Alkyne Oligomerization

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Osmium-Mediated Hexamerization of Phenylacetylene**

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Transition-metal-mediated oligomerization and polymerization reactions of alkynes are attractive atom-economical C–C bond-formation reactions for organic and organometallic synthesis. Previous studies have led to the discovery of catalysts that can mediate selective dimerization,[1] trimerization,[2–4] tetramerization,[5,6] and polymerization[7] of alkynes. Parallel to this development, a number of organometallic complexes derived from dimerization, trimerization, and tetramerization of alkynes have been isolated, including interesting metallacycles,[8] complexes with cyclobutadiene,[9a–c] vinylvinylidene,[9d–e] benzene,[10] fulvene,[11–13] hexadienyne,[14] and unusual ligands derived from the tetramerization of alkynes.[15] In contrast, reactions of alkynes to give selectively well-defined oligomers of medium molecular weight (for example, pentamers, hexamers) of alkynes, either stoichiometric or catalytic in nature, are very scarce.[16] Herein we report a rare example of selective hexamerization of $HC\equiv CPh$ to give bimetallic osmium complexes with bridging μ-1,2-bis(η^5-cyclopentadienyl)-1,2-diphenyl-ethane ligands from the reaction of $[OsCl(PCP)(PPh_3)]$ (PCP = $2,6\text{-}(Ph_2PCH_2)_2C_6H_3$) with $HC\equiv CPh$.

Treatment of $[OsCl(PCP)(PPh_3)]$ (**1**) with excess $HC\equiv CPh$ in benzene rapidly produced a brownish solution of the vinylidene complex $[OsCl(=C=CHPh)(PCP)(PPh_3)]$ (**2**).[17] When the solution was left standing, complex **2** was consumed gradually. After four days, the reaction produced an orange-red precipitate and a dark brown solution. The orange-red precipitate was identified to be the racemic mixture of the (*R*,*R*) and (*S*,*S*) isomers of the dicationic bimetallic complex **4** (Scheme 1). From the filtrate, the neutral bimetallic complex **5** and a small amount of the cationic monomeric complex **3** could be isolated (Scheme 1). The reaction of isolated vinylidene complex **2** with excess $HC\equiv CPh$ gave the same result.

Complex **3** has been characterized by elemental analysis, FAB-MS, and multinuclear NMR spectroscopy. The structure has also been confirmed by an X-ray diffraction study.[18] The molecular structure of the complex cation of **3**, shown in Figure 1, clearly reveals that the complex is a four-legged piano stool cyclopentadienyl osmium(IV) complex with a facially bound PCP ligand and a chloride ligand. The solution NMR spectroscopic data are consistent with the solid-state structure. The facial arrangement of the PCP ligand in **3** is worth noting. Numerous complexes with PCP and related ligands have been reported in recent years.[19] In most of these reported complexes, the PCP and related ligands usually adopt a meridional geometry. Complex **3** represents a rare example of a PCP complex with a facially arranged PCP ligand.[20]

The most interesting result from the reaction of **1** with $HC\equiv CPh$ is the formation of the bimetallic complexes **4** and **5**, which contain a μ-1,2-bis(η^5-cyclopentadienyl)-1,2-diphenylethane bridging ligand (Scheme 1). The bridging ligand is formally derived from selective hexamerization of $HC\equiv CPh$. As a result of the different configurations (*R* or *S*) of the CHPh carbon atoms, both the neutral and dicationic complexes are expected to have (*R*,*R*), (*S*,*S*), and *meso* stereoisomers. Experimentally, all three isomers of the neutral complex **5** have been isolated and identified: the *meso* isomer **5c** was obtained as a yellow solid, and the (*R*,*R*) isomer **5a** and (*S*,*S*) isomer **5b** were obtained in the form of a racemic mixture. For the cationic complex, we have isolated the (*R*,*R*) and (*S*,*S*) isomers (**4a** and **4b**) as a racemic mixture.

