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Substituted Cyclopentadienyl Osmium Complexes from the Reactions of $OsH_3Cl(PPh_3)_3$ with Fulvenes and Cyclopentadienes

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Two methodologies were developed for the preparation of half-sandwich osmium complexes with the general formula (η^5-cyclopentadienyl)$OsCl(PPh_3)_2$. The first approach involves the reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadienes. Treatment of $OsH_3Cl(PPh_3)_3$ with cyclopentadienes gives (η^5-cyclopentadienyl)$OsCl(PPh_3)_2$ via C−H oxidative addition of cyclopentadienes followed by reductive elimination of hydrogen. The methodology has enabled us to synthesize a series of half-sandwich osmium complexes containing Cp, Cp*, indenyl, and C_5Me_4R (R = H, Et, *n*-Pr). The second approach involves the insertion reactions of $OsH_3Cl(PPh_3)_3$ with fulvenes. Treatment of $OsH_3Cl(PPh_3)_3$ with C6-substituted fulvenes produces cleanly monosubstituted cyclopentadienyl osmium complexes (η^5-C_5H_4CHRR')$OsCl(PPh_3)_2$ (R = H, R′ = *p*-$C_6H_4CH_3$, *p*-$C_6H_4OCH_3$, CMe_3; R = R′ = Ph) via hydride transfer to the electrophilic exocyclic carbon of fulvenes. Under similar conditions, $OsH_3Cl(PPh_3)_3$ reacts with C6-monosubstituted 1,2,3,4-tetramethylfulvenes to give pentasubstituted cyclopentadienyl osmium complexes (η^5-$C_5Me_4CH_2R$)$OsCl(PPh_3)_2$ (R = *p*-$C_6H_4CH_3$, *p*-$C_6H_4OCH_3$, pyrenyl).

Introduction

Half-sandwich group 8 transition metal cyclopentadienyl complexes play a key role in the development of organometallic chemistry and homogeneous catalysis.[1] It has been demonstrated that replacement of one or more of the hydrogens of the cyclopentadienyl (C_5H_5) ring by other substituents can lead to significant changes in the reactivity and catalytic properties of these complexes due to steric and electronic effects induced by these substituents. For example, $Cp^*RuCl(PPh_3)_2$ can efficiently mediate the coupling reactions of azides with terminal alkynes to give selectively 1,5-disubstituted 1,2,3-triazoles, whereas the analogous complex $CpRuCl(PPh_3)_2$ is much less effective in terms of both activity and selectivity.[2] In this regard, it is desirable to prepare half-sandwich group 8 transition metal cyclopentadienyl complexes with various substituents on the Cp ring.

In fact, a number of half-sandwich ruthenium complexes of various substituted cyclopentadienyl ligands have been synthesized in the past.[3] In contrast, the chemistry of

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half-sandwich osmium complexes with a substituted cyclopentadienyl ligand, with the exception of Cp*Os complexes,[4] is still underdeveloped, despite the considerable interest in the chemistry of half-sandwich CpOs complexes.[5] Until now, a very limited number of half-sandwich osmium complexes with a substituted cyclopentadienyl ligand other than Cp* and indenyl are known. Notable examples of these complexes include those with C_5Ar_5,[6] iPr_4C_5H,[7] and C_5H_4R[8−10] groups.

This work concerns syntheses of half-sandwich osmium cyclopentadienyl complexes of the type (η^5-cyclopentadienyl)-$OsCl(PPh_3)_2$. Osmium halo complexes (η^5-cyclopentadienyl)-$OsX(PR_3)_2$ are very useful precursors for organometallic synthesis. For example, $CpOsBr(PPh_3)_2$ is one of the commonly used starting materials to make other half-sandwich CpOs complexes;[11] $CpOsCl(PiPr_3)_2$ is another versatile starting material that has also been used to make over 200 new compounds and for the development of interesting organometallic chemistry of osmium.[5e,f,12]

Previously reported osmium halo complexes (η^5-cyclopentadienyl)$OsX(PR_3)_2$ are mainly those containing Cp, Cp*, and indenyl ligands. Several approaches have been used to synthesize such complexes depending on the ligands. The cyclopentadienyl complex $CpOsBr(PPh_3)_2$ could be synthesized by refluxing a mixture of H_2OsBr_6/PPh_3/CpH in alcohols.[13−15] $CpOsX(PPh_3)_2$ (X = Cl, Br) and $CpOsCl(PiPr_3)_2$ have been prepared by the metathesis reactions of cyclopentadienyl anion (e.g., LiCp, TlCp) with haloosmium complexes $OsX_2(PPh_3)_3$[16] and $OsH_2Cl_2(PiPr_3)_2$,[17] respectively. It was reported very recently that the complex $CpOsCl(PPh_3)_2$ can be prepared directly from the reaction of $OsCl_2(PPh_3)_3$ with cyclopentadiene.[18] Other half-sandwich Cp complexes $CpOsX(PR_3)_2$ were usually obtained by ligand substitution reactions of $CpOsX(PPh_3)_2$ (X = Cl, Br)[19] and $CpOsCl(PiPr_3)_2$.[17] The Cp* complexes $Cp^*OsX(PR_3)_2$ were usually prepared from the reactions of PR_3 with $[Cp^*OsBr_2]_2$ or Cp*OsX(COD) (X = Br, Cl),[4c,16,20,21] which were in turn prepared from the reactions of H_2OsBr_6 with C_5Me_5H in alcohols and reactions of $K_2[OsO_2(OH)_4]$/HX with C_5Me_5H/COD,[16] respectively. The indenyl complexes (η^5-C_9H_7)$OsX(PPh_3)_2$ (X = Cl, Br) have been synthesized by the reactions of indenyllithium with $OsX_2(PPh_3)_3$.[22,23] Half-sandwich indenyl complexes containing other phosphine

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(23) Examples of other osmium sandwich complexes prepared from the reactions of indenyl lithium with osmium precursors. (a) (η^5-C_9H_7)$OsH(PiPr_3)_2$: Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2005**, *24*, 5780. (b) (η^5-C_9H_7)$Os{\equiv}N(Ph)_2$: Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071.

ligands have been obtained by ligand substitution reactions of $(\eta^5\text{-}C_9H_7)OsX(PPh_3)_2$..[21a]

Until now very few osmium complexes (η^5-cyclopentadienyl)$OsX(PR_3)_2$ with a substituted cyclopentadienyl ligand other than Cp* and indenyl were known. As rare examples, Esteruelas et al. reported the synthesis of $OsCl(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)(PiPr_3)$ from the reaction of CCl_4 with $OsH(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)(PiPr_3)$,[8] and we reported the synthesis of aryl-substituted indenyl complexes $(\eta^5\text{-}C_9H_6(Ar))OsCl(PPh_3)_2$ from the reductions of carbyne complexes $OsCl_3(\equiv CCH{=}CAr_2)(PPh_3)_2$ with zinc.[24]

In this work, we report two general methods for the preparation of half-sandwich osmium complexes of the type (η^5-cyclopentadienyl)$OsCl(PPh_3)_2$ based on the reactions of the readily available complex $OsH_3Cl(PPh_3)_3$ with fulvene derivatives and cyclopentadienes. The methodologies have enabled us to synthesize a series of half-sandwich osmium complexes containing Cp, Cp*, indenyl, and various substituted cyclopentadienyls.

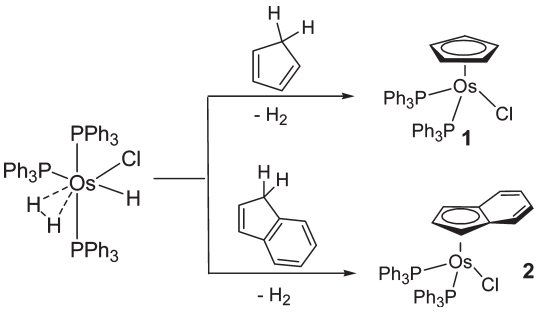
Results and Discussion

Preparation of Cyclopentadienyl Complexes from the Reactions of $OsH_3Cl(PPh_3)_3$ with Cyclopentadienes. It is known that cyclopentadienes can react with hydride complexes to give cyclopentadienyl complexes. For example, treatment of $Re(PPh_3)_2H_7$ with cyclopentadiene gives $CpReH_2(PPh_3)$,[25,26] and photolysis of $ReH_5(PMe_2Ph)_3$ with cyclopentadiene in hexane led to $CpReH_4(PMe_2Ph)$ and $CpReH_2(PMe_2Ph)_2$.[27] The reactions presumably proceed through oxidative addition of C−H of cyclopentadiene (C_5H_6) followed by elimination of H_2. These observations prompted us to investigate the reactions of $OsH_3Cl(PPh_3)_3$ with several cyclopentadienes with the hope of obtaining (η^5-cyclopentadienyl)$OsCl(PPh_3)_2$.

