Metallacycles

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Conversion of Metallabenzynes into Carbene Complexes**

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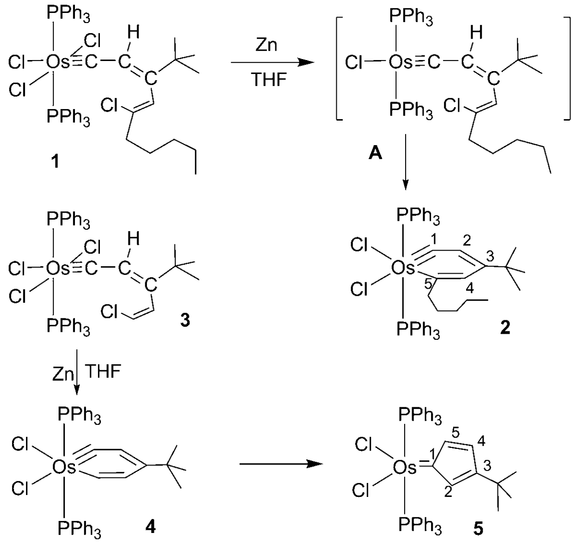
The chemistry of transition metal-containing metallabenzenes has attracted considerable attention.[1] Previous studies have led to the isolation and characterization of a number of stable metallabenzenes, especially those of osmium,[2–4] iridium,[5–8] platinum,[9] ruthenium,[10,11] and rhenium.[12] Many interesting chemical properties of metallabenzenes have also been discovered. For example, it has been demonstrated that metallabenzenes can undergo electrophilic substitution reactions,[2a,5d] cycloaddition reactions,[8d,9c] nucleophilic addition reactions,[13] and nucleophilic aromatic substitution of hydrogen.[14] Another common reactivity of metallabenzenes is that they can undergo migratory insertion reactions to give cyclopentadienyl complexes. The transformation has been demonstrated with well-characterized metallabenzenes[2e,6b,d,e,10b] as well as a spectroscopically characterized ruthenabenzene,[15] and it has been proposed as a key step in the formation of cyclopentadienyl complexes.[1]

Compounds closely related to metallabenzenes are metallabenzynes.[16] Compared with the chemistry of metallabenzenes, that of metallabenzynes is much less developed, which is partly due to the lack of convenient methods to synthesize such compounds.[17] Structurally, metallabenzynes are similar to metallabenzenes in that both have a delocalized structure. Thus it might be expected that metallabenzynes should have properties similar to those of metallabenzenes. Indeed, previous studies have demonstrated that metallabenzynes, like metallabenzenes, can also undergo electrophilic substitution reactions[18] and nucleophilic addition reactions.[17c] As formation of cyclopentadienyl complexes from metallabenzenes by migratory insertion reactions is well-known, one might expect that metallabenzynes could also undergo migratory insertion reactions to give carbene complexes. However, such reactions have not been previously observed. Herein, we present a reliable method to prepare osmabenzynes along with the first examples of conversion of metallabenzynes into carbene complexes.

We recently observed that reaction of zinc with the osmium vinyl carbyne complex $[OsCl_3\{\equiv C{-}CH{=}C(2\text{-}ClC_6H_4)_2\}(PPh_3)_2]$ produced a osmanaphthalyne complex.[19] The reaction was proposed to proceed through a 16e four-coordinate square planar osmium carbyne complex, which undergoes an oxidative addition reaction involving a C−Cl bond. Inspired by the observation, we envisioned that reactions of zinc with carbyne complexes of the type $[OsCl_3\{\equiv C{-}CH{=}CR{-}CR'{=}CClR''\}(PPh_3)_2]$ might lead to the formation of new osmabenzynes.

To test this hypothesis, we first prepared the meridional osmium carbyne complex **1** and then treated it with zinc in THF at room temperature. An in situ ^{31}P NMR study showed that osmabenzyne **2** with substituents on the C3 and C5 positions was produced as the major phosphorus-containing product (Scheme 1), which can be isolated in 62 % yield after column chromatography.



Scheme 1. Preparation of complexes **2**, **4**, and **5**.

