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Synthesis and Characterization of Trimetallic Ruthenium and Bimetallic Osmium Complexes with Metal−Vinyl Linkages

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Treatment of $RuHCl(CO)(PPh_3)_3$ with 1,3,5-triethynylbenzene produces the trimetallic complex 1,3,5-$[Cl(CO)(PPh_3)_2RuCH{=}CH]_3C_6H_3$, which reacts with PMe_3 to give 1,3,5-$[Cl(CO)(PMe_3)_3RuCH{=}CH]_3C_6H_3$. 1,3,5-$[Cl(CO)(PPh_3)_2RuCH{=}CH]_3C_6H_3$ also reacts with pyridine (Py) and 4-phenylpyridine (PhPy) to give 1,3,5-$[Cl(CO)(L)(PPh_3)_2RuCH{=}CH]_3C_6H_3$ (L = Py, PhPy). Reactions of $OsHCl(CO)(PPh_3)_3$ with $ArC{\equiv}CH$ (Ar = Ph, *p*-tolyl) produce the six-coordinated insertion products $OsCl(CH{=}CHAr)(CO)(PPh_3)_3$. Reaction of $OsHCl(CO)(PPh_3)_3$ with 1,3,5-triethynylbenzene produces the bimetallic complex 1-$HC{\equiv}C$-3,5-$[Cl(CO)(PPh_3)_3OsCH{=}CH]_2C_6H_3$, which reacts with PMe_3 to give 1-$HC{\equiv}C$-3,5-$[OsCl(CO)(PPh_3)_2(PMe_3)OsCH{=}CH]_2C_6H_3$. The electrochemical and second-order NLO properties of some of the new complexes have been investigated.

Introduction

Hyperbranched and dendritic organometallic compounds with metal centers linked by conjugated bridges are attracting considerable attention because of their material and catalytic properties.[1] A number of such complexes, either trimetallic or polymetallic in nature, have been synthesized in recent years, especially for those with a 1,3,5-substituted benzene core.[2−16] Most of the reported complexes have $M{-}C{\equiv}C$,[2b,c,3−14] $M{=}C{=}CHR$,[2d,7,8] M−aryl,[15] or M−L (L = η^2-$RC{\equiv}CR'$,[2a,f,16a−c] η^6-arene,[16e] N,[2g,16f−g] or P[16h] donors) linkages, for example, 1,3,5-$[L_nMC{\equiv}C]_3C_6H_3$ (M = Fe,[3] Ru,[5] Rh,[8] Ir,[9] Pd,[10,11] Pt,[11−13] and Au[14]), 1,3,5-$[L_nMC{\equiv}CC_6H_4C{\equiv}C]_3C_6H_3$ (M = Ru,[6a,7] Os[2b]), 1,3,5-$[(P(i\text{-}Pr)_3)_2ClRh{=}C{=}CH]_3C_6H_3$,[8] $\{$1,3,5-$[(dppe)_2ClRu{=}C{=}CHC_6H_4C{\equiv}C]_3C_6H_3\}(PF_6)_3$,[7] 1,3,5-$[(4\text{-}C_6H_3(3,5\text{-}CH_2NMe_2)_2)ClPd]_3C_6H_3$,[15] and

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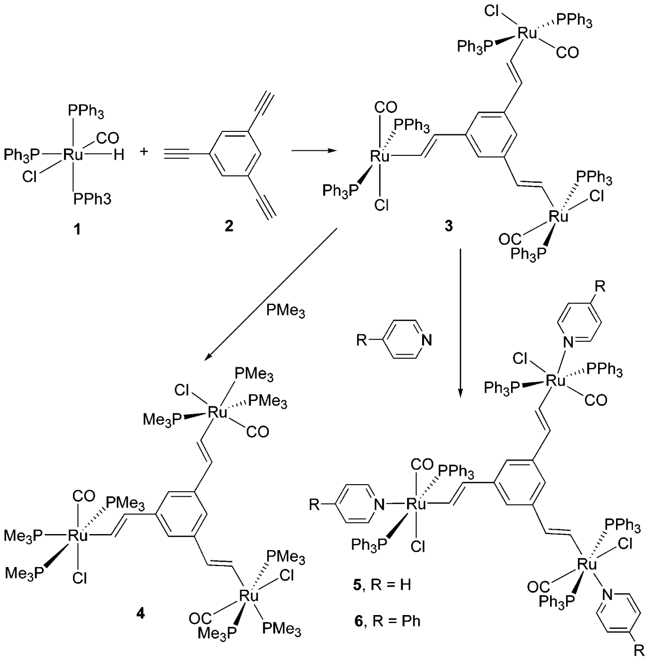
1,3,5-[$(Co_2(CO)_6)(H{\equiv}C{-})]_3C_6H_3$.[16a] These complexes can have interesting physical properties. For example, complexes such as 1,3,5-[$Cl(PEt_3)_2MC{\equiv}CC_6H_4C{\equiv}C]_3C_6H_3$ (M = Pd, Pt) exhibit luminescent properties,[10,11] complexes such as 1,3,5-[$(PPh_3)AuC{\equiv}C]_3C_6H_3$,[14a] 1,3,5-[Cl-(dppe)$_2$RuC≡CC$_6H_4$C≡C]$_3C_6H_3$,[6a] and 1,3,5-[Cl(dppm)$_2$-RuC≡CC$_6$H$_4$CH=CH]$_3$C$_6$H$_3$[6c] have good NLO properties, and complexes such as 1,3,5-[Cp*(dppe)FeC≡C]$_3$C$_6$H$_3$[3] and [Cp(PPh$_3$)$_2$RuC≡C]$_3$C$_6$H$_3$[4] show electronic cooperation between individual metal centers.

Although a number of trimetallic acetylide complexes of the type 1,3,5-[$L_nMC{\equiv}C]_3C_6H_3$ have been reported,[3,5−14] the related vinyl complexes 1,3,5-[$L_nMCH{=}CH]_3C_6H_3$ are still unknown. These vinyl complexes are interesting especially in view of the fact that tris(vinyl)benzenes,[17] 1,3,5-[$L_nMC{\equiv}C]_3C_6H_3$, and related complexes show NLO and interesting electrochemical properties. In this report, we wish to report the synthesis and characterization of trimetallic ruthenium vinyl complexes of the type 1,3,5-[$L_nRuCH{=}CH]_3C_6H_3$.

Results and Discussion

Synthesis and Characterization of 1,3,5-[Cl(CO)-(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ and Related Compounds. Reactions of RuHCl(CO)(PPh$_3$)$_3$ (**1**) with HC≡CR have been shown to readily give RuCl((*E*)-CH=CHR)(CO)-(PPh$_3$)$_2$.[18,19] The reaction has been used previously to prepare bimetallic complexes such as [RuCl(CO)(PPh$_3$)$_2$]$_2$-(μ-CH=CH−Ar−CH=CH)[20] and [RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-(CH=CH)$_n$) (n = 2, 3, 4).[21] Thus it is expected that reaction of **1** with 1,3,5-triethynylbenzene (**2**) will produce the trimetallic complex 1,3,5-[Cl(CO)(PPh$_3$)$_2$-RuCH=CH]$_3$C$_6$H$_3$. Indeed, addition of **2** to a suspension of RuHCl(CO)(PPh$_3$)$_3$ (**1**) in dichloromethane rapidly produced 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (**3**), which can be isolated as an orange-red solid in 92% yield (Scheme 1).