The structures of all these bimetallic complexes have been determined by X-ray diffraction. As an illustration, the molecular structures of cationic complex **4a** ((*R*,*R*) isomer), neutral complexes **5a** ((*R*,*R*) isomer), and **5c** (*meso* isomer) are shown in Figures 2, 3, and 4, respectively. Complex **4a** has crystallographic C_2 symmetry with the twofold axis passing

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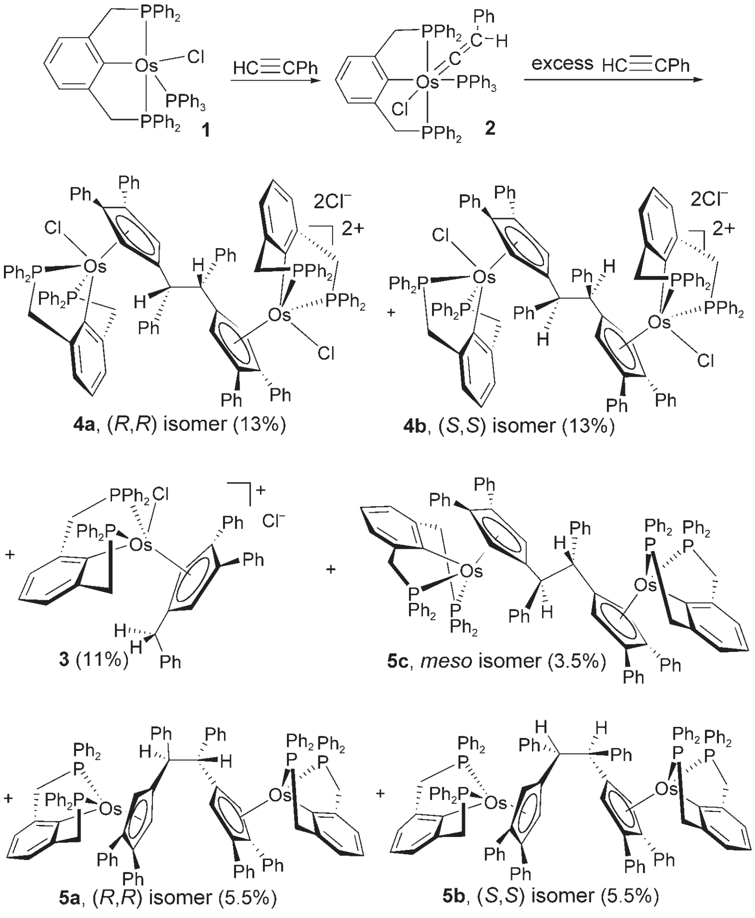


Scheme 1. Synthesis of complexes **3**–**5**.

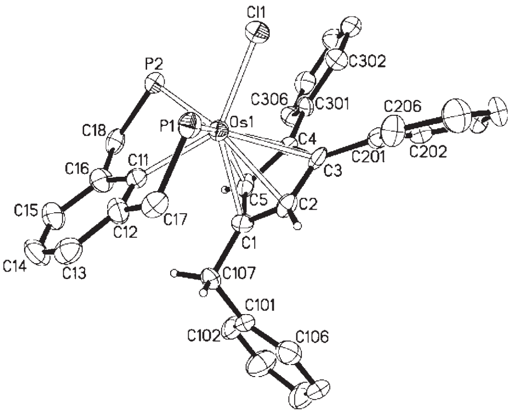


Figure 1. Molecular structure for the cation of **3**. The PPh_2 phenyl rings of the PCP ligands are omitted for clarity.

through the midpoint of C06 and C06A. The *meso* complex **5c** has idealized C_i symmetry with the crystallographic inversion center at the midpoint of C06 and C06A. All the complexes contain a facially bound PCP ligand. The solid-state structures are supported by their solution NMR spectroscopic data.

As indicated by the plausible mechanism shown in Scheme 2, complexes **3**, **4**, and **5** could all be formed through the fulvene intermediate **D** derived from a formal [2+2+1] cyclotrimerization of HC$\equiv$CPh. Thus, reaction of **1** with HC$\equiv$CPh produces the vinylidene complex $[OsCl(=C=CHPh)(PPh_3)(PCP)]$ (**2**), which has been confirmed experimentally. Complex **2** could dissociate the PPh_3 ligand in solution to give the unsaturated vinylidene **A**. Complex **A** undergoes a cycloaddition reaction with HC$\equiv$CPh to give first the metallacyclobutene complex **B** and then the metallacyclohexadiene complex **C**, which could undergo a reductive elimination to give the η^4-fulvene complex **D**. Protonation of **D** at the exocyclic CHPh carbon atom would give **3**. Couplings of vinylidenes at M=C bonds with alkynes are known reactions.[21] Although relatively rare, formation of fulvene metal complexes from formal [2+2+1] cyclotrimerizations of terminal alkynes has been reported in the stoichiometric reactions of rhodium,[11] iridium,[12] and palladium[13] complexes with alkynes. It is interesting to note that HC$\equiv$CR is dimerized on related metal fragments such as {Cp*Ru} (or {CpRu}; $Cp^* = C_5Me_5$, $Cp = C_5H_5$) and {TpRu} (Tp = hydrotris(pyrazolyl)borate) to give metallacyclopentadienes by oxidative coupling,[8b,c] or vinylvinylidenes by coupling of vinylidenes at C=C bonds with alkynes.[9d,e]

