

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

Haiping Xia,[†] Ting Bin Wen,[†] Quan Yuan Hu,[†] Xin Wang,[†] Xingguo Chen,[†] Lai Yung Shek,[†] Ian D. Williams,[†] Kam Sing Wong,^{*,‡} George K. L. Wong,^{*,‡} and Guochen Jia^{*,†}

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis and Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received May 2, 2004

Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 1,3,5-triethynylbenzene produces the trimetallic complex $1,3,5\text{-}[\text{Cl}(\text{CO})(\text{PPh}_3)_2\text{RuCH}=\text{CH}]_3\text{C}_6\text{H}_3$, which reacts with PMe_3 to give $1,3,5\text{-}[\text{Cl}(\text{CO})(\text{PMe}_3)_3\text{RuCH}=\text{CH}]_3\text{C}_6\text{H}_3$. $1,3,5\text{-}[\text{Cl}(\text{CO})(\text{PPh}_3)_2\text{RuCH}=\text{CH}]_3\text{C}_6\text{H}_3$ also reacts with pyridine (Py) and 4-phenylpyridine (PhPy) to give $1,3,5\text{-}[\text{Cl}(\text{CO})(\text{L})(\text{PPh}_3)_2\text{RuCH}=\text{CH}]_3\text{C}_6\text{H}_3$ ($\text{L} = \text{Py}, \text{PhPy}$). Reactions of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ with $\text{ArC}\equiv\text{CH}$ ($\text{Ar} = \text{Ph}, p\text{-tolyl}$) produce the six-coordinated insertion products $\text{OsCl}(\text{CH}=\text{CHAr})(\text{CO})(\text{PPh}_3)_3$. Reaction of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ with 1,3,5-triethynylbenzene produces the bimetallic complex $1\text{-HC}\equiv\text{C-3,5-}[\text{Cl}(\text{CO})(\text{PPh}_3)_3\text{OsCH}=\text{CH}]_2\text{C}_6\text{H}_3$, which reacts with PMe_3 to give $1\text{-HC}\equiv\text{C-3,5-}[\text{OsCl}(\text{CO})(\text{PPh}_3)_2(\text{PMe}_3)\text{OsCH}=\text{CH}]_2\text{C}_6\text{H}_3$. 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 $\text{M}-\text{C}\equiv\text{C}$,^{2b,c,3–14} $\text{M}=\text{C}=\text{CHR}$,^{2d,7,8} $\text{M}-\text{aryl}$,¹⁵ or $\text{M}-\text{L}$ ($\text{L} = \eta^2\text{-RC}=\text{CR}'$,^{2a,f,16a–c} $\eta^6\text{-arene}$,^{16e} $\text{N}_{2g,16f–g}$ or P^{16h} donors) linkages, for example, $1,3,5\text{-}[\text{L}_n\text{MC}\equiv\text{C}]_3\text{C}_6\text{H}_3$ ($\text{M} = \text{Fe},^3 \text{Ru},^5 \text{Rh},^8 \text{Ir},^9 \text{Pd},^{10,11} \text{Pt},^{11–13}$ and Au^{14}), $1,3,5\text{-}[\text{L}_n\text{MC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv$

$\text{C}]_3\text{C}_6\text{H}_3$ ($\text{M} = \text{Ru},^{6a,7} \text{Os}^{2b}$), $1,3,5\text{-}[(\text{P}(i\text{-Pr})_3)_2\text{ClRh}=\text{C}=\text{CH}]_3\text{C}_6\text{H}_3$,⁸ $\{1,3,5\text{-}[(\text{dppe})_2\text{ClRu}=\text{C}=\text{CHC}_6\text{H}_4\text{C}\equiv\text{C}]_3\text{C}_6\text{H}_3\}\text{-}(\text{PF}_6)_3$,⁷ $1,3,5\text{-}[(4\text{-C}_6\text{H}_3(3,5\text{-CH}_2\text{NMe}_2)_2\text{ClPd}]_3\text{C}_6\text{H}_3$,¹⁵ and

[†] Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis.

[‡] Department of Physics.

(1) Oosterom, G. E.; Beck, J. N. H.; Kamer, P. C.; van Leeuwen, P. W. N. *M. Angew. Chem., Int. Ed.* **2001**, *40*, 1828. (b) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586.