The osmabenzyne **2** has been characterized by NMR, elemental analysis, and X-ray diffraction.[20] As shown in Figure 1, it contains an essentially planar six-membered metallacycle. The sum of angles in the six-membered ring of **2** is 720.0° and the maximum deviation from the least-squares plane is 0.020 Å for the C3 atom. The Os−C5 and Os−C1 bond lengths of **2** are 2.097(5) and 1.751(7) Å, respectively. The ring C−C distances for **2** (1.361–1.419 Å) are typical of a regular aromatic system. The overall geometry of **2** resembles that of other reported osmabenzynes.[16c]

Consistent with the solid-state structure, the ^1H NMR spectrum of **2** has signals for the two protons of Os≡C−C*H*

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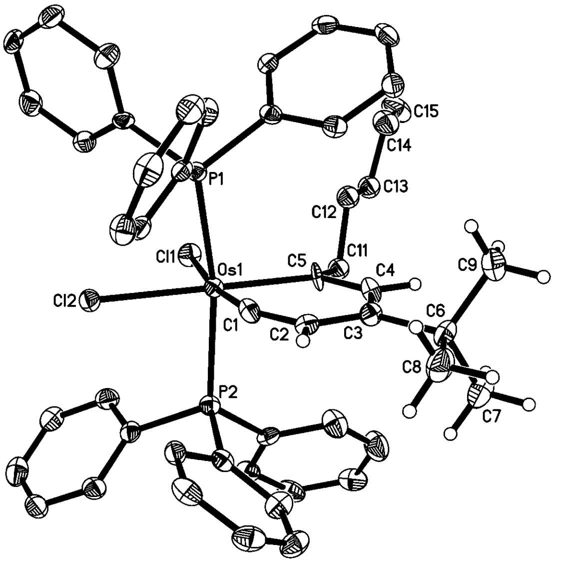


Figure 1. ORTEP drawing of **2**. Ellipsoids are set at 35% probability; the H atoms on PPh_3 and the *n*-pentyl group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 1.751(7), Os1–C5 2.097(5), C1–C2 1.375(8), C2–C3 1.374(8), C3–C4 1.419(8), C4–C5 1.361(8); C1-Os1-C5 79.8(2), C2-C1-Os1 153.3(4), C3-C2-C1 112.3(6), C2-C3-C4 121.4(5), C5-C4-C3 128.4(5), C4-C5-Os1 124.8(4).

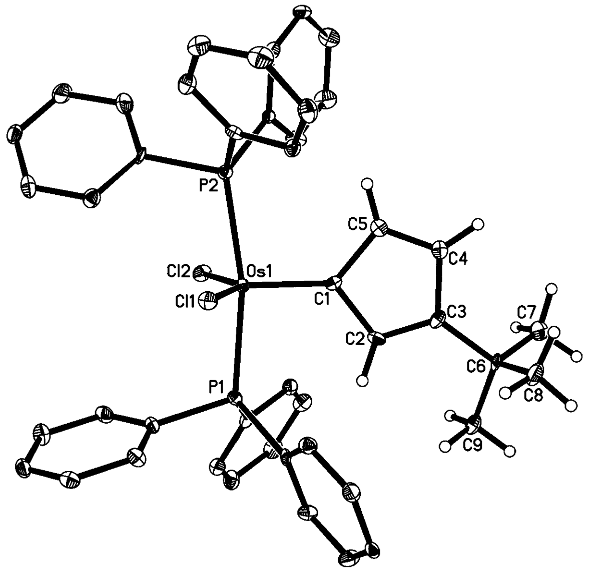


Figure 2. ORTEP drawing of **5**. Ellipsoids are set at 35% probability; the H atoms on PPh_3 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 1.897(5), C1–C2 1.483(7), C1–C5 1.486(7), C2–C3 1.337(8), C3–C4 1.474(8), C4–C5 1.344(8); Cl1-Os1-Cl2 140.85(5), P2-Os1-P1 167.78(5), C1-Os1-Cl1 109.07(15), C1-Os1-Cl2 110.08(15), C1-Os1-P1 94.90(15), C1-Os1-P2 97.28(15), C2-C1-Os1 126.5(4), C2-C1-C5 103.5(5), C5-C1-Os1 130.0(4), C3-C2-C1 110.2(5), C2-C3-C4 108.0(5), C5-C4-C3 109.3(5), C4-C5-C1 109.0(5).

and OsC=C*H* at $\delta = 3.93$ and 6.72 ppm, respectively. The $^{13}C\{^1H\}$ NMR spectrum of **2** (in CD_2Cl_2) has an Os≡*C* signal at $\delta = 297.0$ ppm, and the signal corresponding to the other metal-bound carbon atom (Os*C*) at $\delta = 224.0$ ppm. The ^{13}C signals for the remaining carbon atoms of the metallacycle can also be assigned unambiguously, with the aid of DEPT 135 and ^1H–^{13}C HSQC techniques, at $\delta = 183.8$, 123.5 and 103.7 ppm, corresponding to C3, C4, and C2, respectively.