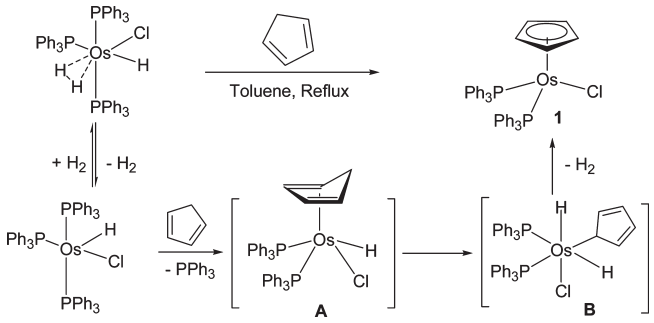
In our initial experiments, we studied the reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadiene and indene. Treatment of $OsH_3Cl(PPh_3)_3$ with 3 equiv of freshly distilled cyclopentadiene in toluene at 110 °C for 2 h affords $CpOsCl(PPh_3)_2$ (**1**), which can be isolated as a yellow, air-stable solid in 61% yield by recystallization from diethyl ether and hexane (Scheme 1). The reaction can also be carried out at room temperature in THF, although it takes 2 days to complete the reaction.

The reaction of the hydride complex $OsHCl(CO)(PiPr_3)_2$ with cyclopentadiene was known to give the cyclopentadienyl complex $OsH(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)$ due to elimination of HCl instead of H_2.[28] Reactions between C_5R_5H (R = H, Me) and $OsX_2(CO)_4$ or $[OsX_2(CO)_3]_2$ (X = Cl, Br, I) also give $(\eta^5\text{-}C_5R_5)OsX(CO)_2$ with the elimination of HX.[29] Thus

Scheme 1



Scheme 2



reaction of $OsH_3Cl(PPh_3)_3$ with cyclopentadiene may also afford $CpOsH(PPh_3)_2$. However, the hydride complex was not detected in our experiments.

A plausible pathway for the formation of the osmium cyclopentadienyl complex **1** from the reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadiene is shown in Scheme 2. $OsH_3Cl(PPh_3)_3$ can lose a molecule of hydrogen to give the unsaturated 16-electron complex $OsHCl(PPh_3)_3$. A cyclopentadiene molecule can then coordinate to the osmium center to give $(\eta^4\text{-}C_5H_6)OsHCl(PPh_3)_2$, which gives intermediate **A**. Oxidative addition of a C−H bond in cyclopentadiene would give intermediate **B**, which can undergo reductive elimination of H_2 to give the final product **1**. The mechanism is similar to that proposed by Jones et al. for the reaction of $Re(PPh_3)_2H_7$ with cyclopentadiene to give $CpReH_2(PPh_3)$.[25] In the rhenium system, $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ has been identified as the key intermediate. We have failed to identify the reaction intermediates in our case.

Similarly, treatment of $OsH_3Cl(PPh_3)_3$ with 1.5 equiv of indene affords osmium indenyl complex $(C_9H_7)OsCl(PPh_3)_2$ (**2**). Complexes **1**[16] and **2**[21b] have been previously prepared from the reactions of $OsCl_2(PPh_3)_3$ with LiCp/cyclopentadiene and indenyllithium. Our work provided an alternative route to the complexes.

Encouraged by the successful preparation of cyclopentadienyl and indenyl osmium complexes **1** and **2**, we sought to extend the synthetic protocol to synthesize substituted cyclopentadienyl complexes. Reaction of $OsH_3Cl(PPh_3)_3$ with pentamethylcyclopentadiene in a 1:1.5 molar ratio in refluxing toluene leads to the formation of the complex $Cp^*OsCl(PPh_3)_2$ (**3**) (Scheme 3). As monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the reaction is completed in ca. 4 h to give $Cp^*OsCl(PPh_3)_2$ as the only product. From the reaction mixture, $Cp^*OsCl(PPh_3)_2$ was isolated in 85% yield. To the best of our knowledge, $Cp^*OsCl(PPh_3)_2$ has not been reported previously, although the analogous complexes

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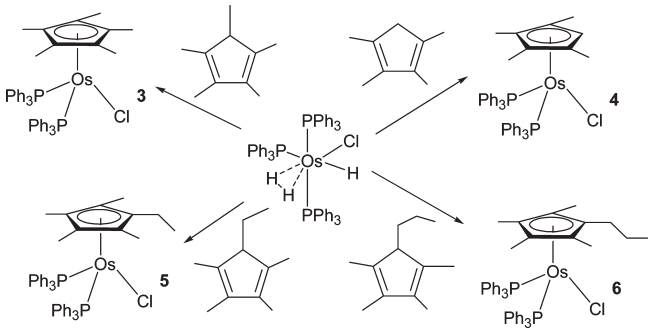
Scheme 3



$Cp^*RuCl(PPh_3)_2$[30] and $Cp^*OsBr(PPh_3)_2$[19c] have been known for a long time.

Under similar conditions, reactions between $OsH_3Cl(PPh_3)_3$ and other tetramethyl-substituted cyclopentadienes (C_5Me_4R, R = H, Et, *n*-Pr) give the corresponding (η^5-C_5Me_4R)$OsCl(PPh_3)_2$ (R = H (**4**), Et (**5**), *n*-Pr (**6**)) in moderate to high yields.

The new substituted tetramethylcyclopentadienyl complexes (η^5-C_5Me_4R)$OsCl(PPh_3)_2$ (R = Me (**3**), H (**4**), Et (**5**), *n*-Pr (**6**)) are characterized by multinuclear NMR and elemental analysis. In the $^{31}P\{^1H\}$ NMR spectra, these complexes show a sharp singlet for the two equivalent phosphine ligands in the region of −2.5 to −3.5 ppm. In the ^1H NMR spectrum of **3**, the Cp* ring shows a singlet at 1.3 ppm for the methyl groups. Complexes **4**−**6** display a characteristic set of two singlets at ca. 1.4 and 1.3 ppm for the two distinguishable methyl groups of the cyclopentadienyl ring.

The structures of complexes (C_5Me_5)$OsCl(PPh_3)_2$ (**3**, Figure 1), (η^5-C_5Me_4H)$OsCl(PPh_3)_2$ (**4**, Figure 2), and (η^5-C_5Me_4Pr)$OsCl(PPh_3)_2$ (**6**, Figure 3) have been confirmed by X-ray diffraction studies. In all cases, the complexes adopt a piano stool structure with PPh_3 and Cl ligands as the legs. To prevent steric interaction between PPh_3 and the substituent on the cyclopentadienyl ligand, the Cl ligand is situated under the *n*-propyl substituent in the (η^5-C_5Me_4Pr)$OsCl(PPh_3)_2$ complex. In the case of (η^5-C_5Me_4H)$OsCl(PPh_3)_2$, the Cl ligand is situated under the methyl group of the cyclopentadienyl ligand, while the PPh_3 is located under the C−H substituent. The average Os−C bond distances (2.247−2.250 Å) between the cyclopentadienyl carbons and the osmium center in these complexes are similar and are slightly longer than the one in $CpOsCl(PPh_3)_2$ (2.214 Å).[16] The bond lengths of Os−Cl and Os−P agree with those of $CpOsCl(PPh_3)_2$.

Preparation of Monosubstituted Cyclopentadienyl Complexes from the Reactions of Monosubstituted Fulvenes with $OsH_3Cl(PPh_3)_3$. Substituted fulvenes are more easily accessible and handled than cyclopentadiene derivatives. Therefore they are attractive starting materials for the preparation of cyclopentadienyl complexes.[31] In fact, a number of cyclopentadienyl complexes have been obtained from fulvenes by first converting fulvenes to cyclopentadienyl anions via their reactions with reducing agents such as sodium, calcium,[32] or nucleophiles such as lithium or Grignard reagents,[33] $LiAlH_4$ and $LiBHEt_3$,[34] followed by the reactions of cyclopentadienyl anions with suitable precursors. Cyclopentadienyl complexes could also be obtained from the insertion reactions of fulvenes with metal alkyl or hydride complexes. For example, complexes $M(CH_2Ph)_4$ (M = Zr, Hf) react with 6,6′-disubstituted fulvenes to give the insertion products (C_5H_4-CMe_2CH_2Ph)$M(CH_2Ph)_3$,[35] and Bu_2ZrCl_2 reacts with 6-aryl-substituted fulvenes to give a bis(benzylic cyclopentadienyl)-zirconium dichloride complex presumably through the insertion reaction of a hydride intermediate generated in situ from *β*-hydrogen elimination.[36] We have recently demonstrated that monosubstituted cyclopentadienyl ruthenium complexes (η^5-$C_5H_4CH_2R$)$RuCl(PPh_3)_2$ can be readily prepared from the reaction between $RuHCl(PPh_3)_3$ and fulvenes.[3c]

In light of the success of the preparation of cyclopentadienyl complexes via insertion reactions of fulvene derivatives with metal hydride or alkyl complexes, we envisioned that a variety of osmium cyclopentadienyl complexes (η^5-cyclopentadienyl)$OsCl(PPh_3)_2$ may be prepared from the reactions of fulvenes with the osmium hydride complex $OsH_3Cl(PPh_3)_3$.

To explore the possibility, the reactions between C6-substituted fulvenes **7S**−**10S** and the osmium hydride complex $OsH_3Cl(PPh_3)_3$ were investigated (Scheme 4). At room temperature, the reaction between $OsH_3Cl(PPh_3)_3$ and fulvene **7S** (in 1.5:1 molar ratio) in dichloromethane proceeded to give complex (η^5-$C_5H_4CH_2$tolyl)$OsCl(PPh_3)_2$ (**7**) cleanly. However the reaction occurred slowly and was completed in 72 h. When the reaction was carried out in THF at 80 °C, the reaction was completed in 4 h, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The completion of the reaction is also indicated by the change in the color of the reaction mixture from initial orange to pale orange. The desired cyclopentadienyl complex **7** can be isolated as an air-stable yellow solid by column chromatography on aluminum oxide using *n*-hexane followed by 5:1 *n*-hexane/diethyl ether as the eluents. Under similar conditions, fulvenes **8S**−**10S** reacted with $OsH_3Cl(PPh_3)_3$ to give the corresponding monosubstituted cyclopentadienyl osmium complexes **8**−**10**, which can be isolated in moderate to high yields.