(2) Examples of recent work, see: (a) Lucas, N. T.; Notaras, E. G. A.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2003**, *22*, 284. (b) Morrall, J. P.; Powell, C. E.; Stranger, R.; Cifuentes, M. P.; Humphrey, M. G.; Heath, G. A. *J. Organomet. Chem.* **2003**, *670*, 248. (c) McDonagh, A. M.; Powell, C. E.; Morrall, J. P.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2003**, *22*, 1402. (d) Weiss, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 2209. (e) Huang, C. H.; Lin, Y. C.; Huang, S. L.; Liu, Y. H.; Wang, Y. *Organometallics* **2003**, *22*, 1512. (f) Yao, H.; Sabat, M.; Grimes, P. N.; Zanello, P.; Febrizia, de Biani, F. *Organometallics* **2003**, *22*, 2581. (g) Liu, Q. D.; Jia, W. L.; Wu, G.; Wang, S. *Organometallics* **2003**, *22*, 3781.

(3) (a) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J. F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228. (b) Weyland, T.; Costuas, K.; Mari, A.; Halet, J. F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569. (c) Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J. F.; Toupet, L. *Organometallics* **1997**, *16*, 2024.

(4) Long, N. J.; Martin, A. J.; de Biani, F. F.; Zanello, F. *J. Chem. Soc., Dalton Trans.* **1998**, 2017.

(5) Long, N. J.; Martin, A. J.; White, A. J. P.; Williams, D. J.; Fontani, M.; Laschi, F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3387.

(6) (a) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A. *J. Am. Chem. Soc.* **1999**, *121*, 1405. (b) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Organometallics* **1999**, *18*, 5195. (c) Hurst, S. K.; Humphrey, M. G.; Isoshima, T.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Samoc, M.; Luther-Davies, B. *Organometallics* **2002**, *21*, 2024. (d) Hurst, S. K.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2002**, *21*, 2353.

(7) Uno, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1714.

(8) Werner, H.; Bachmann, P.; Laubender, M.; Gevert, O. *Eur. J. Inorg. Chem.* **1998**, 1217.

(9) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203.

(10) Yam, V. W. W.; Zhang, L.; Tao, C. H.; Wong, K. M. C.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **2001**, 1111.

(11) Yam, V. W. W.; Tao, C. H.; Zhang, L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 453.

(12) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981.

(13) (a) Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S. *J. Organomet. Chem.* **1998**, *569*, 195. (b) Onitsuka, K.; Fujimoto, M.; Ohshiro, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 689.

(14) (a) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 277. (b) Irwin, M. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Yufit, D. S. *Chem. Commun.* **1997**, 219.

(15) Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Cauty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159.

(16) For additional work, see for example: (a) Moreno, C.; Marcos, M. L.; Dominguez, G.; Arnanz, A.; Farrar, D. H.; Teeple, R.; Lough, A.; González-Velasco, J.; Delgado, S. *J. Organomet. Chem.* **2001**, *631*, 19. (b) Draper, S. M.; Delamesiere, M.; Champeil, E.; Twamley, B.; Byrne, J. J.; Long, C. J. *Organomet. Chem.* **1999**, *589*, 157. (c) Pellny, P. M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1999**, *18*, 2906. (d) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646. (e) Muller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 604. (f) Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094. (g) Tzalis, D.; Tor, Y. *Chem. Commun.* **1996**, 1043. (h) Constable, E. C.; Housecroft, C. E.; Krattinger, B.; Neuburger, M.; Zehnder, M. *Organometallics* **1999**, *18*, 2565.

1,3,5-[(Co₂(CO)₆(H≡C-))₃C₆H₃.^{16a} These complexes can have interesting physical properties. For example, complexes such as 1,3,5-[Cl(PEt₃)₂MC≡CC₆H₄C≡C]₃C₆H₃ (M = Pd, Pt) exhibit luminescent properties,^{10,11} complexes such as 1,3,5-[(PPh₃)₂AuC≡C]₃C₆H₃,^{14a} 1,3,5-[Cl(dppe)₂RuC≡CC₆H₄C≡C]₃C₆H₃,^{6a} and 1,3,5-[Cl(dppm)₂RuC≡CC₆H₄CH=CH]₃C₆H₃^{6c} have good NLO properties, and complexes such as 1,3,5-[Cp*(dppe)FeC≡C]₃C₆H₃³ and [Cp(PPh₃)₂RuC≡C]₃C₆H₃⁴ show electronic cooperation between individual metal centers.

Although a number of trimetallic acetylide complexes of the type 1,3,5-[L_nMC≡C]₃C₆H₃ have been reported,^{3,5–14} the related vinyl complexes 1,3,5-[L_nMCH=CH]₃C₆H₃ are still unknown. These vinyl complexes are interesting especially in view of the fact that tris(vinyl)-benzenes,¹⁷ 1,3,5-[L_nMC≡C]₃C₆H₃, 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]₃C₆H₃.