Inspired by the success of synthesis of **2**, we then tried to prepare osmabenzyne with only one substituent at the C3 position by using osmium carbyne complex **3** as the starting material (Scheme 1). The in situ $^{31}P\{^1H\}$ NMR study shows that osmabenzyne **4** was produced in 2 h as the major phosphorus-containing product. However, the complex is unstable in solution and completely isomerized to osmium carbene complex **5** in 24 h. Complex **5**, a rare osmium analogue of Grubbs catalysts,[21] can be isolated as a brownish-yellow solid in 72% yield after column chromatography.

The carbene complex **5**, which is structurally related to the known five-coordinate vinylidene complexes $OsCl_2(=C=CHR)(PR'_3)_2$,[22] was also characterized by NMR, elemental analysis, and X-ray diffraction. As shown in Figure 2, the complex can be described as a distorted trigonal bipyramidal complex with two PPh_3 ligands at the axial positions, and two chloride atoms and the carbene ligand at the equatorial positions. The Cl-Os-Cl angle is 140.85(5)°, which is close to that observed in the related vinylidene complex $[OsCl_2(=C=CHCMe_3)(PPh_3)_2]$ (149.31(2)°),[22a] and significantly smaller than that in $[RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2]$ (167.6(1)°).[21b]

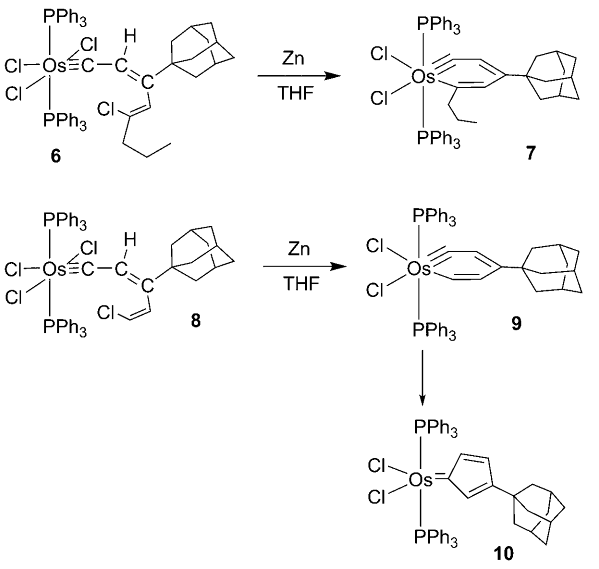
Consistent with the solid-state structure, the ^1H NMR spectrum of **5** (in CD_2Cl_2) had three proton signals at $\delta = 6.23$, 6.54, and 6.70 ppm for the protons attached to C2, C5, and C4, respectively. The $^{13}C\{^1H\}$ NMR spectrum of **5** (in CD_2Cl_2) had a signal for Os=*C* at $\delta = 224.8$ ppm. The ^{13}C signals for the remaining carbon atoms of the cyclopentadienylene ring were observed at $\delta = 142.7$, 142.4, 137.8, and 117.6 ppm corresponding to C3, C5, C2, and C4, respectively.

While there are many reported examples of rearrangement of metallabenzenes to η^5-cyclopentadiene complexes by migratory insertion, formation of **5** from **4** is the first example of conversion of a metallabenzyne into a metal carbene by migratory insertion.

Compound **2** can be stored as a solid at room temperature for at least two weeks without decomposition. In a toluene solution, it also survived when heated at 100 °C for 50 min. The question arises as to why **2** is more stable than **4**. A close examination of the structure of **5** shows that the carbene ligand is oriented parallel to the P1-Os-P2 axis. The protons attached to the C2 and C5 carbons are pointing to the PPh_3 ligands. If **2** underwent migratory insertion to form a similar carbene complex, it would be expected that the pentyl group will have a steric interaction with one of the two PPh_3 ligands. Such a steric effect may help to stabilize the metallabenzyne complex **2** relative to the corresponding carbene complex.