Scheme 1



Compound **3** has been characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in C$_6$D$_6$ showed a singlet at 29.9 ppm, the chemical shift of which is typical for RuCl((*E*)-CH=CHR)(CO)(PPh$_3$)$_2$.[21] The ^1H NMR spectrum in CD$_2$Cl$_2$ displayed the RuC*H* signal at 8.84 ppm and the β-C*H* signal at 6.20 ppm with a ^3J(HH) coupling constant of 13.2 Hz. The magnitude of the coupling constant indicates that the two vinylic protons are in trans geometry and that the acetylene is cis inserted into the Ru−H bond. The core C$_6$*H*$_3$ proton signal was observed at 6.72 ppm in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum (in C$_6$D$_6$), the Ru*C*H signal and the RuCH=*C*H signal were observed at 146.7 and 137.2 ppm, respectively. Monomeric complexes RuCl(RC=CHR′)(CO)(PPh$_3$)$_2$ are known to adopt a distorted trigonal bipyramidal geometry around ruthenium with the two PPh$_3$ ligands in the apical positions.[19] Thus it is assumed that complex **3** has a similar geometry around ruthenium. [RuCl(CO)-(PPh$_3$)$_2$(CH=CH)]$_3$B$_3$N$_3$Me$_3$[22] is a reported trimetallic complex structurally related to **3**.

Three new trimetallic complexes were prepared from complex **3**. Treatment of **3** with PMe$_3$ produced the six-coordinated complex 1,3,5-[Cl(CO)(PMe$_3$)$_3$RuCH=CH]$_3$-C$_6$H$_3$ (**4**) (Scheme 1). The PMe$_3$ ligands in **4** are meridionally coordinated to ruthenium as indicated by the AM$_2$ pattern $^{31}P\{^1H\}$ NMR spectrum. The presence of the 1,3,5-(CH=CH)$_3$C$_6$H$_3$ unit is indicated by the ^1H NMR spectrum (in acetone-d_6), which showed the RuC*H*=C*H* proton signals at 8.13 (RuC*H*) and 6.65 (β-C*H*) ppm and the C$_6$*H*$_3$ signal at 7.02 ppm. In addition, the $^{13}C\{^1H\}$ NMR spectrum (in CD$_2$Cl$_2$) showed three CH signals at 163.0 (Ru*C*H), 135.9 (β-*C*H), and 117.3 (*C*$_6$H$_3$) ppm. The vinyl group is trans to the unique PMe$_3$ ligand, as indicated by the large $^2J(PC)_{trans}$ coupling constant (76.9 Hz).

Reactions of **3** with pyridine (Py) and 4-phenylpyridine (PhPy) gave the corresponding six-coordinated complexes [Cl(Py)(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (**5**) and [Cl(PhPy)(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (**6**), respectively. Related mononuclear complexes RuCl(CH=CHR)(L)-(CO)(PPh$_3$)$_2$ (L = 2e nitrogen donor ligands) have been previously prepared from the reactions of HC≡CR with RuHCl(L)(CO)(PPh$_3$)$_2$.[23] In contrast, complex **3** does not react with PPh$_3$ to give the corresponding six-coordinated complex, due to the steric bulkiness.

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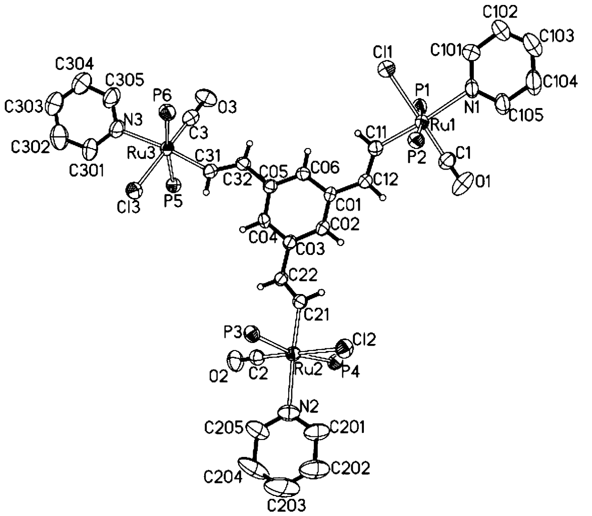

Figure 1. Molecular structure of 1,3,5-[Cl(CO)(Py)$(PPh_3)_2$-RuCH=CH]$_3C_6H_3$ (**5**). The phenyl rings and the H atoms of pyridine are omitted for clarity.

Table 1. Crystal Data and Structure Refinement for Complexes 1,3,5-[Cl(CO)(Py)$(PPh_3)_2$RuCH=CH]$_3C_6H_3 \cdot CH_2Cl_2$ (5·CH_2Cl_2) and OsCl(CH=CH(*p*-tolyl))(CO)$(PPh_3)_3 \cdot 2CH_2Cl_2$ (8b·$2CH_2Cl_2$)

	5·CH_2Cl_2	**8b**·$2CH_2Cl_2$
empirical formula	$C_{139}H_{116}Cl_5N_3O_3P_6Ru_3$	$C_{66}H_{58}Cl_5OOsP_3$
fw	2542.63	1327.48
temperature, K	294(2)	100(2)
radiation (Mo Ka), Å	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbca*
a, Å	22.6945(2)	18.9198(10)
b, Å	19.0662(2)	24.2415(12)
c, Å	30.4423(2)	24.7661(12)
β, deg	105.5780(10)	
volume, Å^3	12688.44(17)	11358.8(10)
Z	4	8
density(calcd), g cm^{-3}	1.331	1.533
absorp coeff, mm^{-1}	0.586	2.609
F(000)	5208	5344
cryst size, mm^3	0.50 × 0.45 × 0.38	0.20 × 0.15 × 0.12
θ range, deg	1.27 to 25.08	1.59 to 26.00
no. of reflns collected	48 046	85 130
no. of indep reflns	22 423 [*R*(int) = 0.0682]	11 096 [*R*(int) = 0.1870]
no. of obsd reflns [$I > 2\sigma(I)$]	11 791	6510
absorp corr	SADABS	SADABS
max. and min. transmn	1.000 and 0.7316	1.000 and 0.8534
no. of data/ restraints/ params	22 423/78/1432	11 096/6/685
goodness-of-fit on F^2	1.069	0.828
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0721$, $wR_2 = 0.1622$	$R_1 = 0.0524$, $wR_2 = 0.1012$
largest diff peak/ hole, e Å^{-3}	0.931/−0.447	1.032/−0.902

The structure of **5** has been confirmed by X-ray diffraction, and its molecular structure is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. As shown in Figure 1, the compound contains three ruthenium centers linked by a 1,3,5-$(CH{=}CH)_3C_6H_3$ bridge. The three ruthenium centers are related by a pseudo-C_3 rotation axis. The carbon atoms of $(CH{=}CH)_3C_6H_3$ are nearly coplanar, with the dihedral angles between the core benzene ring and the three vinyl groups at 13.3°, 15.0°, and 15.0°. The geometry around each ruthenium center can be described as a distorted octahedron with two mutually trans disposed PPh_3 ligands. The vinyl group is trans to the pyridine ligand, and the chloride is trans to the CO, as suggested by the solution NMR data. The mutually trans PPh_3 ligands are bent away from the pyridine ligands but toward the vinyl ligands. The Ru−C and C(α)−C(*β*) bond distances of complex **5** are within the range of those reported for other ruthenium vinyl complexes.[24] In complexes such as [RuCl(CO)$(PEt_3)_3]_2$(*μ*-CH=CHCH=CH)[21b] and [RuCl(CO)$(PMe_3)_3]_2$(*μ*-CH=CHCH=CHCH=CHCH=CH),[21d] the vinyl groups are essentially coplanar with Ru−CO.[25] However, similar coplanarity was not observed for complex **5**.