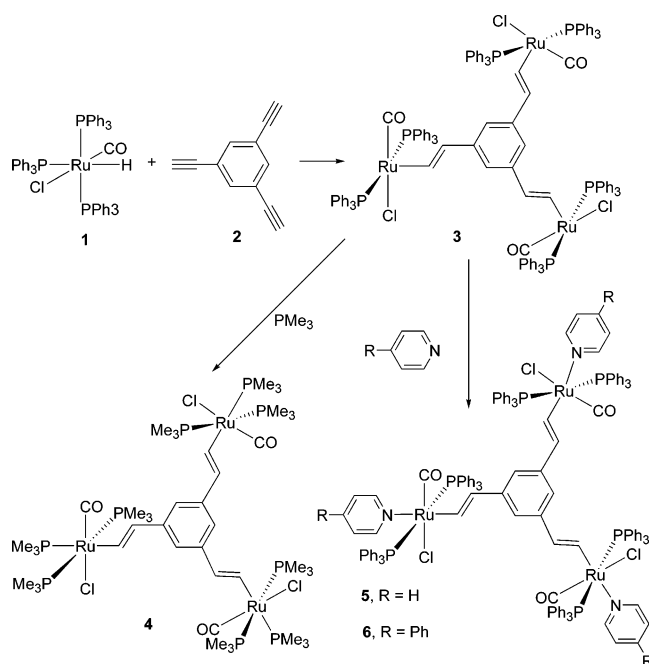
Results and Discussion

Synthesis and Characterization of 1,3,5-[Cl(CO)-(PPh₃)₂RuCH=CH]₃C₆H₃ and Related Compounds.

Reactions of RuHCl(CO)(PPh₃)₃ (**1**) with HC≡CR have been shown to readily give RuCl((E)-CH=CHR)(CO)-(PPh₃)₂.^{18,19} The reaction has been used previously to prepare bimetallic complexes such as [RuCl(CO)(PPh₃)₂]₂(μ-CH=CH-Ar-CH=CH)²⁰ and [RuCl(CO)(PPh₃)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)(PPh₃)₂RuCH=CH]₃C₆H₃. Indeed, addition of **2** to a suspension of RuHCl(CO)(PPh₃)₃ (**1**) in dichloromethane rapidly produced 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ (**3**), which can be isolated as an orange-red solid in 92% yield (Scheme 1).

Compound **3** has been characterized by NMR and elemental analysis. The ³¹P{¹H} NMR spectrum in C₆D₆ showed a singlet at 29.9 ppm, the chemical shift of which is typical for RuCl((E)-CH=CHR)(CO)(PPh₃)₂.²¹ The ¹H NMR spectrum in CD₂Cl₂ displayed the RuCH signal at 8.84 ppm and the β-CH signal at 6.20 ppm

Scheme 1



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 C₆H₃ proton signal was observed at 6.72 ppm in the ¹H NMR spectrum. In the ¹³C{¹H} NMR spectrum (in C₆D₆), the RuCH signal and the RuCH=CH signal were observed at 146.7 and 137.2 ppm, respectively. Monomeric complexes RuCl(RC=CHR')(CO)(PPh₃)₂ are known to adopt a distorted trigonal bipyramidal geometry around ruthenium with the two PPh₃ ligands in the apical positions.¹⁹ Thus it is assumed that complex **3** has a similar geometry around ruthenium. [RuCl(CO)-(PPh₃)₂(CH=CH)]₃B₃N₃Me₃²² is a reported trimetallic complex structurally related to **3**.

Three new trimetallic complexes were prepared from complex **3**. Treatment of **3** with PMe₃ produced the six-coordinated complex 1,3,5-[Cl(CO)(PMe₃)₃RuCH=CH]₃C₆H₃ (**4**) (Scheme 1). The PMe₃ ligands in **4** are meridionally coordinated to ruthenium as indicated by the AM₂ pattern ³¹P{¹H} NMR spectrum. The presence of the 1,3,5-(CH=CH)₃C₆H₃ unit is indicated by the ¹H NMR spectrum (in acetone-*d*₆), which showed the RuCH=CH proton signals at 8.13 (RuCH) and 6.65 (β-CH) ppm and the C₆H₃ signal at 7.02 ppm. In addition, the ¹³C{¹H} NMR spectrum (in CD₂Cl₂) showed three CH signals at 163.0 (RuCH), 135.9 (β-CH), and 117.3 (C₆H₃) ppm. The vinyl group is trans to the unique PMe₃ 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)(PPh₃)₂RuCH=CH]₃C₆H₃ (**5**) and [Cl(PhPy)(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ (**6**), respectively. Related mononuclear complexes RuCl(CH=CHR)(L)-(CO)(PPh₃)₂ (L = 2e nitrogen donor ligands) have been previously prepared from the reactions of HC≡CR with RuHCl(L)(CO)(PPh₃)₂.²³ In contrast, complex **3** does not react with PPh₃ to give the corresponding six-coordinated complex, due to the steric bulkiness.