In an effort to confirm this proposition, we studied zinc reduction reactions of analogous carbyne complexes **6** and **8**. As expected, reaction of **6** with zinc gave osmabenzyne complex **7**, which can be isolated as a green solid and stored as a solid at room temperature for at least two weeks without decomposition. Reaction of **8** with zinc gave osmabenzyne **9**, which slowly isomerized to carbene complex **10** (Scheme 2).

It is of interest to note that osmabenzynes **4** and **9**, which have a *tert*-butyl (**4**) or a 1-adamantyl (**9**) group at the C3 position, are unstable at room temperature and rearrange to

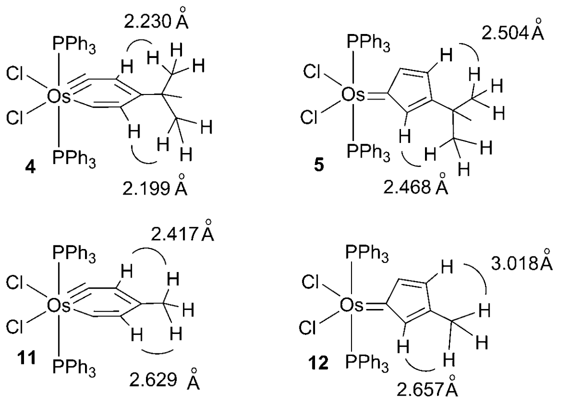


Scheme 2. Preparation of complexes **7**, **9**, and **10**.

the carbene complexes **5** and **10**, respectively. In contrast, the reported osmabenzyne $[OsCl_2(\equiv C{-}CH{=}CMe{-}CH{=}CH)(PPh_3)_2]$ (**11**)[18] with a methyl group at the C3 position is relatively stable and does not rearrange to the corresponding carbene complex, even when heated in toluene at 100 °C for 4 h.

To understand how the subtle change in the substituents on the metallacycle influences the stability of the metallabenzynes studied in this work, we have calculated themodynamics and kinetics of the conversion of **2**, **4**, and **11** into their corresponding carbene complexes.[23,24] The theoretical calculations reproduced the stability trend observed experimentally. Compound **4** was calculated to be less stable than the corresponding carbene complex **5**, while **2** and **11** were calculated to be more stable than their corresponding carbene complexes. Significant barriers (ca. 35 $kcal\,mol^{-1}$)[23] were calculated for these conversions. The significant barrier for the conversion of **4** is in agreement with the experimental observation that **4** can be detected spectroscopically.

A plausible explanation for the difference in the stability of the metallabenzynes is as follows. The optimized structure of osmabenzyne **4** has very short H···H contacts of 2.199 and 2.230 Å involving the *tert*-butyl group and H atoms of the metallacycle at the C2- and C4-positions (Scheme 3). The contacts are shorter than those in the eclipsed conformer of ethane (2.36 Å). The carbene complex **5**, the conversion product from **4**, shows the shortest H···H distance of 2.468 Å, which is close to that in the staggered conformer of ethane (2.54 Å). In contrast, the shortest H···H distances in the structures of **11** (2.417 Å) and **12** (a hypothetical carbene complex formed from the conversion of **11**; 2.657 Å) are all close to or longer than that in the staggered conformer of ethane. It is well known that eclipsed conformer of ethane is less stable than the staggered conformer by 12 $kJ\,mol^{-1}$, which is primarily due to steric effects.[25] Therefore, the lower stability of **4** and **9** compared to **11** could be related to the steric repulsion between the hydrogens at the C2- and C4-positions of the metallacycle and the *tert*-butyl or 1-adamantyl group. Conversion into the carbene structural form releases the steric congestion.



Scheme 3. Short H···H contacts in the optimized structures of **4**, **5**, **11**, and **12**.

As mentioned previously, sterically repulsive interaction in the resultant carbene complex involving pentyl and one of the two PPh_3 ligands may prevent the metallabenzyne complex **2** from conversion into the corresponding carbene complex. Indeed, the calculation shows that the carbene ligand in the resultant carbene complex adopts the electronically unfavorable conformation in which the carbene ligand is oriented perpendicular to the P-Os-P axis to avoid unfavorable steric repulsions,[26] and for this reason the rearrangement of **2** to the corresponding carbene complex is unfavorable. The same argument can be used to explain the failure of **7** to rearrange to the corresponding carbene complex.