Reactions of Terminal Alkynes with OsHCl(CO)$(PPh_3)_3$. We were also interested in preparing analogous trimetallic osmium complexes using similar chemistry starting from OsHCl(CO)$(PPh_3)_3$. To test the feasibility of using OsHCl(CO)$(PPh_3)_3$ as the starting material to prepare trimetallic osmium complexes analogous to **3**−**6**, we have studied the reactions of OsHCl(CO)$(PPh_3)_3$ with PhC≡CH and HC≡C(*p*-tolyl).

Although insertion reactions of alkynes with osmium hydride complexes such as OsHCl(CO)$(PR_3)_2$ (PR_3 = P(*i*-Pr)$_3$,[26] P(t-Bu)$_2$Me[26c]), OsH(O_2CCF_3)(CO)(PPh_3),[27] and OsHCl(CO)((BTD)$(PPh_3)_2$ (BTD = 2,1,3-benzothiadiazole)[28] are known, the insertion reactions of alkynes with OsHCl(CO)$(PPh_3)_3$ have not been well studied. While insertion reaction of OsHCl(CO)$(PPh_3)_3$ with HC≡CCH(OH)Ph_2 apparently occurred in the formation of $OsCl_2$(=CHCH=CPh_2)(CO)$(PPh_3)_2$ from the reaction of OsHCl(CO)$(PPh_3)_3$ with HC≡CCH(OH)Ph_2 and Cl_2PPh_3,[29] it has been briefly mentioned previously that the insertion product from the reaction of OsHCl(CO)$(PPh_3)_3$ with phenylacetylene could not be obtained.[28] However, we now found that OsHCl(CO)$(PPh_3)_3$ does undergo insertion reactions with PhC≡CH and HC≡C(*p*-tolyl).

Addition of PhC≡CH to a solution of OsHCl(CO)$(PPh_3)_3$ (**7**) in dichloromethane produced an orange

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Table 2. Selected Bond Distances and Angles for 1,3,5-[Cl(CO)(Py)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (5)

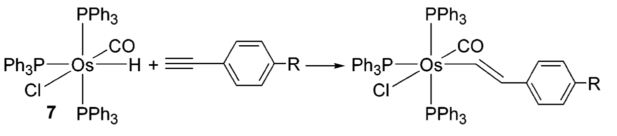
Bond Distances (Å)

Ru(1)−P(1)	2.397(2)	Ru(2)−P(4)	2.395(2)	Ru(3)−P(5)	2.404(2)
Ru(1)−P(2)	2.389(2)	Ru(2)−P(3)	2.389(2)	Ru(3)−P(6)	2.404(2)
Ru(1)−Cl(1)	2.475(2)	Ru(2)−Cl(2)	2.454(2)	Ru(3)−Cl(3)	2.474(2)
Ru(1)−C(1)	1.809(10)	Ru(2)−C(2)	1.814(9)	Ru(3)−C(3)	1.806(10)
Ru(1)−C(11)	2.050(8)	Ru(2)−C(21)	2.043(7)	Ru(3)−C(31)	2.038(7)
Ru(1)−N(1)	2.276(7)	Ru(2)−N(2)	2.271(7)	Ru(3)−N(3)	2.243(7)
C(1)−O(1)	1.105(10)	C(2)−O(2)	1.145(9)	C(3)−O(3)	1.167(10)
C(11)−C(12)	1.326(10)	C(21)−C(22)	1.311(9)	C(31)−C(32)	1.330(10)

Bond Angles (deg)

P(2)−Ru(1)−P(1)	172.18(8)	C(1)−Ru(1)−Cl(1)	178.2(3)
C(11)−Ru(1)−N(1)	174.2(3)	C(1)−Ru(1)−C(11)	91.9(4)
C(1)−Ru(1)-N(1)	93.5(3)	C(1)−Ru(1)-P(1)	90.4(3)
C(11)−Ru(1)-P(1)	85.5(2)	C(1)−Ru(1)-P(2)	91.8(3)
C(11)−Ru(1)-P(2)	86.9(2)	N(1)−Ru(1)-P(1)	96.43(19)
N(1)−Ru(1)-P(2)	90.90(19)	P(1)−Ru(1)-Cl(1)	91.35(9)
P(2)−Ru(1)-Cl(1)	86.34(8)	C(11)−Ru(1)-Cl(1)	87.8(2)
N(1)−Ru(1)-Cl(1)	86.7(2)	O(1)−C(1)-Ru(1)	178.6(10)
P(3)−Ru(2)-P(4)	169.78(8)	C(2)−Ru(2)-Cl(2)	179.7(3)
C(21)−Ru(2)-N(2)	175.8(3)	C(2)−Ru(2)-C(21)	91.9(3)
C(2)−Ru(2)-N(2)	92.3(3)	C(2)−Ru(2)-P(3)	90.5(2)
C(21)−Ru(2)-P(3)	86.8(2)	C(2)−Ru(2)-P(4)	92.7(2)
N(2)−Ru(2)-P(4)	96.5(2)	C(21)−Ru(2)-P(4)	83.4(2)
N(2)−Ru(2)−P(3)	93.05(19)	P(3)−Ru(2)−Cl(2)	89.16(8)
P(4)−Ru(2)−Cl(2)	87.63(7)	C(21)−Ru(2)−Cl(2)	88.2(2)
N(2)−Ru(2)−Cl(2)	87.6(2)	O(2)−C(2)−Ru(2)	177.4(8)
P(6)−Ru(3)−P(5)	172.09(8)	C(3)−Ru(3)−Cl(3)	177.0(3)
C(31)−Ru(3)−N(3)	173.4(3)	C(3)−Ru(3)−C(31)	91.0(3)
C(3)−Ru(3)−N(3)	95.4(3)	C(3)−Ru(3)−P(5)	90.1(3)
C(31)−Ru(3)−P(5)	83.4(2)	C(3)−Ru(3)−P(6)	90.4(3)
N(3)−Ru(3)−P(6)	92.6(2)	C(31)−Ru(3)−P(6)	88.7(2)
N(3)−Ru(3)−P(5)	95.2(2)	P(5)−Ru(3)−Cl(3)	92.59(8)
P(6)−Ru(3)−Cl(3)	86.75(8)	C(31)−Ru(3)−Cl(3)	87.8(2)
N(3)−Ru(3)−Cl(3)	85.8(2)	O(3)−C(3)−Ru(3)	178.2(7)
C(02)−C(01)−C(12)	118.9(6)	C(06)−C(01)−C(12)	123.2(7)
C(02)−C(03)−C(22)	123.1(7)	C(04)−C(03)−C(22)	119.3(7)
C(04)−C(05)−C(32)	122.3(7)	C(06)−C(05)−C(32)	120.4(7)
C(11)−C(12)−C(01)	127.3(7)	C(12)−C(11)−Ru(1)	134.5(6)
C(21)−C(22)−C(03)	126.7(7)	C(22)−C(21)−Ru(2)	134.4(6)
C(31)−C(32)−C(05)	123.8(7)	C(32)−C(31)−Ru(3)	136.5(6)