(17) (a) Cho, B. R.; Lee, S. J.; Lee, S. H.; Son, K. K.; Kim, Y. H.; Doo, J. Y.; Lee, G. J.; Kang, T. I.; Lee, Y. K.; Cho, M.; Jeon, S. J. *J. Chem. Mater.* **2001**, *13*, 1438. (b) Cho, B. R.; Park, S. P.; Lee, S. J.; Son, K. K.; Lee, S. H.; Lee, M. J.; Yoo, J.; Lee, Y. K.; Lee, G. J.; Kang, T. I.; Cho, M.; Jeon, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 6421.

(18) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169.

(19) For recent work, see for example: (a) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308. (b) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421. (c) Harlow, K. J.; Hill, A. F.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1911. (d) Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. *T. Chem. Commun.* **1997**, 2207. (e) Harlow, K. J.; Hill, A. F.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **1998**, *17*, 1916. (f) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. J. *Organomet. Chem.* **1997**, *538*, 31.

(20) (a) Gómez-Lor, B.; Santos, A.; Ruiz, M.; Echavarren, A. M. *Eur. J. Inorg. Chem.* **2001**, 2305. (b) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. P. *J. Organomet. Chem.* **1997**, *539*, 53. (c) Santos, A.; López, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605.

(21) (a) Xia, H. P.; Jia, G. *Organometallics* **1997**, *16*, 1. (b) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1997**, *16*, 3557. (c) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1998**, *17*, 4762. (d) Liu, S. H.; Chen, Y.; Wan, K. L.; Wen, T. B.; Zhou, Z.; Lo, M. F.; Williams, I. D.; Jia, G. *Organometallics* **2002**, *21*, 4984. (e) Liu, S. H.; Xia, H. P.; Wen, T. B.; Zhou, Z.; Jia, G. *Organometallics* **2003**, *22*, 737.

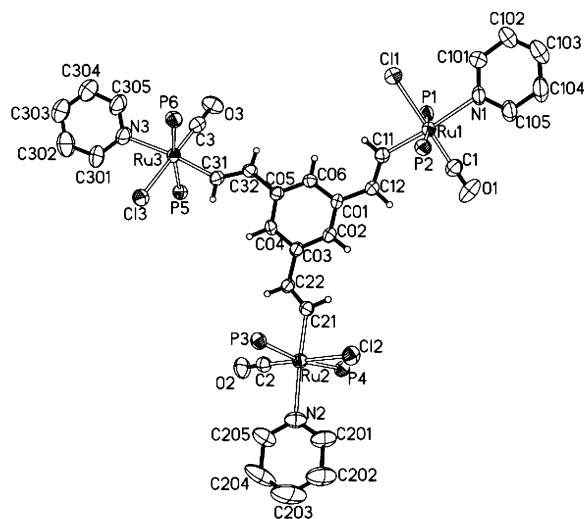


Figure 1. Molecular structure of 1,3,5-[Cl(CO)(Py)(PPh₃)₂]-RuCH=CH]₃C₆H₃ (**5**). The phenyl rings and the H atoms of pyridine are omitted for clarity.

Table 1. Crystal Data and Structure Refinement for Complexes
1,3,5-[Cl(CO)(Py)(PPh₃)₂RuCH=CH]₃C₆H₃·CH₂Cl₂
(5·CH₂Cl₂) and
OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)₃·2CH₂Cl₂
(8b·2CH₂Cl₂)

	5·CH₂Cl₂	8b·2CH₂Cl₂
empirical formula	C ₁₃₉ H ₁₁₆ Cl ₅ N ₃ O ₃ P ₆ Ru ₃	C ₆₆ H ₅₈ Cl ₅ OsP ₃
fw	2542.63	1327.48
temperature, K	294(2)	100(2)
radiation (Mo Kα), Å	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> , Å	22.6945(2)	18.9198(10)
<i>b</i> , Å	19.0662(2)	24.2415(12)
<i>c</i> , Å	30.4423(2)	24.7661(12)
β, deg	105.5780(10)	
volume, Å ³	12688.44(17)	11358.8(10)
<i>Z</i>	4	8
density(calcd), g cm ⁻³	1.331	1.533
absorp coeff, mm ⁻¹	0.586	2.609
<i>F</i> (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 [<i>R</i> (int) = 0.0682]	11 096 [<i>R</i> (int) = 0.1870]
no. of obsd reflns [<i>I</i> > 2σ(<i>I</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 <i>F</i> ²	1.069	0.828
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0721, <i>wR</i> ₂ = 0.1622	<i>R</i> ₁ = 0.0524, <i>wR</i> 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)₃C₆H₃ bridge. The three ruthenium centers