All these complexes have been characterized by NMR and elemental analysis. As expected, the $^{31}P\{^1H\}$ spectra of the complexes show a singlet at ca. −2.0 ppm for the two equivalent PPh_3 ligands. The ^1H NMR spectra display two singlet signals at ca. 3.95 and 3.65 ppm for the protons of the cyclopentadienyl ligands. The structures of complexes (η^5-$C_5H_4CH_2C_6H_4OMe$)$OsCl(PPh_3)_2$ (**8**) and (η^5-$C_5H_4CH_2t$Bu)-$OsCl(PPh_3)_2$ (**10**) have been confirmed by X-ray diffraction. As shown in Figures 4 and 5, both osmium complexes adopt a

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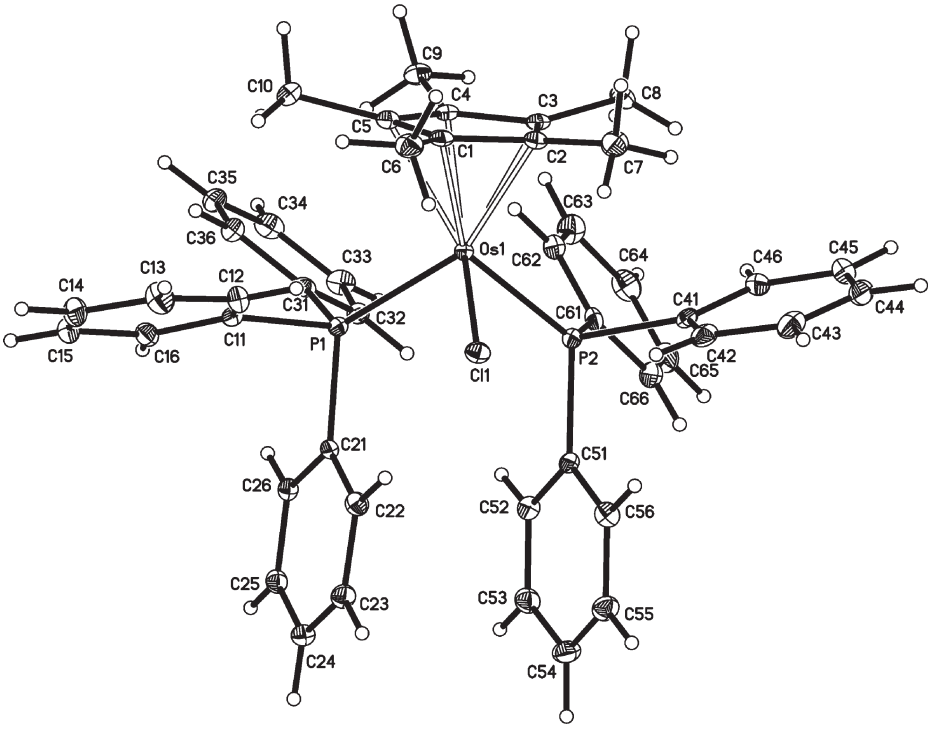


Figure 1. ORTEP drawing of $Cp^*OsCl(PPh_3)_2$ (**3**). Thermal ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5Me_5), 2.247; Os−P(1), 2.3243(7); Os−P(2), 2.3132(7); Os−Cl(1), 2.4544(6); P(1)−Os(1)−Cl(1), 93.24(2); P(2)−Os(1)−P(1), 96.51(2).

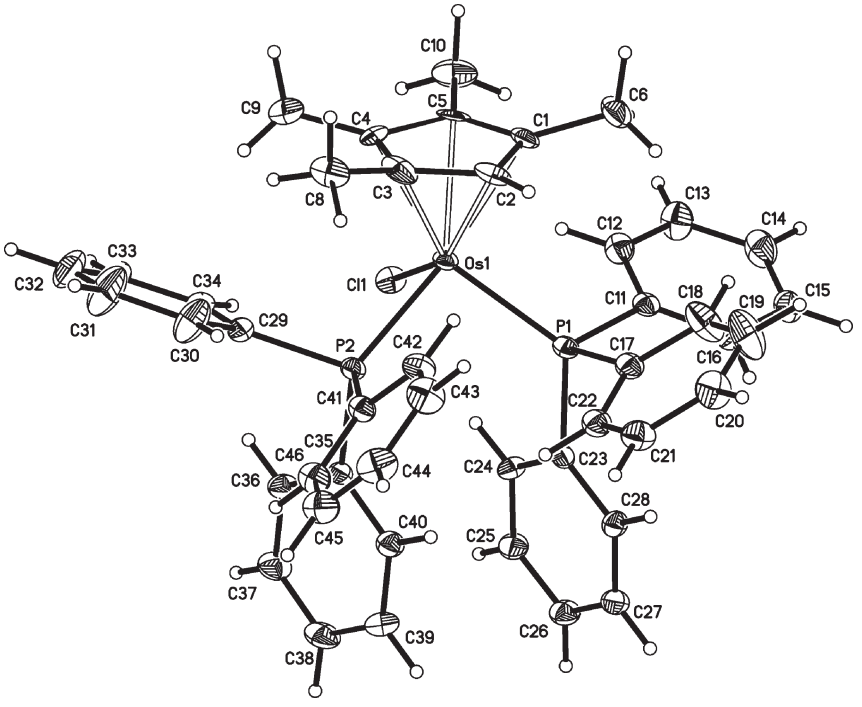


Figure 2. ORTEP drawing of (η^5-C_5Me_4H)$OsCl(PPh_3)_2$ (**4**). Thermal ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5Me_4H), 2.252; Os−P(1), 2.3274(13); Os−P(2), 2.3174(12); Os−Cl(1), 2.4430(13); P(1)−Os(1)−Cl(1), 93.72(4); P(2)−Os(1)−P(1), 96.86(4).

three-legged piano stool structure with the Cl ligand located under the pendent group for steric reasons. The pendent group bends away from the metal center.

In our previous work, we found that reactions between $RuHCl(PPh_3)_3$ and fulvenes having an sp^3-CH proton at the carbon α to the exocyclic carbon give the expected cyclopentadienyl complexes together with a small amount of vinylcyclopentadienyl complexes due to dehydrogenation.[3c] A similar result was observed in the reactions of $OsH_3Cl(PPh_3)_3$ with fulvene **11S**. Treatment of $OsH_3Cl(PPh_3)_3$ with fulvene **11S**

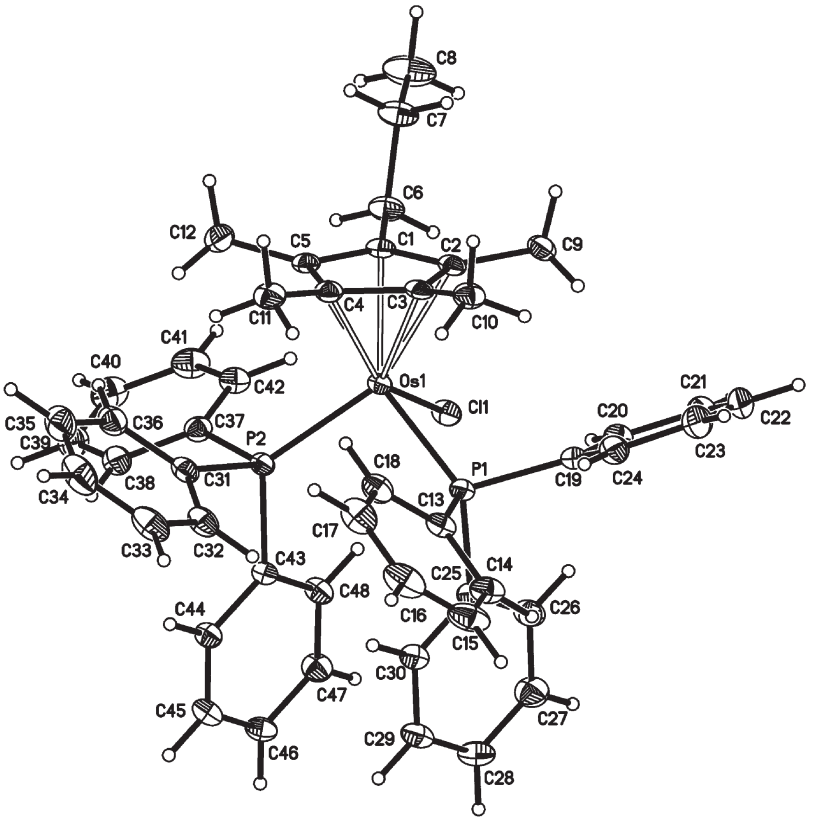
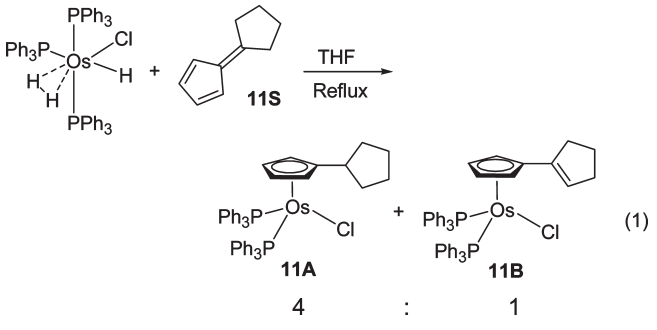