solution, from which the six-coordinated insertion product OsCl(CH=CHPh)(CO)(PPh$_3$)$_3$ (**8a**) can be isolated as a light pink solid in 71% yield (eq 1). The insertion reaction is different from the reaction of HC≡CPh with RuHCl(CO)(PPh$_3$)$_3$ in that the latter reaction gives the five-coordinated complex RuCl(CH=CHPh)(CO)(PPh$_3$)$_2$.[18] Compound **8a** has been characterized by NMR and elemental analysis. The ^{31}P{^{1}H} NMR spectrum in CDCl$_3$ at room temperature showed two broad signals at −11.6 and −22.7 ppm, indicating that the compound is fluxional. In toluene-d_8 at 203 K, the fluxional process is slowed and the ^{31}P{^{1}H} NMR spectrum showed a doublet at −11.6 ppm and a triplet at −24.6 ppm with a coupling constant of 12.1 Hz. The NMR data clearly indicate that compound **8a** has three PPh$_3$ ligands meridionally coordinated to osmium. The presence of the vinyl ligand is supported by the ^{1}H NMR spectrum (in toluene-d_8 at 203 K), which displayed the OsC*H* signal at 8.32 ppm. In addition, the ^{13}C{^{1}H} NMR spectrum showed OsCH=CH signals at 147.7 and 135.5 ppm, respectively. Under similar conditions, reaction of HC≡C(*p*-tolyl) with OsHCl(CO)(PPh$_3$)$_3$ gave the analogous insertion product OsCl(CH=CH(*p*-tolyl))(CO)(PPh$_3$)$_3$ (**8b**). The spectroscopic data of **8b** are similar to that of **8a**, indicating that they have similar structures.



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(1)

8a, R = H; **8b**, R = Me

The structure of **8b** has been confirmed by X-ray diffraction. The molecular structure of **8b** is depicted in Figure 2. The crystallographic details and selected bond distances and angles are given in Tables 1 and 3, respectively. As shown in Figure 2, the compound contains three meridionally bound PPh$_3$ ligands and a

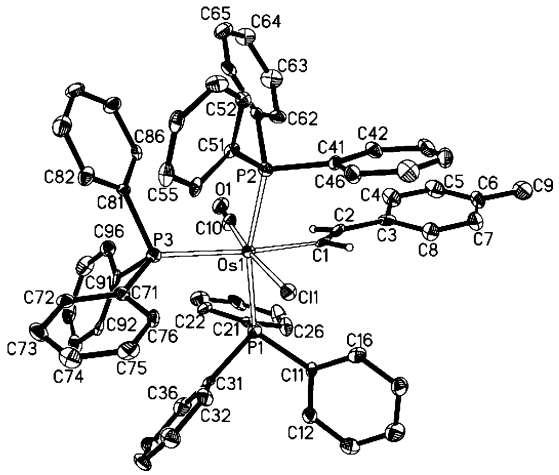


Figure 2. Molecular structure of [OsCl(CH=CH(*p*-tolyl)-(CO)(PPh$_3$)$_3$ (**8b**).

Table 3. Selected Bond Distances and Angles for OsCl(CH=CH(*p*-tolyl))(CO)(PPh$_3$)$_3$ (8b)

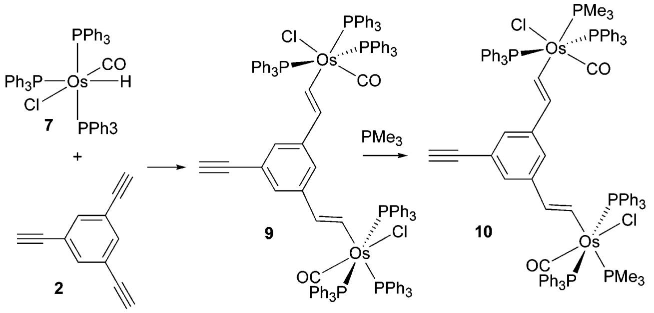
Bond Distances (Å)

Os(1)−C(10)	1.837(7)	Os(1)−C(1)	2.105(7)	Os(1)−P(1)	2.4041(19)
Os(1)−P(2)	2.4386(19)	Os(1)−Cl(1)	2.4772(16)	Os(1)−P(3)	2.500(19)
C(1)−C(2)	1.366(10)	C(2)−C(3)	1.464(10)	C(10)−O(1)	1.146(8)

Bond Angles (deg)

C(10)−Os(1)−C(1)	86.9(3)	C(10)−Os(1)−P(1)	91.3(2)
C(10)−Os(1)−P(2)	95.6(2)	C(10)−Os(1)−P(3)	85.9(2))
C(10)−Os(2)−Cl(1)	172.8(2)	C(1)−Os(1)−P(1)	84.23(8)
C(1)−Os(1)−P(2)	83.28(18)	C(1)−Os(1)−P(3)	172.61(9)
C(1)−Os(1)−Cl(1)	85.9(2)	P(1)−Os(1)−P(3)	165.36(7)
P(1)−Os(1)−P(3)	97.59(6)	P(1)−Os(1)−Cl(1)	88.53(6)
P(2)−Os(1)−P(3)	95.77(6)	P(2)−Os(1)−Cl(1)	83.00(6)
P(3)−Os(1)−Cl(1)	101.30(6)	Os(1)−C(1)−C(2)	130.6)
Os(1)−C(10)−O(1)	176.0(6)		

Scheme 2



vinyl ligand trans to the unique PPh$_3$ ligand. The Os−C(1) and C(1)−C(2) bond distances are normal compared to those reported for other osmium vinyl complexes.[30]