The fulvene intermediate **D** could undergo an intramolecular electron transfer (or "electron tautomerism") to generate the transient cyclopentadienyl osmium complex **E**, featuring an Os^{III} center and a carbon-centered radical, which then undergoes intermolecular radical coupling to produce the paramagnetic Os^{III} complex **F**. The 19-electron Os^{III} species **F** may undergo

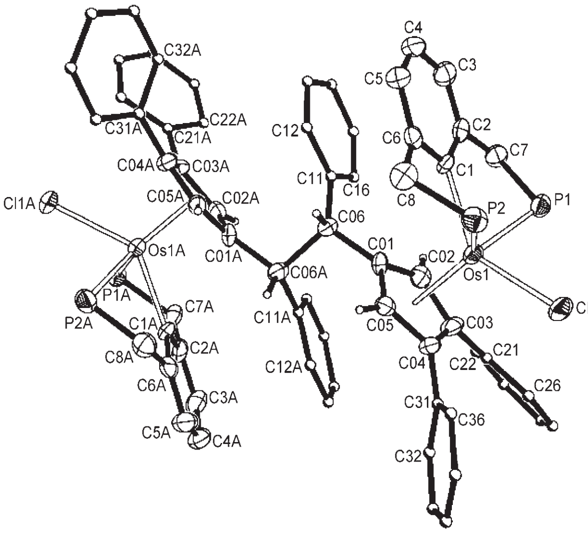


Figure 2. Molecular structure for the cation of **4a** ((R,R) isomer). The PPh_2 phenyl rings of the PCP ligands are omitted for clarity.

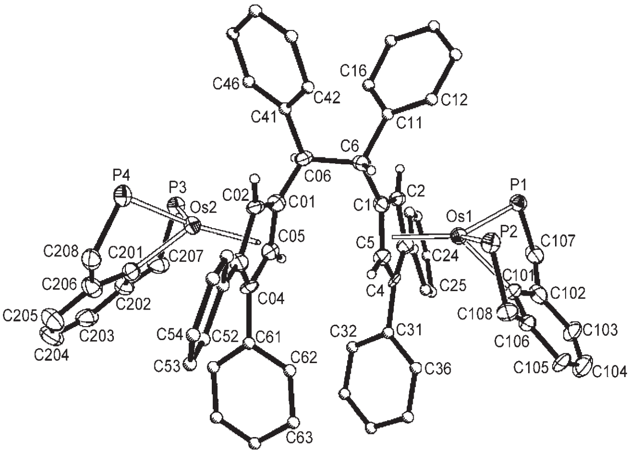


Figure 3. Molecular structure for **5a** ((*R*,*R*) isomer). The PPh_2 phenyl rings of the PCP ligands are omitted for clarity.

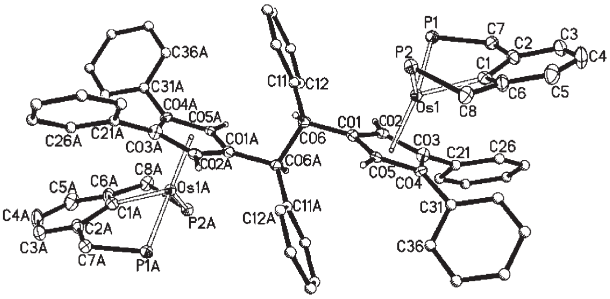


Figure 4. Molecular structure for **5c** (*meso* isomer). The PPh_2 phenyl rings of the PCP ligands are omitted for clarity.

disproportionation to give the neutral Os^{II} complex **5** and the dicationic Os^{IV} complex **4** with Cl^- as the counteranion. Radical dimerization involving coordinated fulvene has been proposed previously, for example, in the reaction of [CpCo(C_2H_4)$_2$] with 6,6-dimethylpentafulvene to give paramagnetic (1,1,2,2-tetramethyl-1,2-ethanediyl)biscobaltocene,[22] and in the dimerization of ferrocenylmethyl carbocations to give the paramagetic iron(III) 1,2-bis(ferroceniumyl)ethane complexes.[23]