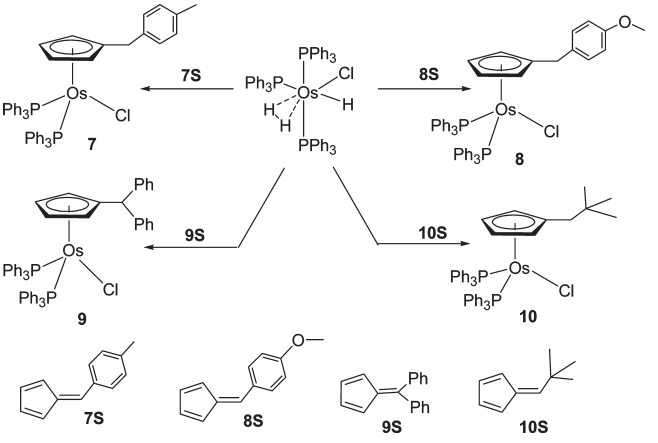
Figure 3. ORTEP drawing of (η^5-C_5Me_4Pr)$OsCl(PPh_3)_2$ (**6**). Thermal ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5Me_4Pr), 2.248; Os−P(1), 2.3224(6); Os−P(2), 2.3234(5); Os−Cl(1), 2.4632(6); P(1)−Os(1)−Cl(1), 87.94(2); P(2)−Os(1)−P(1), 97.76(2).

in THF at 80 °C for 4 h gives the cyclopentadienyl product **11A** and the vinyl-cyclopentadienyl product **11B** in a molar ratio of 4:1 (eq 1), as determined by the integrals of proton signals of the Cp ring in the ^{1}H NMR spectrum.



Preparation of Pentasubstituted Cyclopentadienyl Complexes from the Reactions of Pentasubstituted Fulvenes with $OsH_3Cl(PPh_3)_3$. Having succeeded in the preparation of monosubstituted cyclopentadienyl osmium complexes from fulvenes, we have tried to prepare substituted tetramethylcyclopentadienyl osmium complexes via the reactions of $OsH_3Cl(PPh_3)_3$ with C6-substituted 1,2,3,4-tetramethylfulvenes.

Scheme 4



Polysubstituted fulvenes can be prepared by organic transformation[37] or by metal-catalyzed reactions.[38] The desired fulvene derivatives used in this work were prepared from the reactions of 1,2,3,4-tetramethylcyclopentadiene with the corresponding aldehydes in methanol in the presence of excess KO*t*Bu as the base, as shown in eq 2 in Scheme 5.

Thus, 6-tolyl-1,2,3,4-tetramethylfulvene (**12S**) was produced from the condensation reaction between *p*-tolylaldehyde and

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tetramethylcyclopenta-1,3-diene in the presence of KO*t*Bu. The ligand was isolated as an orange oil by column chromatography using basic Al_2O_3 as the solid phase and pentane as the eluent. Following the same procedure, 6-anisolyl-1,2,3,4-tetramethylfulvene (**13S**) and 6-pyrenyl-1,2,3,4-tetramethylfulvene (**14S**) were prepared in high yield from the corresponding aldehydes.

The identities of the new fulvenes were assigned on the basis of NMR and MS spectroscopy. The solid-state structure of **14S** has also been confirmed by X-ray diffraction (Figure 6). The pyrene group of **14S** is not perfectly coplanar with the fulvene unit, but has a torsion angle of 13.68°. The bond distances of C(1)−C(2), C(3)−C(4), and C(5)−C(10) are slightly shorter than those of C(2)−C(3) and C(4)−C(5), which confirms the structure of the fulvene system.

Having the new ligands in hand, we examined their reactions with $OsH_3Cl(PPh_3)_3$ for the synthesis of substituted tetramethylcyclopentadienyl osmium complexes. Treatment of ligand **12S** with $OsH_3Cl(PPh_3)_3$ in a molar ratio of 1.3:1 in refluxing toluene resulted in the formation of (η^5-$C_5Me_4CH_2$tolyl)$OsCl(PPh_3)_2$ (**12**), which can be isolated in 75.9% yield after purification by column chromatography. In a similar fashion, (η^5-$C_5Me_4CH_2$anisolyl)$OsCl(PPh_3)_2$ (**13**)

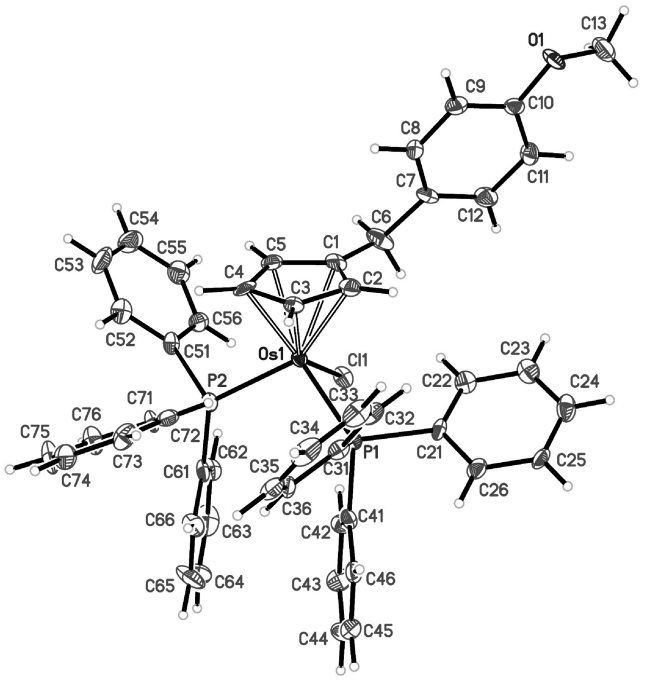
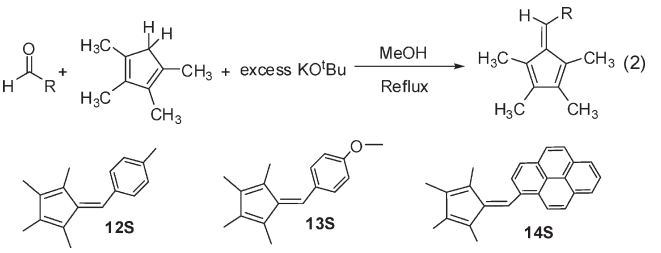


Figure 4. ORTEP drawing of (η^5-$C_5H_4CH_2C_6H_4OMe$)$OsCl(PPh_3)_2$ (**8**). Thermal ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5H_4R), 2.209; Os−P(1), 2.320(2); Os−P(2), 2.308(2); Os−Cl(1), 2.4582(19); P(1)−Os(1)−Cl(1), 91.39(7); P(2)−Os(1)−P(1), 103.28(7).

Scheme 5



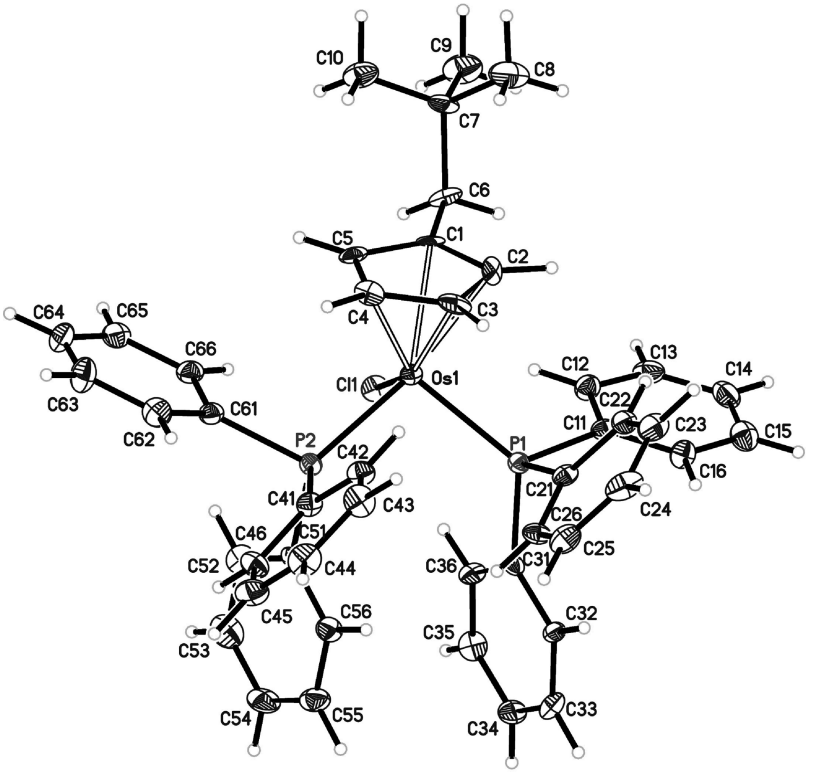


Figure 5. ORTEP drawing of (η^5-$C_5H_4CH_2CMe_3$)$OsCl(PPh_3)_2$ (**10**). Thermal ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5H_4R), 2.220; Os−P(1), 2.3088(15); Os−P(2), 2.3049(14); Os−Cl(1), 2.4565(15); P(1)−Os(1)−Cl(1), 94.56(5); P(2)−Os(1)−P(1), 99.16(5).