In summary, we have demonstrated that zinc reduction of osmium vinylcarbyne complexes of the type $[OsCl_3\{\equiv C{-}CH{=}CR{-}CR'{=}CClR''\}(PPh_3)_2]$ can be a reliable method to prepare osmabenzynes. We also observed for the first time that osmabenzynes can rearrange to carbene complexes. A subtle change in the substituents in the metallacyle can have a drastic effect on the transformation.

Experimental Section

$[OsCl_2\{\equiv C{-}CH{=}C\mathit{t}Bu{-}CH{=}C(\mathit{n}C_5H_{11}){-}\}(PPh_3)_2]$ (**2**): A mixture of **1** (501 mg, 0.48 mmol) and zinc dust (35 mg, 0.53 mmol) in THF (30 mL) was stirred at room temperature for 12.5 h to give a brown solution. The solvent then was removed completely under vacuum. The residue was dissolved in benzene (ca. 5 mL) and was loaded onto a silica gel column. The column was flashed with benzene and dichloromethane subsequently, and then eluted with dichloromethane/diethyl ether (8:1) to give a purple solution. The solvent was removed under vacuum to give a purple solid, which was dried under vacuum. Yield: 290 mg, 62.2 %. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): $\delta = -3.8$ ppm (s). ^1H NMR (400.13 MHz, CD_2Cl_2): $\delta = 7.68$ (dt, $J(HH) = 7.1$ Hz, $J(PH) = 5.2$ Hz, 12 H, P*Ph*), 7.40 (t, $J(HH) = 7.0$ Hz, 6 H, P*Ph*), 7.34 (t, $J(HH) = 7.2$ Hz, 12 H, P*Ph*), 6.72 (s, 1 H, Os-C=C*H*), 3.93 (s, 1 H, Os≡CC*H*), 2.83 (t, J(HH) = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 1.10 (qn, $J(HH) = 7.2$ Hz, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 0.99 (s, 9 H, $C(CH_3)_3$), 0.91 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 0.83 ppm (m, 5 H, $CH_2CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): $\delta = 297.0$ (t, $J(PC) = 11.8$ Hz,

$\text{Os}{\equiv}C$), 224.0 (t, $J(\text{PC}) = 5.8$ Hz, $\text{Os-}C{=}\text{CH}$), 183.8 (s, $C\text{C(CH}_3)_3$), 123.5 (s, $\text{Os-C}{=}C\text{H}$), 103.7 (s, $\text{Os}{\equiv}\text{C}C\text{H}$), 52.2 (s, $C\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 37.8 (s, $C(\text{CH}_3)_3$), 31.4 (s, $\text{CH}_2\text{CH}_2C\text{H}_2\text{CH}_2\text{CH}_3$), 29.2 (s, $\text{C}(C\text{H}_3)_3$), 29.0 (s, $\text{CH}_2C\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.0 (s, $\text{CH}_2\text{CH}_2\text{CH}_2C\text{H}_2\text{CH}_3$), 13.4 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2C\text{H}_3$), 134.3 (t, $J(\text{PC}) = 4.9$ Hz, P*Ph*), 130.7 (t, $J(\text{PC}) = 26.3$ Hz, P*Ph*), 129.5 (s, P*Ph*), 126.7 ppm (t, $J(\text{PC}) = 4.9$ Hz, P*Ph*). Anal. calcd (%) for $\text{C}_{50}\text{H}_{52}\text{Cl}_2\text{OsP}_2$: C 61.53, H 5.37; found: C 61.70, H 5.37.