Synthesis and Characterization of 1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_3$OsCH=CH]$_2$C$_6$H$_3$ and Related Compounds. Treatment of OsHCl(CO)(PPh$_3$)$_3$ (**7**) with 1,3,5-triethynylbenzene in dichloromethane produced the bimetallic complex 1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_3$OsCH=CH]$_2$C$_6$H$_3$ (**9**) (Scheme 2). The expected trimetallic complex could not be obtained, however, even when more than 3 equiv of OsHCl(CO)(PPh$_3$)$_3$ was used. Compound **9** has been characterized by NMR and elemental analysis. The ^{31}P{^{1}H} NMR data are similar to those of **8**. The ^{1}H NMR spectrum in C$_6$D$_6$ displayed the OsC*H* signal at 7.85 ppm, the OsCH=C*H* signal at 6.07 ppm, and the two C$_6$H$_3$ signals at 6.37 and 6.79 ppm. Reported bimetallic complexes closely related to **9** include [MCl(P(*i*-Pr)$_3$)$_2$]CH=CH(CH$_2$)$_4$CH=CH[MCl(P(*i*-Pr)$_3$)$_2$] (M = Ru, Os) and [RuCl(P(*i*-Pr)$_3$)$_2$]CH=CH(CH$_2$)$_4$CH=CH[OsCl(P(*i*-Pr)$_3$)$_2$].[31]

It is interesting to note that the reaction of 1,3,5-(HC≡C)$_3$C$_6$H$_3$ with OsHCl(CO)(PPh$_3$)$_3$ gives the bimetallic complex **9**, but the reaction of 1,3,5-(HC≡C)$_3$C$_6$H$_3$ with RuHCl(CO)(PPh$_3$)$_3$ produces the trimetallic complex 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$. Probably, the presence of three bulky PPh$_3$ ligands in the osmium centers of **9** prevents the further insertion reaction of **9** with OsHCl(CO)(PPh$_3$)$_3$ to give a trimetallic complex. Complex **9** also failed to react with **1** to give a trimetallic complex. We have tried to replace the PPh$_3$ ligands with PMe$_3$, to reduce the steric effect. Reaction of **9** with PMe$_3$ produced 1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_2$(PMe$_3$)OsCH=CH]$_2$C$_6$H$_3$ (**10**). The PPh$_3$ ligands cannot be completely exchanged with PMe$_3$, even when excess PMe$_3$ was used. As expected, complex **10** also failed to react with OsHCl(CO)(PPh$_3$)$_3$.

Table 4. Electrochemical Data for Compounds 3−6[a]

compound	E_{pa}, V	E_{pc}, V	$E_{1/2}$, V	ΔE_p, mV
3	0.98[b]			
4	0.76[b]			
5	0.60	0.48	0.54	120
	1.01	0.82	0.92	190
	1.28	1.08	1.19	200
6	0.58	0.49	0.54	90
	0.96	0.84	0.94	120
	1.16	1.03	1.10	130

[a] All data were obtained in CH$_2$Cl$_2$ containing 0.10 M *n*-Bu$_4$NClO$_4$ as the supporting electrolyte with a scan rate of 100 mV/s, $E_{1/2} = (E_{pa} + E_{pc})/2$, $\Delta E_p = E_{pa} - E_{pc}$. [b] Irreversible oxidation peak.

Electrochemistry. Electrochemistry has often be used to assess the electronic communication of metal centers in bi- and polymetallic complexes. The redox behavior of trimetallic complexes **3**−**6** in CH$_2$Cl$_2$ have been investigated by cyclic voltammetry with *n*-Bu$_4$NClO$_4$ as the supporting electrolyte, and the results are collected in Table 4.

Three oxidation waves are expected for the trimetallic complexes if the metal centers interact with each other electronically. The three oxidation waves were resolved for complexes **5** and **6**. As an illustration, the cyclic voltammogram of complex **5** is shown in Figure 3. As can be seen from Figure 3, the cyclic votammogram of complex **5** showed three oxidation waves at 0.54, 0.92, and 1.19 V vs Ag/AgCl, which can be tentatively attributed to the formation of **5**$^+$(Ru(II)/Ru(II)/Ru(III)), **5**$^{2+}$(Ru(II)/Ru(III)/Ru(III)), and **5**$^{3+}$(Ru(III)/Ru(III)/Ru(III)), respectively. The peak separation between the first and the second oxidation waves and that between the second and the third oxidation waves are at 0.38 and 0.27 V, respectively. Similarly, complex **6** exhibited three oxidation waves at 0.54, 0.90, and 1.10 V vs Ag/AgCl with peak separations of 0.36 and 0.20 V. The appreciable peak separations in the oxidation of complexes **5** and **6** indicate that there exist appreciable interactions between the metal centers. Interestingly, the peak separations between the first and the second oxidation waves of **5** and **6** are larger than those between the second and the third oxidation waves.

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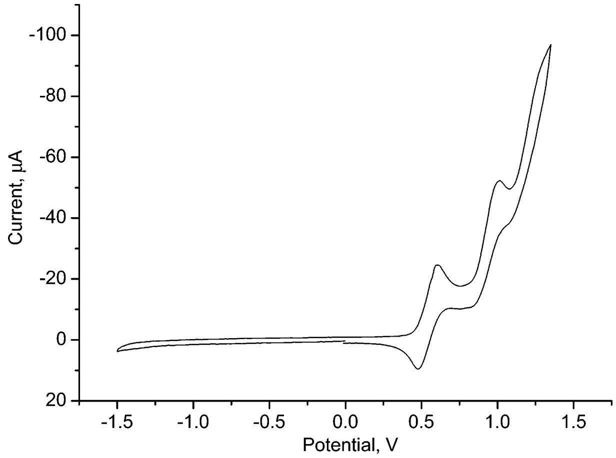

Figure 3. Cyclic voltammogram of 1,3,5-[Cl(CO)(Py)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (**5**) in 0.10 M *n*-Bu$_4$NClO$_4$/CH$_2$Cl$_2$ (Pt electrode, V vs Ag/AgCl, scan rate 100 mV/s, 25 °C).

The three oxidation waves were not resolved in the cyclic votammogram of complexes **3** and **4**, however. The cyclic votammogram of complex **3** showed an irreversible oxidation peak at 0.98 V vs Ag/AgCl. The cyclic votammogram of complex **4** showed two irreversible oxidation peaks at 0.76 and 1.05 V vs Ag/AgCl, which can be tentatively attributed to the formation of $\mathbf{4}^{+}$ (Ru(II)/Ru(II)/Ru(III)) and $\mathbf{4}^{3+}$ (Ru(III)/Ru(III)/Ru(III)), respectively. Apparently, the peak separation between the second and the third oxidation wave is too small to be observed. We have conducted the CV experiments at lower temperature (0 °C) to improve the reversibility. However, the cyclovotamograms did not change appreciably.

The electrochemical behaviors of complexes **3**–**6** can be related to those of recently reported {Cp*Co(2,3-Et$_2$C$_2$B$_4$H$_3$-7-C$\equiv$C)}$_3$C$_6$H$_3$ (**11**), {Cp*Co(2,3-Et$_2$C$_2$B$_4$H$_3$-5-C$\equiv$C)}$_3$C$_6$H$_3$ (**12**), and {Cp*Co(2,3-Et$_2$C$_2$B$_3$H$_4$-5-C$\equiv$C)}$_3$C$_6$H$_3$ (**13**).[2f] Complex **11** has three oxidation waves where the separation between the first and second waves (0.2 V) is larger than that between the second and third waves (0.1 V). Complex **12** shows only two oxidation waves, and the second and third oxidation waves are not resolved. Complexes **13** has only one reduction wave.