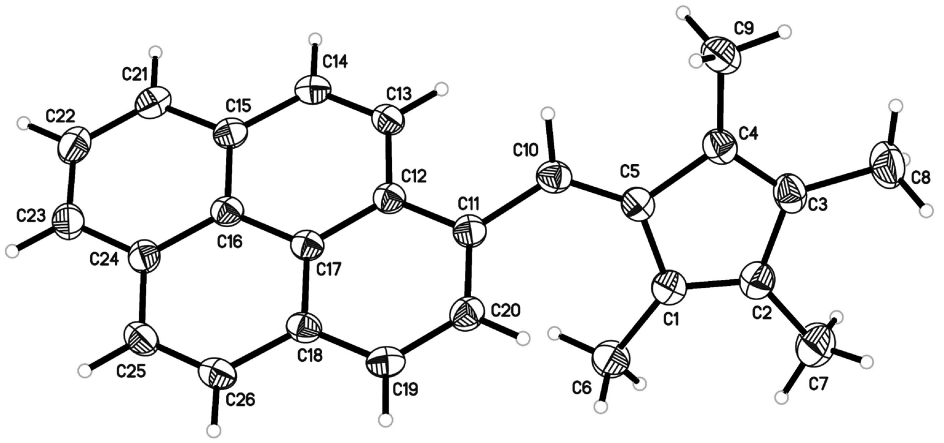
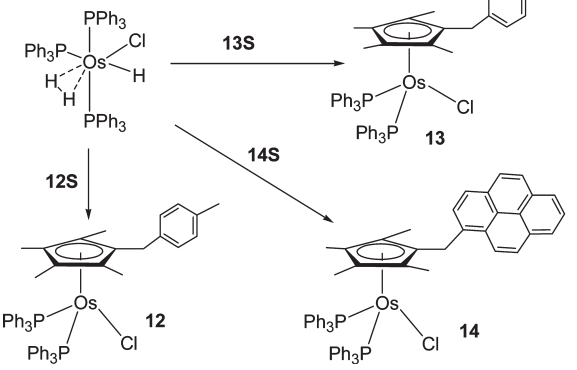


Figure 6. ORTEP drawing of **14S**. Thermal ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (deg): C(1)−C(2), 1.339(2); C(2)−C(3), 1.482(2); C(3)−C(4), 1.345(2); C(4)−C(5), 1.491(2); C(5)−C(10), 1.342(2).

Scheme 6



and (η^5-$C_5Me_4CH_2$pyrenyl)OsCl(PPh_3)$_2$ (**14**) were obtained from the reactions using **S13** and **S14**, respectively.

All these complexes have been characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of complex **12**−**14** show a singlet at ca. −2 to −3 ppm. The ^1H NMR spectra display a set of three singlets at ca. 2.8, 1.2, and 1.1 ppm with an intensity ratio of 1:3:3 for the CH_2 and the methyl groups. The solid-state structure of complex **12** (containing a tolyl pendant group) has been determined by X-ray analysis. Like the monosubstituted cyclopentadienyl complexes, the substituted tetramethylcyclopentadienyl complex **12** also adopts a piano stool structure (Figure 7). The bond lengths and bond angles are also similar to those of the cyclopentadienyl complexes.

Conclusion

In conclusion, we have developed two methodologies for the preparation of half-sandwich osmium complexes with the general formula (η^5-cyclopentadienyl)OsCl(PPh_3)$_2$ using $OsH_3Cl(PPh_3)_3$ as the starting material. The first approach involves the reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadienes. Thus, (η^5-cyclopentadienyl)OsCl(PPh_3)$_2$ can be conveniently synthesized from the reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadienes through C−H oxidative addition of cyclopentadiene followed by reductive elimination of hydrogen. The methodology has enabled us to synthesize a series of half-sandwich osmium complexes containing Cp, Cp*, indenyl, and several substituted cyclopentadienyls. The second approach involves the reactions of $OsH_3Cl(PPh_3)_3$ with fulvenes. Treatment of $OsH_3Cl(PPh_3)_3$ with C6-substitued fulvenes gives monosubstituted cyclopentadienyl complexes. 6-Substituted-1,2,3,4-tetramethylfulvenes can be efficiently synthesized by condensation reactions between 1,2,3,4-tetramethylcyclopentadiene and aldehydes in the presence of KO*t*Bu. The new fulvenes readily react with $OsH_3Cl(PPh_3)_3$ to give complexes (η^5-$C_5Me_4CH_2R$)OsCl(PPh_3)$_2$.

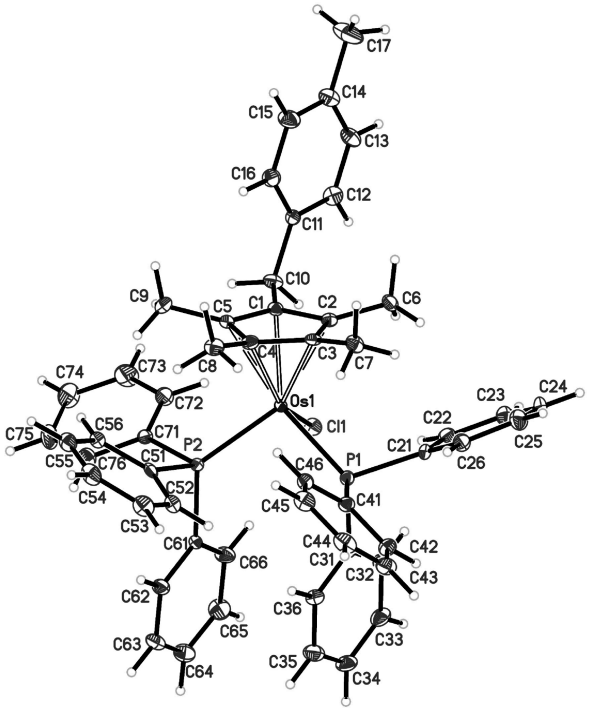


Figure 7. ORTEP drawing of (η^5-$C_5Me_4CH_2C_6H_4Me$)OsCl(PPh_3)$_2$ (**12**). Thermal ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): average Os−C (C_5Me_4R), 2.243; Os−P(1), 2.3153(9); Os−P(2), 2.3317 (10); Os−Cl(1), 2.4727(10); P(1)−Os(1)−Cl(1), 87.14(3); P(2)−Os(1)−P(1), 99.48(4).

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium

and benzophenone (*n*-hexane, diethyl ether), sodium (THF, benzene), or calcium hydride (CH_2Cl_2). The starting materials $OsH_3Cl(PPh_3)_3$,[39] **S7**/**S8**,[40] **S9**,[41] and **S10**/**S11**[42] were prepared following the procedures described in the literature. All other reagents were used as purchased from Aldrich Chemical Co. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts are relative to 85% H_3PO_4. MS spectra were recorded on a Finnigan TSQ7000 spectrometer.

Synthesis of $CpOsCl(PPh_3)_2$ (1). A mixture of freshly distillated cyclopentadiene (50 μL, 0.61 mmol) and $OsH_3Cl(PPh_3)_3$ (208 mg, 0.20 mmol) in 10 mL of toluene was refluxed for 2 h. After removal of the solvent, the residue was washed with *n*-hexane and diethyl ether and dried under vacuum to give a yellow solid. Yield: 102 mg, 61.1%. The NMR data match with the literature values.[16] ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.11 (m, 30H, PPh_3), 4.31 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$): δ −2.51 ppm (s).

Synthesis of $(C_9H_7)OsCl(PPh_3)_2$ (2). A mixture of indene (90%) (50 μL, 0.38 mmol) and $OsH_3Cl(PPh_3)_3$ (260 mg, 0.26 mmol) in 10 mL of toluene was refluxed for 18 h. The product was purified by column chromatography using Al_2O_3 as the solid phase. The indene and PPh_3 were first eluted out by a *n*-hexane/DCM (6:1) mixture. The product was then eluted out with DCM. The product was isolated as an orange solid. Yield: 68.0 mg, 30.7%. The NMR data match with the literature values. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.14−7.11 (m, 6H, PPh_3 and indenyl), 7.03 (br s, 25H, PPh_3), 6.84−6.82 (m, 3H, indenyl), 4.84 (s, 1H, indenyl), 4.18 (s, 2H, indenyl). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ −1.58 ppm (s).

General Procedure for the Synthesis of (η^5-C_5Me_4R)OsCl(PPh_3)$_2$ from Substituted Tetramethylcyclopentadienes (3−6). A mixture of cyclopentadiene (ca. 1.5 equiv) and $OsH_3Cl(PPh_3)_3$ in 20 mL of toluene was refluxed for 4 h. After the completion of the reaction, the solvent was removed by evaporation under vacuum. The residue was washed with *n*-hexane and Et_2O and dried under vacuum to give a yellow solid.