Consistent with this proposition, treatment of vinylidene complex **2** with HC≡CPh in benzene in the presence of added HEt_3NCl produced **3** as the major product [Eq. (1)]. Isolated **3** readily undergoes H/D exchange with D_2O to give CD_2Ph-deuterated [D_2]-**3**, thus suggesting that the transient intermediate **D** can be generated by deprotonation of **3**. Treatment of **3** with NEt_3 can also produce the bimetallic complexes **4** and **5**, presumably via the fulvene intermediate **D** that is generated by deprotonation of **3** with NEt_3. Following the proposed mechanism, one would expect that the reaction of **1** with PhC≡CH would lead to the formation of a mixture of (*R*,*R*), (*S*,*S*), and *meso* stereoisomers for both neutral and cationic complexes. Experimentally, we have isolated and identified all three isomers of the neutral complex **5**, though *meso* isomer **5c** was obtained in a relatively low yield. For the cationic complexes, we have been able to isolate and characterize the (*R*,*R*) and (*S*,*S*) isomers **4a** and **4b**. In line with the low yield of **5c**, isolation of the dicationic meso isomer **4c** was not successful. It is noted that only racemic isomers of bis(ferroceniumyl)ethane were obtained in the dimerization reaction of [Cp*Fe(C_5H_4CHPh)]$^+$.[23b]

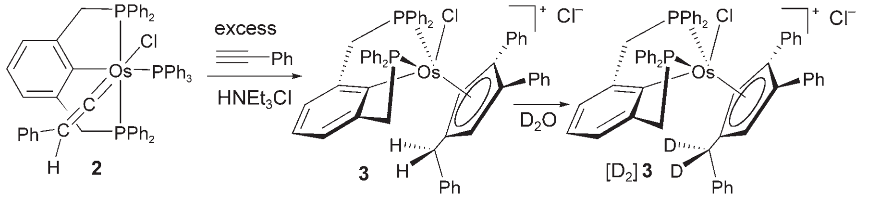
In summary, reaction of [OsCl(PPh_3)(PCP)] with excess HC≡CPh led to the unprecedented formation of bimetallic osmium complexes containing a μ-1,2-bis(η^5-cyclopentadienyl)-1,2-diphenyl-ethane bridging ligand, which are presumably formed through a fulvene intermediate which is generated from a formal [2+2+1] cylotrimerization of HC≡CPh.