The electrochemical properties of the related acetylide compounds such as 1,3,5-[Cp(PPh$_3$)$_2$RuC$\equiv$C]$_3$C$_6$H$_3$,[4] 1,3,5-[Cp*(dppe)FeC$\equiv$C]$_3$C$_6$H$_3$,[3] and 1,3,5-[Cl(dppe)$_2$MC$\equiv$CC$_6$H$_4$C$\equiv$C]$_3$C$_6$H$_3$ (M = Ru,[7] Os[2b]) have also been reported. Three separated one-electron-oxidation waves were also observed in complexes such as 1,3,5-[Cp(PPh$_3$)$_2$RuC$\equiv$C]$_3$C$_6$H$_3$ (0.22, 0.35, and 0.50 V vs SCE)[4] and 1,3,5-[Cp*(dppe)FeC$\equiv$C]$_3$C$_6$H$_3$ (−0.225, −0.125, and 0.000 V vs SCE).[3] The peak separations of 1,3,5-[Cp(PPh$_3$)$_2$RuC$\equiv$C]$_3$C$_6$H$_3$ are at 0.12 and 0.15 V. The peak separations of 1,3,5-[Cp*(dppe)FeC$\equiv$C]$_3$C$_6$H$_3$ are at 0.13 and 0.13 V. However, only one single oxidation wave was observed for the ferrocenyl complex 1,3,5-[CpFe(η^5-C$_5$H$_4$)]$_3$C$_6$H$_3$[16d] and 1,3,5-[Cl(dppe)$_2$MC$\equiv$CC$_6$H$_4$C$\equiv$C]$_3$C$_6$H$_3$ (M = Ru,[7] Os[2b]).

Hyperpolarizability. The nonlinear optical properties of octupolar molecules are receiving increasing attention in recent years.[32,33] The second-order optical nonlinearities of complexes **4** and **5** have been determined by hyper-Raleigh scattering at 1064 nm. Complexes **4** and **5** have β_{HRS} values of 14.0×10^{-30} and 18.3×10^{-30} esu, respectively. Using the three-level model,[34] the static β_0 values were calculated to be 8.7×10^{-30} and 13.8×10^{-30} esu, respectively. The β_0 values are close to those of 1,3,5-[(PPh$_3$)AuC$\equiv$C]$_3$C$_6$H$_3$ ($\beta_0 = 4 \times 10^{-30}$ esu),[14a] 1,3,5-(CN)$_3$-2,4,6-[Me$_2$NCH=CH]$_3$-C$_6$H$_3$ ($\beta_0 = 35 \times 10^{-30}$ esu),[17b] and 1,3,5-(NO$_2$)$_3$-2,4,6-[Me$_2$NCH=CH]$_3$C$_6$H$_3$ ($\beta_0 = 24 \times 10^{-30}$ esu).[17a] It is noted that organometallic complexes 1,3,5-[Cl(dppe)$_2$RuC$\equiv$CC$_6$H$_4$C$\equiv$C]$_3$C$_6$H$_3$ ($\beta_0 = 94 \times 10^{-30}$ esu)[6a] and 1,3,5-[Cl(dppm)$_2$RuC$\equiv$CC$_6$H$_4$CH=CH]$_3$C$_6$H$_3$ ($\beta_0 = 165 \times 10^{-30}$ esu),[6c] which have a more extended structure, have significantly larger β_0 values.

Summary. By reacting RuHCl(CO)(PPh$_3$)$_3$ with 1,3,5-triethynylbenzene, the trimetallic complex 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ was obtained. 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ was found to react with PMe$_3$ and pyridine ligands L (L = pyridine (Py) and 4-phenylpyridine (PhPy)) to give 1,3,5-[Cl(CO)(PMe$_3$)$_3$RuCH=CH]$_3$C$_6$H$_3$ and 1,3,5-[Cl(CO)(L)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (L = Py, PhPy). It was reported previously that OsHCl(CO)(PPh$_3$)$_3$ does not undergo an insertion reaction with PhC$\equiv$CH. However, we found that OsHCl(CO)(PPh$_3$)$_3$ does undergo insertion reactions with ArC$\equiv$CH (Ar = Ph, *p*-tolyl) to produce the six-coordinated insertion products OsCl(CH=CHAr)(CO)(PPh$_3$)$_3$. Reaction of OsHCl(CO)(PPh$_3$)$_3$ with 1,3,5-triethynylbenzene was found to produce the bimetallic complex 1-HC$\equiv$C-3,5-[Cl(CO)(PPh$_3$)$_3$OsCH=CH]$_2$C$_6$H$_3$ rather than a trimetallic complex. The electrochemical studies show the metal centers in 1,3,5-[Cl(CO)(L)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (L = Py, PhPy) interact with each other electronically. The complexes [Cl(CO)(PMe$_3$)$_3$RuCH=CH]$_3$C$_6$H$_3$ and [Cl(CO)(Py)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ exhibit second-order NLO properties as suggested by HRS measurements.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, CHCl$_3$). The starting materials 1,3,5-(HC$\equiv$C)$_3$C$_6$H$_3$,[12] RuHCl(CO)(PPh$_3$)$_3$,[35] and OsHCl(CO)(PPh$_3$)$_3$[35] were prepared according to literature methods.

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

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The electrochemical measurements were performed with a PAR model 273 potentiostat. A three-component electrochemical cell was used with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were collected with a scan rate of 100 mV/s in CH_2Cl_2 containing 0.10 M n-Bu_4NClO_4 as the supporting electrolyte. The peak potentials reported were referenced to Ag/AgCl. Under our experimental conditions, the oxidation wave of Fc/Fc^+ occurred at 0.51 V.

1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (3). To a suspension of $RuHCl(CO)(PPh_3)_3$ (3.00 g, 3.15 mmol) in CH_2Cl_2 (80 mL) was slowly (in 20 min) added 1,3,5-triethynylbenzene (0.190 g, 1.27 mmol in 10 mL of CH_2Cl_2). The reaction mixture was stirred for an additional 15 min to give a red solution. The volume of the reaction mixture was then reduced to ca. 10 mL under vacuum. Addition of ether (250 mL) to the residue produced an orange-red solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 2.15 g, 92%. Anal. Calcd for $C_{123}H_{99}Cl_3O_3P_6Ru_3$: C, 66.53; H, 4.79. Found: C, 66.70; H, 4.61. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 29.9 (s). ^1H NMR (C_6D_6, 300.13 MHz): δ 6.20 (d, J(HH) = 13.2 Hz, 3 H, RuCH=C*H*), 6.72 (s, 3 H, CH of C_6H_3), 7.25 (m, 54 H, PPh_3), 8.03 (m, 36 H, PPh_3), 8.84 (d, J(HH) = 13.2 Hz, 3 H, RuCH). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 118.5 (s, CH of C_6H_3), 127.3−134.5 (m, PPh_3), 137.2 (s, RuCH=*C*H), 139.1 (s, C of C_6H_3), 146.7 (t, J(PC) = 8.3 Hz, RuCH), 202.4 (t, J(PC) = 13.7 Hz, CO).