are related by a pseudo-*C*₃ rotation axis. The carbon atoms of (CH=CH)₃C₆H₃ 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 PPh₃ 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 PPh₃ 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)-(PEt₃)₃]₂(μ-CH=CHCH=CH)^{21b} and [RuCl(CO)(PMe₃)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)-(PPh₃)₃. We were also interested in preparing analogous trimetallic osmium complexes using similar chemistry starting from OsHCl(CO)(PPh₃)₃. To test the feasibility of using OsHCl(CO)(PPh₃)₃ as the starting material to prepare trimetallic osmium complexes analogous to **3–6**, we have studied the reactions of OsHCl(CO)(PPh₃)₃ with PhC≡CH and HC≡C(*p*-tolyl).

Although insertion reactions of alkynes with osmium hydride complexes such as OsHCl(CO)(PR₃)₂ (PR₃ = *P*(-i-Pr)₃,²⁶ *P*(*t*-Bu)₂Me^{26c}), OsH(O₂CCF₃)(CO)(PPh₃)₂,²⁷ and OsHCl(CO)(BTD)(PPh₃)₂ (BTD = 2,1,3-benzothiadiazole)²⁸ are known, the insertion reactions of alkynes with OsHCl(CO)(PPh₃)₃ have not been well studied. While insertion reaction of OsHCl(CO)(PPh₃)₃ with HC≡CCH(OH)Ph₂ apparently occurred in the formation of OsCl₂(=CHCH=CPh₂)(CO)(PPh₃)₂ from the reaction of OsHCl(CO)(PPh₃)₃ with HC≡CCH(OH)Ph₂ and Cl₂-PPh₃,²⁹ it has been briefly mentioned previously that the insertion product from the reaction of OsHCl(CO)-(PPh₃)₃ with phenylacetylene could not be obtained.²⁸ However, we now found that OsHCl(CO)(PPh₃)₃ does undergo insertion reactions with PhC≡CH and HC≡C(*p*-tolyl).

Addition of PhC≡CH to a solution of OsHCl(CO)-(PPh₃)₃ (**7**) in dichloromethane produced an orange

(22) Hu, Q. Y.; Lo, M. F.; Williams, I. D.; Koda, N.; Uchimarum, Y.; Lo, M. F.; Williams, I. D.; Jia, G. *J. Organomet. Chem.* **2003**, *670*, 243.

(23) (a) Santos, A.; López, J.; Galán, A.; González, J. J.; Tinoco, P.; Echavarren, A. M. *Organometallics* **1997**, *16*, 3482. (b) Romero, A.; Santos, A.; López, J.; Echavarren, A. M. *J. Organomet. Chem.* **1990**, *391*, 219.

(24) See for example: (a) Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 221. (b) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988. (c) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P. *J. Organomet. Chem.* **1989**, *373*, 249. (d) Alcock, N. W.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898. (e) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.

(25) Choi, S. H.; Bytheway, I.; Lin, Z.; Jia, G. *Organometallics* **1998**, *17*, 3974.

(26) (a) Marchenko, A. V.; Gerard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1244. (b) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (c) Werner, H.; Meyer, U.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 2097. (d) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(27) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M. B.; New, L. *Polyhedron* **1985**, *4*, 1119.

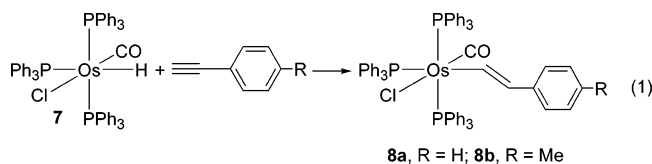
(28) Hill, A. F.; Wilton-Ely, J. D. E. *T. J. Chem. Soc., Dalton Trans.* **1998**, 3501.

(29) Harlow, K. J.; Hill, A. F.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1911.