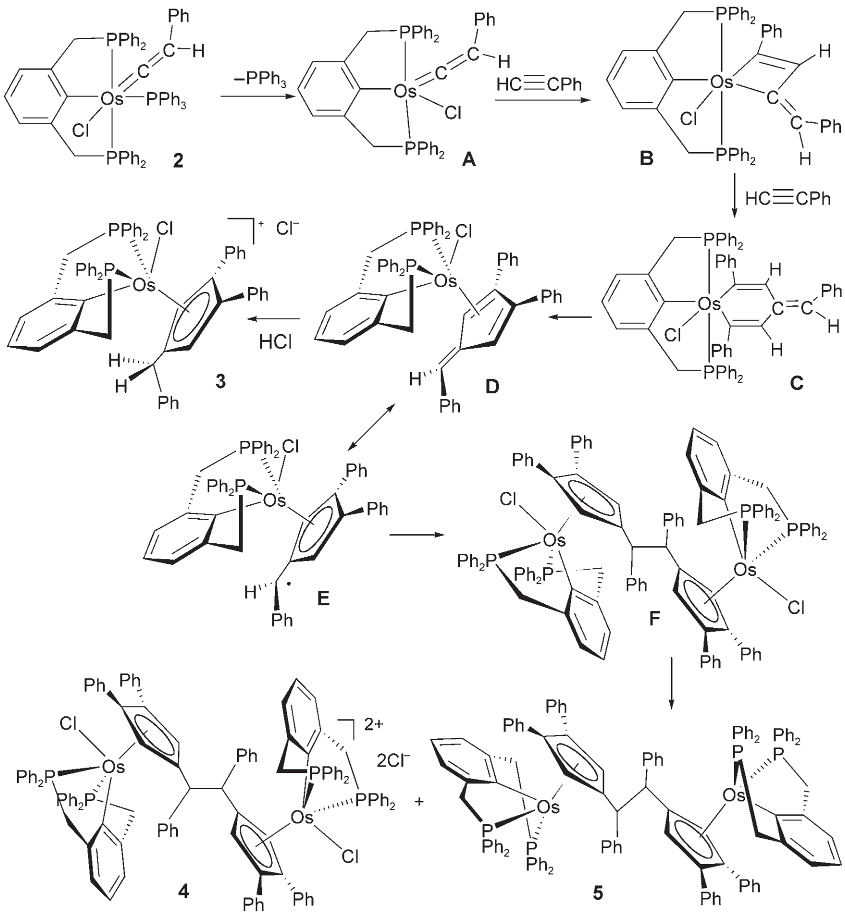
Experimental Section

A mixture of [OsCl(PPh_3)(PCP)] (0.80 g, 0.83 mmol) and phenylacetylene (1.40 mL, 12.7 mmol) in benzene (12 mL) was stirred at room temperature for 4 days to give an orange-red precipitate and a dark brown solution. The orange-red solid was collected by filtration, washed with benzene (2 mL) and diethyl ether (2 × 5 mL), dried in a vacuum overnight, and was identified to be a racemic mixture of **4a** and **4b**. Yield: 221 mg, 26 %. The benzene washings and the mother liquid were collected and combined. The solution was concentrated to about 1 mL to give **3** as an orange-yellow crystalline solid, which was collected by filtration, washed with benzene (1 mL) and diethyl ether (2 × 2 mL), and dried in a vacuum overnight. Yield: 95 mg, 11 %. The filtrate and the benzene washings were again combined and reduced to about 0.5 mL. Addition of diethyl ether (20 mL) to the residue provided a brownish-yellow solid, which was isolated by filtration and dried in a vacuum. The solid was then recrystallized from a small amount of benzene to give a racemic mixture of **5a** and **5b** as a yellow microcrystalline solid. Yield: 88 mg, 11 %. The solvent of the final filtrate obtained above was removed in a vacuum. The residue was washed with hexane (2 × 20 mL) to give a brown solid, which was dried under vacuum and recrystallized from a small amount of benzene to give **5c** as a yellow microcrystalline solid. Yield: 29 mg, 3.5 %.

3: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 7.6$ ppm (s); ^1H NMR (300.13 MHz, CD_2Cl_2): $\delta = 2.71$ (s, 2H, CH_2Ph), 4.42 (dd, $J(PH) = 14.2$ Hz, $J(HH) = 16.2$ Hz, 2H, PCP-CH_2), 4.57 (d, $J(HH) = 16.2$ Hz, 2H, PCP-CH_2), 6.66 (s, 2H, Cp-CH), 6.78–7.84 ppm (m, 38H, PPh_2, C_6H_3, C_6H_5); $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): $\delta = 147.9$ (t, $J(PC) = 6.6$ Hz, Os-C(aryl)), 137.5–124.5 (m, other aromatic carbon atoms), 114.1 (s, Cp-CCH_2Ph), 108.4 (s, 2 Cp-CPh), 90.6 (s, 2 Cp-CH), 43.9 (dd, $J(PC) = 23.1$, 19.8 Hz, PCP-CH_2), 32.8 ppm (s, CH_2Ph); FAB-MS (*m*-nitrobenzyl alcohol (NBA)): *m*/*z*: 1007.8 ([$M-Cl$]$^+$, calcd 1007.2). Elemental analysis (%) calcd for $C_{56}H_{46}Cl_2P_2Os$: C 64.55, H 4.45; found: C 64.29, H 4.67.

Racemic isomers **4a and 4b**: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 9.1$ (d), 5.2 (d), $J(PP) = 18.4$ Hz; ^1H NMR (300.13 MHz, CD_2Cl_2): $\delta = 2.97$ (dd, $J(HH) = 15.3$ Hz, $J(PH) = 3.1$ Hz, 1H, PCP-CH_2), 3.63 (t, $J(PH) = 15.3$ Hz, $J(HH) = 15.3$ Hz, 1H, PCP-CH_2), 3.79 (s, 1H, CHPh), 4.45 (t, $J(PH) =$

 (1)



Scheme 2. Proposed mechanism for the formation of **3**–**5**.