1,3,5-[Cl(CO)(PMe$_3$)$_3$RuCH=CH]$_3$C$_6$H$_3$ (4). To a Schlenk flask containing 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (1.20 g, 0.540 mmol) was added a THF solution of PMe_3 (10 mL, 1 M, 10 mmol). The reaction mixture was stirred for 5 days to give a light yellow solution with some white suspension. The solvent was removed under vacuum, and acetone (100 mL) was added to the residue. The resulting mixture was stirred for 3 h to give a light yellow solution with a white precipitate, which was removed by filtration. The volume of the yellow filtrate was reduced to ca. 5 mL under vacuum. Addition of ether (100 mL) to the residue produced a light yellow solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.49 g, 68%. Anal. Calcd for $C_{42}H_{90}Cl_3O_3P_6Ru_3$: C, 37.89; H, 6.81. Found: C, 37.91; H, 6.64. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −20.0 (t, J(PP) = 22.6 Hz), −7.8 (d, J(PP) = 22.6 Hz). ^1H NMR (acetone-d_6, 300.13 MHz): δ 1.48 (t, J(PH) = 3.5 Hz, 54 H, PMe_3), 1.57 (d, J(PH) = 6.8 Hz, 27 H, PMe_3), 6.65 (ddt, J(HH) = 17.8 Hz, J(PH) = 6.3, 2.6 Hz, 3 H, RuCH=C*H*), 7.02 (s, 3 H, CH of C_6H_3), 8.13 (ddt, J(HH) = 17.8 Hz, J(PH) = 7.9, 3.4 Hz, 3 H, RuCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.40 MHz): δ 16.9 (t, J(PC) = 15.5 Hz, PMe_3), 20.3 (d, J(PC) = 20.6 Hz, PMe_3), 117.3 (s, CH of C_6H_3), 135.9 (t, J(PC) = 5.1 Hz, RuCH=*C*H), 141.7 (d, J(PC) = 6.4 Hz, C of C_6H_3), 163.0 (dt, J(PC) = 76.9, 16.6 Hz, RuCH), 202.4 (q, J(PC) = 12.2 Hz, CO).

1,3,5-[Cl(CO)(Py)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (5). A mixture of [Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (0.200 g, 0.09 mmol) and pyridine (0.2 mL) in CH_2Cl_2 (10 mL) was stirred for 10 min to give a yellow solution. The volume of the reaction mixture was reduced to ca. 5 mL under vacuum. Addition of ether (40 mL) to the residue produced a yellow solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.16 g, 73%. Anal. Calcd for $C_{138}H_{114}Cl_3N_3O_3P_6Ru_3$: C, 67.39; H, 4.68. Found: C, 67.58; H, 4.57. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 26.1 (s). ^1H NMR (C_6D_6, 300.13 MHz): δ 6.11 (dd, J(HH) = 6.6, 6.3 Hz, 6 H, *m*-H of Py), 6.43 (d, J(HH) = 16.6 Hz, 3 H, RuCH=C*H*), 6.61 (t, J(HH) = 7 0.6 Hz, 3 H, *p*-H of Py), 6.87 (s, 3 H, CH of C_6H_3), 7.0−7.8 (m, 90 H, PPh_3), 8.91 (br, 6 H, *o*-H of Py), 9.02 (dt, J(HH) = 16.3 Hz, J(PH) = 2.9 Hz, 3 H, RuCH).

1,3,5-[Cl(CO)(PhPy)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (6). A mixture of 1,3,5-[Cl(CO)(PPh$_3$)$_2$RuCH=CH]$_3$C$_6$H$_3$ (0.500 g, 0.225 mmol) and 4-phenylpyridine (0.300 g, 1.93 mmol) in CH_2Cl_2 (20 mL) was stirred for 10 min. to give a yellow solution. The volume of the reaction mixture was reduced to ca. 5 mL under vacuum. Addition of ether (150 mL) to the residue produced a yellow solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.54 g, 90%. Anal. Calcd for $C_{156}H_{126}Cl_3N_3O_3P_6Ru_3$: C, 69.75; H, 4.73. Found: C, 69.82; H, 4.85. $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.5 MHz): δ 25.2 (s). ^1H NMR (acetone-d_6, 300.13 MHz): δ 6.00 (d, J(HH) = 16.8 Hz, 3 H, RuCH=C*H*), 6.39 (s, 3 H, CH of C_6H_3), 8.69 (d, J(HH) = 16.8 Hz, 3 H, RuCH), 8.79 (br, 6 H, *o*-H of Py), 7.03−7.78 (m, 111 H, other aromatic protons). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 121.5 (s, CH of C_6H_3), 126.7 (s, *m*-C of Py), 137.5 (s, C of C_6H_3), 140.2 (RuCH=*C*H), 140.5 (s, *p*-C of Py), 147.7 (s, *q*-C of Py-*Ph*), 149.6 (t, J(PC) = 14.0 Hz, RuCH), 203.6 (t, J(PC) = 14.1 Hz, CO), 121.7−134.4 (m, other aromatic signals).

OsCl(CH=CHPh)(CO)(PPh$_3$)$_3$ (8a). To a solution of $OsHCl(CO)(PPh_3)_3$ (0.50 g, 0.48 mmol) in CH_2Cl_2 (50 mL) was added HC≡CPh (0.16 mL, 1.44 mmol). The reaction mixture was stirred at RT for 30 min to give a clear orange solution, which was then concentrated to ca. 1 mL. Addition of diethyl ether (30 mL) to the residue produced a light pink solid. The solid was collected by filtration, washed with diethyl ether (2 × 20 mL), and dried under vacuum. Yield: 0.39 g, 71%. Anal. Calcd for $C_{63}H_{52}ClOP_3Os$: C, 66.16; H, 4.58. Found: C, 66.03; H, 4.70. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K): δ −11.6 (br), −22.7 (br) (with an integration ratio of ca. 2:1). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): δ 6.28 (d br, J(HH) = 17.5 Hz, 1 H, = *CH*Ph), 6.66−7.49 (m, 50 H, PPh_3, Ph), 7.78 (d br, J(HH) = 17.5 Hz, 1 H, OsCH). $^{31}P\{^1H\}$ NMR (161.7 MHz, toluene-d_8, 203 K): δ −11.6 (d, J(PP) = 12.1 Hz), −24.6 (t, J(PP) = 12.1 Hz). ^1H NMR (400 MHz, toluene-d_8, 203 K): δ 6.60−7.60 (m, 51 H, =*C*HPh, PPh_3), 8.32 (d br, J(HH) = 14.0 Hz, 1 H, OsCH). $^{13}C\{^1H\}$ NMR (100.40 MHz, $CDCl_3$, 298 K): δ 123.9−142.3 (m, PPh_3, Ph), 135.5 (br, =*CH*Ph, confirmed by a $^1H-^{13}C$ COSY NMR experiment), 147.7 (br, Os*C*H, confirmed by a $^1H-^{13}C$ COSY NMR experiment), 182.3 (t, J(PC) = 8.4 Hz, *C*O).