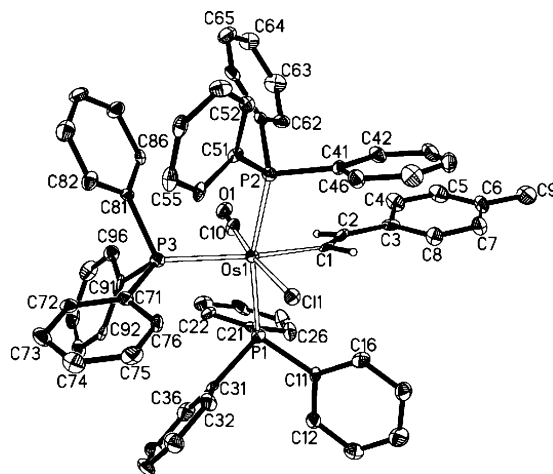
Table 2. Selected Bond Distances and Angles for 1,3,5-[Cl(CO)(Py)(PPh₃)₂RuCH=CH]₃C₆H₃ (**5**)

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)(PPh₃)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)(PPh₃)₃ in that the latter reaction gives the five-coordinated complex RuCl(CH=CHPh)(CO)(PPh₃)₂.¹⁸ Compound **8a** has been characterized by NMR and elemental analysis. The ³¹P{¹H} NMR spectrum in CDCl₃ 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 ³¹P{¹H} 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 PPh₃ ligands meridionally coordinated to osmium. The presence of the vinyl ligand is supported by the ¹H NMR spectrum (in toluene-*d*₈ at 203 K), which displayed the OsCH signal at 8.32 ppm. In addition, the ¹³C{¹H} 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)(PPh₃)₃ gave the analogous

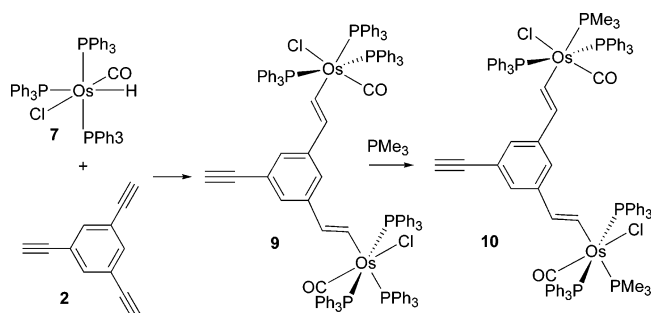
**Figure 2.** Molecular structure of [OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)₃] (**8b**).

insertion product OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)₃ (**8b**). The spectroscopic data of **8b** are similar to that of **8a**, indicating that they have similar structures.

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 PPh₃ ligands and a

Table 3. Selected Bond Distances and Angles for OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)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(1)–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 PPh₃ 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)(PPh₃)₂OsCH=CH]₂C₆H₃ and Related Compounds. Treatment of OsHCl(CO)(PPh₃)₃ (**7**) with 1,3,5-triethynylbenzene in dichloromethane produced the bimetallic complex 1-HC≡C-3,5-[Cl(CO)(PPh₃)₂OsCH=CH]₂C₆H₃ (**9**) (Scheme 2). The expected trimetallic complex could not be obtained, however, even when more than 3 equiv of OsHCl(CO)(PPh₃)₃ was used. Compound **9** has been characterized by NMR and elemental analysis. The ³¹P{¹H} NMR data are similar to those of **8**. The ¹H NMR spectrum in C₆D₆ displayed the OsCH signal at 7.85 ppm, the OsCH=CH signal at 6.07 ppm, and the two C₆H₃ signals at 6.37 and 6.79 ppm. Reported bimetallic complexes closely related to **9** include [MCl(P(*i*-Pr)₃)₂]₂CH=CH(CH₂)₄CH=CH[MCl(P(*i*-Pr)₃)₂] (M = Ru, Os) and [RuCl(P(*i*-Pr)₃)₂]₂CH=CH(CH₂)₄CH=CH[OsCl(P(*i*-Pr)₃)₂].³¹

It is interesting to note that the reaction of 1,3,5-(HC≡C)₃C₆H₃ with OsHCl(CO)(PPh₃)₃ gives the bimetallic complex **9**, but the reaction of 1,3,5-(HC≡C)₃C₆H₃ with RuHCl(CO)(PPh₃)₃ produces the trimetallic complex 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃. Probably, the presence of three bulky PPh₃ ligands in the osmium centers of **9** prevents the further insertion reaction of **9** with OsHCl(CO)(PPh₃)₃ to give a trimetallic complex. Complex **9** also failed to react with **1** to give a trimetallic