(C_5Me_5)$OsCl(PPh_3)_2$ (3). $OsH_3Cl(PPh_3)_3$ (1.287 g, 1.27 mmol), C_5Me_5H (300 μL, 1.92 mmol, 1.5 equiv). Reaction time: 4 h. Yield: 949 mg, 85%. ^1H NMR (300 MHz, C_6D_6): δ 7.86 (br, 12H, PPh_3), 7.04 (br, 18H, PPh_3), 1.30 (s, 15H, CH_3 of Cp*). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2): δ 138.60 (d, J = 46.9 Hz), 135.08 (s), 128.49 (s), 126.83 (s) (PPh_3), 86.50 (s) (C_5Me_5), 9.00 (s) (C_5Me_5). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −2.54 ppm (s). Anal. Calcd for $C_{46}H_{45}ClOsP_2$: C, 62.39; H, 5.12. Found: C, 62.37; H, 5.08.

(η^5-C_5Me_4H)$OsCl(PPh_3)_2$ (4). $OsH_3Cl(PPh_3)_3$ (331 mg, 0.33 mmol), $C_5Me_4H_2$ (85%) (87 μL, 0.49 mmol, 1.5 equiv). Reaction time: 4 h. Yield: 230 mg, 84.1%. ^1H NMR (300 MHz, C_6D_6): δ 7.81 (br, 10H, PPh_3), 7.05 (br, 20H, PPh_3), 4.14 (s, 1H, CH of C_5Me_4H), 1.38 (s, 6H, CH_3 of C_5Me_4H), 1.23 (s, 6H, CH_3 of C_5Me_4H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 138.98 (d, J = 47.9 Hz), 134.61 (s), 128.39 (s), 126.87 (s) (PPh_3), 91.32 (s), 82.42 (s), 78.20 (s) (C_5Me_4H), 9.50 (s), 8.54 (s) (C_5Me_4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −2.73 ppm (s). Anal. Calcd for $C_{45}H_{43}ClOsP_2$: C, 62.02; H, 4.97. Found: C, 62.06; H, 4.77.

(η^5-C_5Me_4Et)$OsCl(PPh_3)_2$ (5). $OsH_3Cl(PPh_3)_3$ (211 mg, 0.21 mmol), C_5Me_4HEt (97%) (55 μL, 0.31 mmol, 1.5 equiv). Reaction time: 6 h. Yield: 125.6 mg, 67.5%. ^1H NMR (300 MHz, C_6D_6): δ 7.86 (br, 12H, PPh_3), 7.04 (br, 18H, PPh_3), 1.77 (q, J = 7.4 Hz, 2H, CH_2CH$_2$), 1.40 (s, 6H, CH_3 of C_5Me_4Et), 1.37 (s, 6H, CH_3 of C_5Me_4Et), 0.92 (t, J = 7.4 Hz, 3H, CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 138.55 (d, J = 46.9 Hz), 134.94 (s), 128.47 (s), 126.66 (s) (PPh_3), 90.01 (s), 87.65 (s), 83.84 (s) (C_5Me_4), 17.06 (s), 12.48 (s) (-Et), 8.86 (s), 8.60 (s) (C_5Me_4). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −3.38 ppm (s). Anal. Calcd for $C_{47}H_{47}ClOsP_2$: C, 62.76; H, 5.27. Found: C, 62.87; H, 5.17.

(η^5-C_5Me_4Pr)$OsCl(PPh_3)_2$ (6). $OsH_3Cl(PPh_3)_3$ (506 mg, 0.50 mmol), C_5Me_4H*n*-Pr (116 mg, 0.71 mmol, 1.4 equiv). Reaction time: 8 h. Yield: 341 mg, 75.1%. ^1H NMR (300 MHz, C_6D_6): δ 7.89 (br, 12H, PPh_3), 7.04 (br, 18H, PPh_3), 1.67 (t, J = 7.6 Hz, 2H, $CH_2CH_2CH_3$); 1.44 (s, 6H, CH_3 of C_5Me_4nPr); 1.37−1.34 (m, 8H, CH_3 of C_5Me_4Pr and CH$_2$CH_2CH$_3$), 0.87 (t, J = 7.2 Hz, 3H, CH$_2$CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 138.73, (d, J = 47.3 Hz), 135.12 (s), 128.46 (s), 126.80 (s) (PPh_3), 90.03 (s), 87.29 (s), 85.15 (s) (C_5Me_4), 26.32 (s), 21.95 (s), 14.65 (s) (*n-Pr*), 9.05 (s) (C_5Me_4). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −3.46 ppm (s). Anal. Calcd for $C_{48}H_{49}ClOsP_2$: C, 63.11; H, 5.41. Found: C, 63.05; H, 5.35.

General Procedure for the Synthesis of (η^5-C_5H_4R)OsCl(PPh_3)$_2$ (7−11) Using Fulvenes 7S−11S. A solution of fulvene in THF (5 mL) was added to a solution of $OsH_3Cl(PPh_3)_3$ in THF (5 mL). The mixture was refluxed for 4 h. After the completion of the reaction, all volatiles were removed under reduced pressure. The residue was purified by column chromatography on aluminum oxide using *n*-hexane and 5:1 *n*-hexane/Et_2O as the eluting solvents. Removal of solvents afforded corresponding cyclopentadienyl complexes as yellow solids.

(η^5-$C_5H_4CH_2$tolyl)$OsCl(PPh_3)_2$ (7). 6-Tolylfulvene (**7S**) (107 mg, 0.63 mmol), $OsH_3Cl(PPh_3)_3$ (412 mg, 0.41 mmol). Yield: 259 mg, 69.4%. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.31−7.05 (m, 34H, PPh_3 and aromatic protons of tolyl), 4.03 (s, 2H, C_5H_4), 3.71 (s, 2H, C_5H_4), 3.44 (s, 2H, CH_2), 2.28 (s, 3H, *Me* of tolyl). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): 139.32 (d, J = 48.1 Hz), 133.95 (t, J = 4.7 Hz), 128.71 (s), 127.25 (t, J = 4.4 Hz) (P*Ph*$_3$), 137.68 (s), 135.76 (s), 129.05 (s), 128.89 ($C_{arom.}$ of tolyl), 106.54 (s), 76.03 (s), 75.97 (s), 72.56 (s, C_5H_4), 32.26 (s, $C_5H_4CH_2$-), 20.74 (s, CH_3 of tolyl). $^{31}P\{^1H\}$NMR (121.5 MHz, CD_2Cl_2): δ −2.28 ppm (s). Anal. Calcd for $C_{49}H_{43}ClOsP_2$: C, 64.01; H, 4.71. Found: C, 64.23; H, 4.90.

(η^5-$C_5H_4CH_2C_6H_4OMe$)$OsCl(PPh_3)_2$ (8). 6-Anisolylfulvene (**8S**) (110 mg, 0.60 mmol), $OsH_3Cl(PPh_3)_3$ (403 mg, 0.40 mmol). Yield: 212 mg, 57.1%. ^1H NMR (300 MHz, C_6D_6): δ 7.74 (br, 10H, PPh_3), 7.40 (d, J = 8.5 Hz, C_6H_4OMe), 7.07 (br, 20H, PPh_3), 6.90 (d, J = 8.5 Hz, C_6H_4OMe), 4.33 (s, 2H, C_5H_4), 4.04 (s, 2H, CH_2), 3.95 (s, 2H, C_5H_4), 3.45 (s, 3H, O*Me*). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 139.42 (d, J = 49.1 Hz), 133.96 (s), 128.70 (s), 127.24 (s) (P*Ph*$_3$), 132 (s), 129.99 (s), 113.75 (s), 106.83 (s) ($C_{arom.}$ of anisolyl), 75.90 (s), 72.51 (s) (C_5H_4), 31.73 (s) ($C_5H_4CH_2$), 13.93 (s) (O*Me*). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): −2.38 ppm (s). Anal. Calcd for $C_{49}H_{43}ClOOsP_2$: C, 62.91; H, 4.63. Found: C, 62.83; H, 4.77.

(η^5-$C_5H_4CHPh_2$)$OsCl(PPh_3)_2$ (9). 6,6′-Diphenylfulvene (**9S**) (102 mg, 0.44 mmol), $OsH_3Cl(PPh_3)_3$ (0.300 mg, 0.30 mmol). Yield: 196 mg, 67.6%. ^1H NMR (300 MHz, C_6D_6): δ 7.85 (d, J = 6.4 Hz, 4H, Ph), 7.73 (br, 12H, PPh_3), 7.30 (br, 3H, Ph), 7.16 (t, J = 6.4 Hz, 3H, Ph), 7.02 (br, 18H, PPh_3), 6.35 (s, 1H, C*H*Ph$_2$), 4.17 (s, 2H, C_5H_4), 3.57 (s, 2H, C_5H_4). $^{31}P\{^1H\}$NMR (121.5 MHz, C_6D_6): δ −1.41 ppm (s). Anal. Calcd for $C_{54}H_{45}ClOsP_2$: C, 66.08; H, 4.62. Found: C, 65.97; H, 4.67.