OsCl(CH=CH(*p*-tolyl))(CO)(PPh$_3$)$_3$ (8b). To a solution of $OsHCl(CO)(PPh_3)_3$ (0.45 g, 0.43 mmol) in CH_2Cl_2 (50 mL) was added HC≡C(*p*-tolyl) (0.16 mL, 1.30 mmol). The reaction mixture was stirred at RT for 30 min to give a clear orange solution, which was then concentrated to ca. 1 mL. Addition of diethyl ether (30 mL) to the residue produced a light pink solid. The solid was collected by filtration, washed with diethyl ether (2 × 20 mL), and dried under vacuum. Yield: 0.33 g, 66.3%. Anal. Calcd for $C_{64}H_{54}ClOP_3Os$: C, 66.40; H, 4.70. Found: C, 66.30; H, 4.90. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ −11.1 (br), −22.7 (br) (with an integration in a ratio of ca. 2:1). ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 2.24 (s, 3 H, CH_3), 6.10 (d br, J(HH) = 17.2 Hz, 1 H, = *CH*(*p*-tolyl)), 6.48−7.36 (m, 49 H, PPh_3, *p*-tolyl), 7.63 (d br, J(HH) = 17.5 Hz, 1 H, OsCH). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 200 K): δ −10.9 (d, J(PP) = 11.4 Hz), −23.1 (t, J(PP) = 11.4 Hz). ^1H NMR (300.13 MHz, CD_2Cl_2, 200 K): δ 2.21 (s, 3 H, CH_3), 6.12 (d br, J(HH) = 13.2 Hz, 1 H, *CH*(*p*-toyl)), 6.56−7.70 (m, 50 H, PPh_3, *p*-toyl, OsCH). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 21.0 (s, *C*H_3), 124.8−139.6 (m, other PPh_3, C_6H_4), 135.8 (br, =*CH*(*p*-toyl), confirmed by a $^1H-^{13}C$ COSY NMR experiment), 144.4 (br, OsCH, confirmed by a $^1H-^{13}C$ COSY NMR experiment), 182.2 (t, J(PC) = 8.1 Hz, *C*O).

1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_3$OsCH=CH]$_2$C$_6$H$_3$ (9). To a CH_2Cl_2 solution (20 mL) of $OsHCl(CO)(PPh_3)_3$ (200 mg, 0.192 mmol) was slowly (in 1 h) added 1,3,5-triethynylbenzene (15.8 mg, 0.106 mmol in 10 mL of CH_2Cl_2). The reaction mixture was stirred for 15 min to give a light brown solution. The volume of the reaction mixture was reduced to ca. 5 mL under vacuum. Addition of ether (25 mL) to the residue produced a white solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.169 g, 79%. Anal. Calcd for $C_{122}H_{98}Cl_2O_2P_6Os_2$: C, 65.61; H, 4.42.

Found: C, 65.79; H, 4.85. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −11.9 (br), −23.4 (br). ^1H NMR (C_6D_6, 300.13 MHz, 298 K): δ 3.15 (br, 1 H, C≡CH), 6.07 (br, 2 H, OsCH═C*H*), 6.37 (br, 2 H, CH of C_6H_3), 6.79 (br, 1 H, CH of C_6H_3), 7.85 (br, 2 H, OsCH).

1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_2$(PMe$_3$)OsCH═CH]$_2$C$_6$H$_3$ (10). To a Schlenk flask containing 1-HC≡C-3,5-[Cl(CO)(PPh$_3$)$_3$-OsCH═CH]$_2$C$_6$H$_3$ (0.50 g, 0.22 mmol) was added a THF solution of PMe_3 (10 mL, 1 M, 10 mmol). The reaction mixture was stirred for 2 days to give a light yellow solution. The volume of the mixture was reduced to ca. 3 mL under vacuum. Addition of ether (30 mL) to the residue produced a white solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.367 g, 88%. Anal. Calcd for $C_{92}H_{86}Cl_2O_2P_6Os_2$: C, 59.38; H, 4.66. Found: C, 59.57; H, 4.73. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −55.8 (t, *J*(PP) = 12.9 Hz, PMe_3), −12.4 (d, *J*(PP) = 12.9 Hz, PPh_3). ^1H NMR (C_6D_6, 300.13 MHz): δ 1.26 (d, *J*(PH) = 7.4 Hz, PMe_3), 2.85 (s, 1 H, ≡CH), 6.25 (dm, *J*(HH) = 13.5 Hz, 2 H, OsCH═C*H*), 6.46 (s, 1 H, CH of C_6H_3), 6.89 (s, 2 H, CH of C_6H_3), 7.0−8.1 (m, PPh_3), 8.75 (ddt, *J*(HH) = 13.5 Hz, *J*(PH) = 7.5, 2.2 Hz, 2 H, OsCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 117.0 (s, C of C_6H_3), 122.6 (s, C of C_6H_3), 120.2 (s, CH of C_6H_3), 123.6 (s, CH of C_6H_3), 127.1−135.7 (m, PPh_3), 142.2 (d, *J*(PC) = 6.0 Hz, OsCH═*C*H), 148.5 (dt, *J*(PC) = 62.4, 14.2 Hz, OsCH), 203.6 (q, *J*(PC) = 9.2 Hz, CO).

Crystallographic Details. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solutions of **5** and **8b** layered with hexane. Data collections were performed on a Bruker SMART CCD area detector for **5**, and on a Bruker Apex CCD area detector for **8b**, by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections (SADABS)[36] were applied. Both structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL (Version 5.10)[37] program package. All non-hydrogen atoms were refined anisotropically except those for the solvating CH_2Cl_2 molecule in **5**, which was disordered over two sites and refined with isotropic thermal parameters using fixed C−Cl distances restraints. Some of the PPh_3 ligands in **5** exhibited distorted phenyl rings (C131−C136, C511−C516, C621−C626, C631−C636) after initial full-matrix least-squares refinement due to the rotational disorder, which were then refined with similar C−C distances and planarity restraints. All of the hydrogen atoms in **5** and **8b** were placed in the ideal positions and refined as riding atoms. Further details on crystal data, data collection, and refinements are summarized in Table 1.

HRS Experiments. IR laser pulses generated with an injection-seeded Q-switched and mode-locked Nd:YAG laser (Antares 76-S, 1064 nm, 70 ps, 15 Hz) were focused on a cylindrical cell (6 mL) containing the sample. The fundamental intensity was altered by rotation of a half-wave plate placed between crossed polarizers and measured with a photodiode. An efficient condenser system was used to collect the light scattered at the harmonic frequency (532 nm) that was detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light was accomplished by a monochromator. Actual values of the intensities were retrieved by using fast gated integrators and boxcar averagers. All measurements were performed in chloroform using *p*-nitroaniline ($\beta = 7.0 \times 10^{-30}$ esu) as a reference. The intrinsic β value was obtained after removing the contribution from the multiphoton absorption-induced fluorescence that can interfere with the HRS signal.[38] Further details of the experimental setup, data collection, and treatment can be found elsewhere.[39]

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Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displace coefficients, and anisotropic displacement coefficients for 1,3,5-[Cl(CO)(Py)(PPh$_3$)$_2$RuCH═CH]$_3$C$_6$H$_3$ (**5**) and OsCl(CH═CH(*p*-tolyl))(CO)(PPh$_3$)$_3$ (**8b**). The materials are available free of charge via the Internet at http://pubs.acs.org.

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