Table 4. Electrochemical Data for Compounds 3–6^a

compound	<i>E</i> _{pa} , V	<i>E</i> _{pc} , V	<i>E</i> _{1/2} , V	Δ <i>E</i> _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 CH₂Cl₂ containing 0.10 M *n*-Bu₄NClO₄ as the supporting electrolyte with a scan rate of 100 mV/s, *E*_{1/2} = (*E*_{pa} + *E*_{pc})/2, Δ*E*_p = *E*_{pa} – *E*_{pc}. ^b Irreversible oxidation peak.

complex. We have tried to replace the PPh₃ ligands with PMe₃, to reduce the steric effect. Reaction of **9** with PMe₃ produced 1-HC≡C-3,5-[Cl(CO)(PPh₃)₂(PMe₃)OsCH=CH]₂C₆H₃ (**10**). The PPh₃ ligands cannot be completely exchanged with PMe₃, even when excess PMe₃ was used. As expected, complex **10** also failed to react with OsHCl(CO)(PPh₃)₃.

Electrochemistry. Electrochemistry has often been used to assess the electronic communication of metal centers in bi- and polymetallic complexes. The redox behavior of trimetallic complexes **3–6** in CH₂Cl₂ have been investigated by cyclic voltammetry with *n*-Bu₄NClO₄ 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 voltammogram 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.

(30) (a) Wen, T. B.; Zhou, Z. Y.; Jia, G. *Organometallics* **2003**, *22*, 4947. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. (c) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667. (d) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. (e) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (f) Werner, H.; Meyer, U.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 2097.

(31) (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (b) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798.

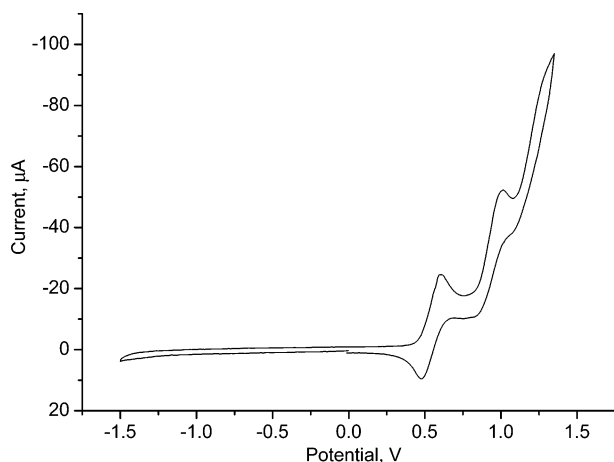


Figure 3. Cyclic voltammogram of 1,3,5-[Cl(CO)(Py)-(PPh₃)₂RuCH=CH]₃C₆H₃ (**5**) in 0.10 M *n*-Bu₄NClO₄/CH₂-Cl₂ (Pt electrode, V vs Ag/AgCl, scan rate 100 mV/s, 25 °C).

The three oxidation waves were not resolved in the cyclic voltammogram of complexes **3** and **4**, however. The cyclic voltammogram of complex **3** showed an irreversible oxidation peak at 0.98 V vs Ag/AgCl. The cyclic voltammogram 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 **4**⁺ (Ru(II)/Ru(III)) and **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 cyclic voltammograms did not change appreciably.

The electrochemical behaviors of complexes **3**–**6** can be related to those of recently reported {Cp*Co(2,3-Et₂C₂B₄H₃-7-C≡C)}₃C₆H₃ (**11**), {Cp*Co(2,3-Et₂C₂B₄H₃-5-C≡C)}₃C₆H₃ (**12**), and {Cp*Co(2,3-Et₂C₂B₄H₃-5-C≡C)}₃C₆H₃ (**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(PPh₃)₂RuC≡C]₃C₆H₃,⁴ 1,3,5-[Cp*(dppe)FeC≡C]₃C₆H₃,³ and 1,3,5-[Cl(dppe)₂MC≡CC₆H₄C≡C]₃C₆H₃ (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(PPh₃)₂RuC≡C]₃C₆H₃ (0.22, 0.35, and 0.50 V vs SCE)⁴ and 1,3,5-[Cp*(dppe)FeC≡C]₃C₆H₃ (−0.225, −0.125, and 0.000 V vs SCE).³ The peak separations of 1,3,5-[Cp(PPh₃)₂RuC≡C]₃C₆H₃ are at 0.12 and 0.15 V. The peak separations of 1,3,5-[Cp*(dppe)FeC≡C]₃C₆H₃ are at 0.13 and 0.13 V. However, only one single oxidation wave was observed for the ferrocenyl complex 1,3,5-[CpFe(η⁵-C₅H₄)₃C₆H₃]^{16d} and 1,3,5-[Cl(dppe)₂MC≡CC₆H₄C≡C]₃C₆H₃ (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. Com-