(η^5-$C_5H_4CH_2t$Bu)$OsCl(PPh_3)_2$ (10). 6-*tert*-Butylfulvene (**10S**) (60.0 mg, 0.45 mmol), $OsH_3Cl(PPh_3)_3$ (203 mg, 0.20 mmol). Yield: 135 mg, 76.3%. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.23−7.02 (m, 30H, PPh_3), 3.95 (s, 2H, C_5H_4), 3.65 (s, 2H, C_5H_4), 1.86 (s, 2H, CH_2), 0.81 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 138.71 (d, J = 50.6 Hz), 133.12 (s), 127.79 (s), 126.37 (s) (P*Ph*$_3$), 102.43 (s), 77.12 (t, J = 4.5 Hz), 71.56 (s, C_5H_4), 40.50 (s, $C_5H_4CH_2$), 29.93 (s, CMe_3), 28.76 (s, CMe_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −1.23 ppm (s). Anal. Calcd for $C_{46}H_{45}ClOsP_2$: C, 62.39; H, 5.12. Found: C, 62.62; H, 5.16.

(η^5-C_5H_4cyclopentyl)$OsCl(PPh_3)_2$ (11A) and (η^5-C_5H_4cyclopentenyl)$OsCl(PPh_3)_2$ (11B). 6-Cyclopentylfulvene (**11S**) (43 mg,

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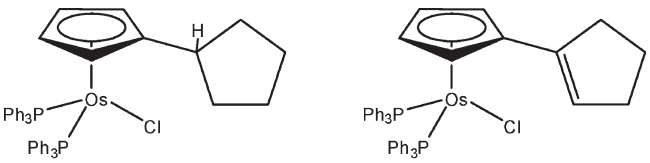
0.32 mmol), $OsH_3Cl(PPh_3)_3$ (203 mg, 0.20 mmol). Yield: 106 mg, 63.9%. Molar ratio of **11A** to **11B** = 4:1 (based on the integrations of Cp proton signals). Characteristic ^1H signals of **11A** (300 MHz, CD_2Cl_2): δ 4.11 (s, 2H, Cp), 3.87 (s, 2H, Cp), 2.90 (quintet, J = 8.3 Hz, 1H, CpC*H* of cyclopentyl), 2.19−2.13 (m, 2H cyclopentyl), 1.82−1.78 (m, 4H, cyclopentyl), 1.63−1.53 (m, 2H, cyclopentyl). Characteristic signals of **11B** (300 MHz, CD_2Cl_2): δ 5.90 (br t, 1H, =C*H*), 4.50 (s, 2H, C_5H_4), 3.83 (s, 2H, C_5H_4), 2.87 (br dt, 2H, cyclopentyl), 2.19−2.13 (m, 2H, cyclopentyl), 1.82−1.78 (m, 2H, cyclopentenyl). The ^1H NMR signals of PPh_3 in **11A** and **11B** are overlapped in the region 7.48−7.15 ppm, and other CH_2 signals are overlapped in the region 2.65−1.28 ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): −2.10 (s, **11A**), −2.80 ppm (s, **11B**). Anal. Calcd for $C_{46}H_{43}ClP_2Os$: C, 62.54; H, 4.91. Found: C, 62.76; H, 4.98.



Preparation of 6-Tolyl-1,2,3,4-tetramethylfulvene (12S). 1,2,3,4-Tetramethylcyclopentadiene (85%) (250 μL, 1.40 mmol) was added dropwisely to a Schlenk flask containing KO*t*Bu (1.558 g, 13.88 mmol, 9.9 equiv) followed by addition of MeOH (8 mL) and *p*-tolylaldehyde (97%) (230 μL, 1.88 mmol, 1.3 equiv). The mixture was heated at 70 °C. The reaction was monitored by TLC. After the completion of the reaction (15 h), the product was extracted with *n*-pentane (10 mL × 3), washed with a brine solution (10 mL × 2), and dried over Na_2SO_4. The product was purified by column chromatography on basic aluminum oxide using *n*-pentane as the eluent. Yield: 189 mg (orange oil), 60.2%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (d, J = 7.9 Hz, 2H, $H_{arom.}$of tolyl), 7.28 (d, J = 7.9 Hz, 2H, $H_{arom.}$of tolyl), 7.22 (s, 1H, C*H*(tolyl)), 2.51 (s, 3H, CH_3 of tolyl), 2.22 (s, 3H, CH_3 of C_5Me_4), 2.02 (s, 3H, CH_3 of C_5Me_4), 1.98 (s, 3H, CH_3 of C_5Me_4), 1.77 (s, 3H, CH_3 of C_5Me_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 146.69 (s), 141.96 (s), 137.32 (s), 137.03 (s), 134.57 (s), 130.49 (s), 129.62 (s), 128.63 (s), 125.66 (s), 122.48 (s), 21.40 (s), 13.59 (s), 11.44 (s), 11.35 (s), 9.84 (s). MS (TOF EI$^+$): m/z 224.15 (M).

Preparation of 6-Anisolyl-1,2,3,4-tetramethylfulvene (13S). 1,2,3,4-Tetramethylcyclopentadiene (85%) (250 μL, 1.40 mmol) was added dropwisely to a Schlenk flask containing KO*t*Bu (1.602 g, 14.28 mmol, 10.2 equiv) followed by addition of MeOH (8 mL) and *p*-anisolylaldehyde (98%) (260 μL, 2.10 mmol, 1.5 equiv). The mixture was heated at 70 °C. The reaction was monitored by TLC. After the completion of the reaction (19 h), the product was extracted with *n*-pentane (10 mL × 3), washed with a brine solution (10 mL × 2), and dried over Na_2SO_4. The product was purified by column chromatography on basic aluminum oxide using hexane/ethyl acetate (10:1) as the eluent. Yield: 188 mg (orange oil), 55.7%. ^1H NMR (300 MHz, *d*-acetone): δ 7.39 (d, J = 8.6 Hz, 2H, aromatic H), 7.14 (s, 1H, CH (anisolyl)), 7.05 (d, J = 8.6 Hz, 2H, aromatic H), 3.98 (s, 3H, OCH_3), 2.04 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.74 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, *d*-acetone): δ 159.53 (s), 146.59 (s), 141.29 (s), 136.05 (s), 131.14 (s), 129.63 (s), 129.36 (s), 125.38 (s), 121.71 (s), 113.36 (s), 154.73 (s), 133.07 (s), 10.50 (s), 10.47 (s), 9.04 (s). MS (TOF LD$^+$): m/z 226.38 (M − CH_3).

Preparation of 6-Pyrenyl-1,2,3,4-tetramethylfulvene (14S). 1,2,3,4-Tetramethylcyclopentadiene (85%) (250 μL, 1.40 mmol) was added dropwisely to a flask containing KO*t*Bu (1.642 g, 14.63 mmol, 10.5 equiv) followed by addition of MeOH (5 mL) and 1-pyrenylcarboxaldehyde (98%) (394 mg, 1.71 mmol, 1.22 equiv) in THF (5 mL). The mixture was heated at 70 °C. The reaction was monitored by TLC. After the completion of the reaction (19 h), the product was extracted with DCM (10 mL × 3), washed with a brine solution (10 mL × 2), and dried over Na_2SO_4. The product was purified by column chromatography on basic aluminum oxide using hexane/ethyl acetate (10:1) as the eluent. Yield: 244 mg (orange solid), 52.1%. ^1H NMR (300 MHz, *d*-acetone): δ 8.41 (d, J = 5.6 Hz, 1H, aromatic H), 8.40 (s, 1H, aromatic H), 8.39 (d, J = 6.0 Hz, 1H, aromatic H), 8.35 (s, 1H, aromatic H), 8.32 (s, 1H, aromatic H), 8.29 (s, 2H, aromatic H), 8.19 (t, J = 7.6 Hz, 1H, aromatic H), 8.09 (d, J = 7.6 Hz, 1H, aromatic H), 7.82 (s, 1H, CH(pyrenyl)), 2.26 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, *d*-acetone): 149.57 (s), 141.71 (s), 137.12 (s), 132.92 (s), 131.53 (s), 131.16 (s), 130.98 (s), 129.05 (s), 128.14 (s), 127.67 (s), 127.55 (s), 127.51 (s), 127.33 (s), 127.27 (s), 126.34 (s), 125.47 (s), 125.39 (s), 125.10 (s), 124.90 (s), 124.63 (s), 124.40 (s), 122.43 (s), 12.26 (s), 10.59 (s), 10.41 (s), 9.11 (s). MS (TOF LD$^+$): m/z 334.11 (M).

Synthesis of (η^5-$C_5Me_4CH_2$tolyl)OsCl(PPh_3)$_2$ (12). 6-Tolyl-1,2,3,4-tetramethylfulvene (**12S**) (53 mg, 0.25 mmol, 1.6 equiv) in toluene (6 mL) was added to a solution of $OsH_3Cl(PPh_3)_3$ (155 mg, 0.15 mmol) in toluene (2 mL). The reaction mixture was refluxed for 3.5 h. After the completion of the reaction, all volatiles were removed under reduced pressure. The residue was purified by column chromatography on Al_2O_3 with pentane/diethyl ether (10:1) followed by pentane/DCM (1:1) as the eluting solvents. Pure product was isolated as a yellow solid. Yield: 113 mg, 75.9%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.45 (br, 13H, PPh_3), 7.17 (br, 7H, PPh_3), 7.08 (br, 10H, PPh_3), 6.95 (d, J = 8 Hz, 2H, aromatic H of tolyl), 6.72 (d, J = 8 Hz, 2H, aromatic H of tolyl), 2.56 (s, 2H, CH_2-tolyl), 2.23 (s, 3H, CH_3 of tolyl), 1.10 (s, 6H, CH_3 of C_5H_4), 1.06 (s, 6H, CH_3 of C_5H_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 138.41 (d, J = 46.9 Hz), 134.99 (s), 128.44 (s), 126.73 (s) (PPh_3), 136.92 (s), 131.92 (s), 128.72 (s), 128.01 (s) ($C_{arom.}$ of tolyl), 87.26 (s), 86.93 (s), 85.88 (s) (C_5Me_4), 29.21 (s) (CH_2-tolyl), 20.64 (s) (CH_3 of tolyl), 9.31 (s), 8.96 (s) (C_5Me_4). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ −3.42 ppm (s). Anal. Calcd for $C_{53}H_{51}ClP_2Os$: C, 65.25; H, 5.27. Found: C, 62.65; H, 5.25.