$[\text{OsCl}_2\{{=}\text{C}({-}\text{CH}{=}\text{C}(t\text{Bu})\text{CH}{=}\text{CH}{-})\}(\text{PPh}_3)_2]$ (**5**)**:** A mixture of **3** (450 mg, 0.46 mmol) and zinc dust (46 mg, 0.70 mmol) in THF (30 mL) was stirred at room temperature for 24 h to give a brown solution. The solvent was removed completely under vacuum. The residue was dissolved in benzene (ca. 5 mL) and was loaded onto a silica gel column. The column was flashed with benzene/hexane (15:1) and then eluted with benzene to give a brownish-yellow solution. The solvent was removed under vacuum to give a brownish-yellow solid, which was dried under vacuum. Yield : 301 mg, 72.2 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2): $\delta = -4.2$ ppm (s). ^{1}H NMR (400.13 MHz, CD_2Cl_2): $\delta = 0.86$ (s, 9 H, $\text{C(CH}_3)_3$), 6.23 (s, 1 H, $\text{Os}{=}\text{C-C}H$), 6.54 (dd, $J(\text{HH}) = 5.6$ Hz, 2.0 Hz, 1 H, $\text{Os}{=}\text{C-C}H{=}\text{CH}$), 6.70 (d, $J(\text{HH}) = 5.2$ Hz, 1 H, $\text{Os}{=}\text{C-CH}{=}\text{C}H$), 7.38–7.40 (m, 12 H, P*Ph*), 7.45–7.50 (m, 6 H, P*Ph*), 7.62 (br, 12 H, P*Ph*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD_2Cl_2): $\delta = 224.8$ (t, $J(\text{PC}) = 5.6$ Hz, $\text{Os}{=}C$), 142.7 (s, CtBu), 142.4 (t, $J(\text{PC}) = 9.1$ Hz, $\text{Os}{=}\text{C-}C\text{H}{=}\text{CH}$), 137.8 (t, $J(\text{PC}) = 9.4$ Hz, $\text{Os}{=}\text{C-}C\text{H}$), 134.1 (br, P*Ph*), 129.5 (s, P*Ph*), 127.6 (t, $J(\text{PC}) = 4.9$ Hz, P*Ph*), 117.6 (s, $\text{Os}{=}\text{C-CH}{=}C\text{H}$), 31.4 (s, $C(\text{CH}_3)_3$), 22.0 ppm (s, $\text{C}(C\text{H}_3)_3$). Anal. calcd (%) for $\text{C}_{45}\text{H}_{42}\text{Cl}_2\text{OsP}_2$: C 59.66, H 4.67; found: C 59.87, H 4.43.

Details of the preparation and characterization of **1**, **3**, **4**, and **6–10** can be found in the Supporting Information.

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[20] Single-crystal X-ray diffraction intensity data of **2** was collected with an Oxford Diffraction Gemini S Ultra X-ray diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) at $T = 133$ K. The intensity data of **5** was collected with a Bruker Smart APEX CCD X-ray diffractometer with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) at $T = 100$ K. Lattice determination, data collection, and data reduction of **2** were carried out using CrysAlisPro 171.33.46, and absorption correction was performed using the built-in SADABS in the CrysAlisPro program suite. Lattice determination and data collection of **5** were carried out using SMART v.5.625 software. Data reduction and absorption correction by semi-empirical methods were performed using SAINT v.6.26 and SADABS v.2.03, respectively. Structure solution and refinement for both **2** and **5** were performed using the OLEX2 software package. All of the structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms, except for those disordered groups that have been re-examined and refined as disorder model with appropriate partial occupancies applied. Crystal data for **2**: $C_{50}H_{52}Cl_2OsP_2$ (from CH_2Cl_2/hexane), $M_r = 975.96$, monoclinic, $P2_1/c$, $a = 14.3894(5)$, $b = 10.5071(5)$, $c = 28.4259(12)$ Å, $\beta = 95.863(4)°$, $V = 4275.3(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.516$ g cm^{-3}, $\mu = 7.744$ mm^{-1}, $F(000) = 1968$, $\theta_{\max} = 67.5°$, 17173 reflections, 7569 independent ($R_{\text{int}} = 0.0638$), $R_1 = 0.0367$, $wR_2 = 0.0727$. A portion of the pentyl group of **2** was disordered over two positions; C11, C12, and C13 were refined as 0.6 occupancies, and C11 A, C12 A, and C13 A were refined as 0.4 occupancies. Crystal data for **5**: $C_{45}H_{42}Cl_2OsP_2$ (from C_6H_6), $M_r = 905.83$, monoclinic, $P2_1$, $a = 9.9551(11)$, $b = 15.5004(18)$, $c = 12.5658(14)$ Å, $\beta = 95.781(2)°$, $V = 1929.1(4)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.559$ g cm^{-3}, $\mu = 3.558$ mm^{-1}, $F(000) = 904$, $\theta_{\max} = 28.09°$, 11273 reflections, 6212 independent ($R_{\text{int}} = 0.0347$), $R_1 = 0.0298$, $wR_2 = 0.0627$. CCDC 816621 (**2**) and CCDC 816622 (**5**) 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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