15.8 Hz, J(HH) = 15.8 Hz, 1 H, PCP-CH_2), 5.54 (s, 1 H, Cp-CH), 6.08–7.88 (m, 39 H, PPh$_2$, C$_6$H$_3$, C$_6$H$_5$, 1 H of PCP-CH_2 at ca. 7.1 ppm (obscured by aromatic proton resonances, assigned by ^{1}H,^{1}H COSY and ^{1}H,^{13}C COSY NMR experiments)), 8.98 (s, 1 H, Cp-CH); ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ = 149.0 (dd, J(PC) = 35.7, 10.4 Hz, Os-C(aryl)), 134.0–122.9 (m, other aromatic carbon atoms), 116.3 (s, Cp), 110.9 (d, J(PC) = 5.9 Hz, Cp), 107.1 (d, J(PC) = 7.4 Hz, Cp), 89.9 (d, J(PC) = 4.5 Hz, Cp-CH), 87.2 (d, J(PC) = 5.9 Hz, Cp-CH), 54.3 (s, CHPh, hidden under CD$_2$Cl$_2$ resonance, confirmed by DEPT-135, ^{1}H,^{13}C COSY experiments), 45.9 (d, J(PC) = 41.6 Hz, PCP-CH$_2$), 45.0 ppm (d, J(PC) = 41.7 Hz, PCP-CH$_2$); FAB-MS (NBA): m/z: 2012.0 ([M−2 Cl]$^+$, calcd 2012.5), 1006.3 ([M−2 Cl]$^{2+}$, calcd 1006.2). Elemental analysis (%) calcd for C$_{112}$H$_{90}$Cl$_4$P$_4$Os$_2$: C 64.61, H 4.36; found: C 64.76, H 4.50.

Racemic isomers **5a** and **5b**: ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 30.7 (d), 15.8 ppm (d), J(PP) = 13.9 Hz; ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ = 3.04 (s, 1 H, CHPh), 3.07 (dd, J(HH) = 14.6 Hz, J(PH) = 5.8 Hz, 1 H, PCP-CH_2), 3.48 (dd, J(HH) = 13.8 Hz, J(PH) = 5.6 Hz, 1 H, PCP-CH_2), 3.78 (t, J(HH) = 13.8 Hz, J(PH) = 13.3 Hz, 1 H, PCP-CH_2), 4.01 (dd, J(HH) = 14.6, J(PH) = 12.8 Hz, 1 H, PCP-CH_2), 4.32 (br s, 1 H, Cp-CH), 4.59 (br s, 1 H, Cp-CH), 5.62–7.47 ppm (m, 38 H, PPh$_2$, C$_6$H$_3$, C$_6$H$_5$); ^{13}C {^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ = 167.0 (t, J(PC) = 6.6 Hz, Os-C(aryl)), 147.1–119.7 (m, other aromatic carbon atoms), 96.4 (s, Cp), 91.2 (d, J(PC) = 6.5 Hz, Cp), 88.1 (s, Cp-CH), 85.4 (d, J(PC) = 8.2 Hz, Cp-CH), 78.9 (d, J(PC) = 13.2 Hz, Cp), 50.1 (d, J(PC) = 44.5 Hz, PCP-CH$_2$), 49.0 (s, CHPh), 48.4 ppm (d, J(PC) = 42.9 Hz, PCP-CH$_2$); FAB-MS (NBA, m/z): 1942.3 (M^+, calcd 1942.5). Elemental analysis (%) calcd for C$_{112}$H$_{90}$P$_4$Os$_2$: C 69.33, H 4.68; found: C 69.50, H 4.69.

5c: ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 298 K): δ = 29.2 (br), 22.9 ppm (d (unresolved), J(PP) = 13.2 Hz); ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, 298 K): δ = 3.29 (br s, 1 H, CHPh), 3.41–3.55 (m, 3 H, PCP-CH_2), 3.94 (br s, 1 H, Cp-CH), 4.19 (t, J(HH) = 14.4 Hz, J(PH) = 13.4 Hz, 1 H, PCP-CH_2), 4.32 (br s, 1 H, Cp-CH), 5.81–7.37 ppm (m, 38 H, PPh$_2$, C$_6$H$_3$, C$_6$H$_5$); ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ = 165.7 (br, Os-C(aryl)), 147.6–120.0 (m, other aromatic carbon atoms), 96.7 (br s, Cp), 95.0 (s, Cp), 85.5 (s, Cp-CH), 80.5 (br s, Cp-CH), 79.0 (br s, Cp), 51.2 (d, J(PC) = 48.5 Hz, PCP-CH$_2$), 51.0 (s, CHPh), 48.4 ppm (d, J(PC) = 42.3 Hz, PCP-CH$_2$); FAB-MS (NBA): m/z: 1941.0 (M^+, calcd 1942.5). Elemental analysis (%) calcd for C$_{112}$H$_{90}$P$_4$Os$_2$: C 69.33, H 4.68; found: C 69.27, H 5.15.

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