Synthesis of (η^5-$C_5Me_4CH_2$anisolyl)OsCl(PPh_3)$_2$ (13). 6-Anisolyl-1,2,3,4-tetramethylfulvene (**13S**) (143 mg, 0.59 mmol, 1.3 equiv) in toluene (6 mL) was added to the solution of $OsH_3Cl(PPh_3)_3$ (461 mg, 0.45 mmol) in toluene (2 mL). The reaction mixture was refluxed for 2 h. After the completion of the reaction, all volatiles were removed under reduced pressure. The product was washed with *n*-hexane and diethyl ether and dried under vacuum. Yield: 345 mg, 76.6%. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.57 (br, 13H, PPh_3), 7.40−7.27 (m, 7H, PPh_3), 7.20 (br, 10H, PPh_3), 6.86 (d, J = 8.6 Hz, 2H, aromatic H of anisolyl), 6.79 (d, J = 8.6 Hz, 2H, aromatic H of anisolyl), 3.82 (s, 3H, OCH_3), 2.47 (s, 2H, CH_2-anisolyl), 1.23 (s, 6H, CH_3 of C_5Me_4), 1.19 (s, 6H, CH_3 of C_5Me_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 157.75 (s), 132.06 (s), 129.04 (s), 113.45 (s) (aromatic C of anisolyl), 138.42 (d, J=47 Hz), 135.01 (s), 128.45 (s), 126.74 (s) (PPh_3), 87.14 (s), 86.96 (s), 86.11 (s) (C_5Me_4), 55.18 (s) (OCH_3), 28.76 (s) (CH_2-anisolyl), 9.31 (s), 8.96 (s) (C_5Me_4). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −3.38 ppm (s). Anal. Calcd for $C_{53}H_{51}ClOOsP_2$: C, 64.20; H, 5.18. Found: C, 64.38; H, 5.09.

Synthesis of (η^5-$C_5Me_4CH_2$pyrenyl)OsCl(PPh_3)$_2$ (14). 6-Pyrenyl-1,2,3,4-tetramethylfulvene (**14S**) (137 mg, 0.41 mmol, 1.3 equiv) in toluene (6 mL) was added to the solution of $OsH_3Cl(PPh_3)_3$ (321 mg, 0.32 mmol) in toluene (2 mL). The reaction mixture was refluxed for 3 h. After the completion of the reaction, all volatiles were removed under reduced pressure. The product was washed with *n*-hexane and diethyl ether and dried under vacuum. Yield: 263 mg, 76.6%. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.36−8.28 (m, 3H, pyrenyl), 8.16−8.04 (m, 5H, pyrenyl), 7.66 (br, 12H, PPh_3), 7.52 (d, J = 7.8, 1H, pyrenyl), 7.31 (br, 8H, PPh_3), 7.25 (br, 10H, PPh_3), 3.42 (s, 2H, CH_2-pyrenyl), 1.35

Table 1. Crystal Data and Structure Refinement for 3, 4, 6, 8, 10, 14S, and 12

	3	4	6	8	10	14S	12
formula	$C_{46}H_{45}ClOsP_2$	$C_{45}H_{43}ClOsP_2$	$C_{48}H_{49}ClOsP_2 \cdot CH_2Cl_2$	$C_{49}H_{43}ClOOsP_2$	$C_{46}H_{45}ClOsP_2$	$C_{26}H_{22}$	$C_{53}H_{51}ClOsP_2 + 0.5CH_2Cl_2$
fw	885.41	871.38	998.39	935.42	885.41	334.44	1017.99
wavelength, Å	0.71073	1.54178	1.54178	0.71073	1.54178	1.54178	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$I2/a$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a, Å	17.135(2)	20.6600(2)	10.8929(3)	17.1453(6)	12.3351(2)	29.3956(9)	12.51560(10)
b, Å	10.6770(13)	10.64450(10)	12.7255(3)	10.1364(4)	10.5747(2)	6.5728(2)	20.4199(2)
c, Å	20.526(3)	34.0135(4)	16.4403(5)	23.1151(8)	29.3780(6)	9.5187(3)	17.1641(2)
α, deg	90	90	78.940(2)	90	90	90	90
β, deg	101.6230(10)	102.7770(10)	71.202(3)	95.258(3)	94.228(2)	99.019(2)	94.4070(10)
γ, deg	90	90	87.621(2)	90	90	90	90
V, Å	3678.2(8)	7294.87(13)	2116.78(10)	4000.3(3)	3821.64(12)	1816.38(10)	4373.61(8)
Z	4	8	2	4	4	4	4
D_{calcd}, g cm^{-3}	1.599	1.587	1.566	1.553	1.539	1.223	1.546
abs coeff, mm^{-1}	3.660	8.343	8.401	3.372	7.972	0.518	3.148
F(000)	1776	3488	1004	1872	1776	712	2052
θ range, deg	2.03−26.00	2.66−67.00	3.54−71.28	2.34−26.00	3.59−67.50	6.91−67.50	2.32−29.04
no. of reflns	36 908	12 670	27 991	30 557	15 058	9931	55 911
no. of indep reflns	7175 (R(int) = 0.0371)	6259 (R(int) = 0.0307)	7679 (R(int) = 0.0252)	7725 (R(int) = 0.1053)	6702 (R(int) = 0.0622)	3204 (R(int) = 0.0405)	10873 (R(int) = 0.0673)
no. of data/restraints/params	7175/0/456	6259/0/451	7679/2/519	7725/0/488	6702/6/454	3204/0/239	10 873/2/531
goodness of fit on F^2	1.010	1.001	1.002	1.057	1.026	1.005	1.027
final R indices ($I > 2\sigma(I)$)	R1 = 0.0213, wR2 = 0.0473	R1 = 0.0367, wR2 = 0.0806	R1 = 0.0210, wR2 = 0.0519	R1 = 0.0687, wR2 = 0.0888	R1 = 0.0392, wR2 = 0.0656	R1 = 0.0432, wR2 = 0.1074	R1 = 0.0422, wR2 = 0.0726
largest diff peak and hole, e Å^{-3}	1.473 and −0.401	3.455 and −1.321	0.932 and −0.958	1.556 and −3.251	0.995 and −0.920	0.198 and −0.131	1.394 and −2.273

(s, 6H, CH_3 of C_5Me_4), 1.21 (s, 6H, CH_3 of C_5Me_4). $^{13}C\{^1H\}$NMR (75.5 MHz, CD_2Cl_2): δ 138.43 (d, J = 48 Hz), 135.05 (s), 128.55 (s), 126.86 (s) (PPh_3), 133.60 (s), 131.48 (s), 130.92 (s), 129.52 (s), 128.68 (s), 127.40 (s), 127.04 (s), 126.55 (s), 125.94 (s), 124.93 (s), 124.83 (s), 124.75 (s), 124.72 (s), 124.60 (s), 124.52 (s), 123.50 (s) (pyrenyl), 88.65 (s), 87.19 (s), 83.99 (s) (C_5Me_4), 26.65 (s) (CH_2-pyrenyl), 9.12 (s), 9.06 (s) (C_5Me_4). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −3.38 ppm (s). Anal. Calcd for $C_{62}H_{53}ClOsP_2$: C, 68.59; H, 4.92. Found: C, 68.65; H, 5.01.

X-ray Crystallography Studies of 3, 4, 6, 8, 10, 14S, and 12. The crystal of **14S** suitable for X-ray analysis was obtained by slow evaporation of solvent of a methanol/hexane (1:3) solution. Single crystals of others were obtained by layer diffusion using a DCM/*n*-hexane mixture at room temperature. The crystals were mounted on a glass fiber. The diffraction intensity data of **3** were collected with a Bruker Smart APEX CCD X-ray diffractometer at T = 100 K. The diffraction intensity data of the rest were collected with an Oxford Diffraction Gemini S Ultra X-ray diffractometer. Data of **4**, **6**, **8**, **10**, and **12** were collected at T = 173 K, while those for **14S** were collected at T = 203 K. Lattice determination and data collection of **3** were carried out using SMART v.5.625 software. Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26 and SADABS v 2.03, respectively. Lattice determination, data collection, and reduction of the rest were carried out using CrysAlisPro 171.33.46. Absorption correction was performed using SADABS built into the CrysAlisPro program suite. Structure solution and refinement for all data were performed using the SHELXTL v.6.10 software package. All 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 a disordered model with appropriate partial occupancies applied. Further details on crystal data, data collection, and refinements are summarized in Table 1.

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Supporting Information Available: X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.