 6.32 [br. s, $W_{1/2}$ = 4.5 Hz, 1 H, C(2)-H], 7.51 [br. t, $^4J_{C(4)\text{-}H,\,C(6)\text{-}H}$ = 1.8 Hz, 1 H, C(6)-H], 6.77–7.77 (m, 15 H, Ph) ppm.

Crystallographic Details for 2a, 3, and 4: Crystals of **2** and **4** suitable for X-ray diffraction were grown from CH_2Cl_2 solutions of **2** and **4** layered with hexane, and crystals of **3** were grown from a CH_2Cl_2 solution layered with benzene. Data collections were performed with a Bruker AXS diffractometer equipped with a SMART APEX CCD area detector. Intensity data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature for **2** and **4**, and at 100 K for **3**. Data reduction and absorption correction were performed using SAINT v.6.26 and SADABS v.2.03, respectively. Structure solution and refinement were performed using the SHELXTL v.6.10 software package. All three structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2. Non-hydrogen atoms were refined anisotropically, except for the CH_2Cl_2 solvent in **4**. This was found to be severely disordered and its atoms were given split occupancies and refined isotropically using C–Cl bond length restraints. Some phenyl rings of the PPh_3 ligands in **4** also exhibited extensive disorder and were refined with ideal C–C distances and planarity restraints. All hydrogen atoms were placed in geometrical positions and with riding parameters. Further crystallographic details are given in Table 5.

CCDC-631969 (for **2a**), -631970 (for **3**), and -631971 (for **4**) 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.

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