plexes **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 β₀ values were calculated to be 8.7 × 10^{−30} and 13.8 × 10^{−30} esu, respectively. The β₀ values are close to those of 1,3,5-[(PPh₃)₃AuC≡C]₃C₆H₃ (β₀ = 4 × 10^{−30} esu),^{14a} 1,3,5-(CN)₃-2,4,6-[Me₂NCH=CH]₃-C₆H₃ (β₀ = 35 × 10^{−30} esu),^{17b} and 1,3,5-(NO₂)₃-2,4,6-[Me₂NCH=CH]₃C₆H₃ (β₀ = 24 × 10^{−30} esu).^{17a} It is noted that organometallic complexes 1,3,5-[Cl(dppe)₂RuC≡CC₆H₄C≡C]₃C₆H₃ (β₀ = 94 × 10^{−30} esu)^{6a} and 1,3,5-[Cl(dppe)₂RuC≡CC₆H₄CH=CH]₃C₆H₃ (β₀ = 165 × 10^{−30} esu),^{6c} which have a more extended structure, have significantly larger β₀ values.

Summary. By reacting RuHCl(CO)(PPh₃)₃ with 1,3,5-triethynylbenzene, the trimetallic complex 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ was obtained. 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ was found to react with PMe₃ and pyridine ligands L (L = pyridine (Py) and 4-phenylpyridine (PhPy)) to give 1,3,5-[Cl(CO)(PMe₃)₃-RuCH=CH]₃C₆H₃ and 1,3,5-[Cl(CO)(L)(PPh₃)₂RuCH=CH]₃C₆H₃ (L = Py, PhPy). It was reported previously that OsHCl(CO)(PPh₃)₃ does not undergo an insertion reaction with PhC≡CH. However, we found that OsHCl(CO)(PPh₃)₃ does undergo insertion reactions with ArC≡CH (Ar = Ph, *p*-tolyl) to produce the six-coordinated insertion products OsCl(CH=CHAr)(CO)(PPh₃)₃. Reaction of OsHCl(CO)(PPh₃)₃ with 1,3,5-triethynylbenzene was found to produce the bimetallic complex 1-HC≡C-3,5-[Cl(CO)(PPh₃)₃OsCH=CH]₂C₆H₃ rather than a trimetallic complex. The electrochemical studies show the metal centers in 1,3,5-[Cl(CO)(L)(PPh₃)₂RuCH=CH]₃C₆H₃ (L = Py, PhPy) interact with each other electronically. The complexes [Cl(CO)(PMe₃)₃RuCH=CH]₃C₆H₃ and [Cl(CO)(Py)(PPh₃)₂RuCH=CH]₃C₆H₃ 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, CHCl₃). The starting materials 1,3,5-(HC≡C)₃C₆H₃,¹² RuHCl(CO)(PPh₃)₃,³⁵ and OsHCl(CO)(PPh₃)₃³⁵ were prepared according to literature methods.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ¹H and ¹³C NMR chemical shifts are relative to TMS, and ³¹P NMR chemical shifts are relative to 85% H₃PO₄.

(32) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.

(33) Examples of recent work: (a) Alcarz, G.; Euzénat, L.; Mongin, O.; Katan, C.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M.; Vaultier, M. *Chem. Commun.* **2003**, 2766. (b) Zyss, J.; Ledoux-Pak, I.; Weiss, H. C.; Blaser, D.; Boese, R.; Thallapally, P. K.; Thalladi, V. R.; Desiraju, G. R. *Chem. Mater.* **2003**, *15*, 3063. (c) Brunel, J.; Mongin, O.; Jutand, A.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M. *Chem. Mater.* **2003**, *15*, 4139. (d) Le Boudier, T.; Maury, O.; Bondon, A.; Costuas, K.; Amouyal, E.; Ledoux, I.; Zyss, J.; Le Bozec, H. *J. Am. Chem. Soc.* **2003**, *125*, 12284. (f) Cui, Y. Z.; Fang, Q.; Lei, H.; Xue, G.; Yu, W. T. *Chem. Phys. Lett.* **2003**, *377*, 507. (g) Zhou, X.; Ren, A. M.; Feng, J. K.; Liu, X. J. *Chem. Phys. Lett.* **2003**, *373*, 167.

(34) Three-level model: Joffe, M.; Yaron, D.; Silbey, R. J.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607.

(35) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F.; Wonchoba, E. R.; Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 45.

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 CH₂Cl₂ containing 0.10 M *n*-Bu₄NClO₄ 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)(PPh₃)₂RuCH=CH]₃C₆H₃ (3). To a suspension of RuHCl(CO)(PPh₃)₃ (3.00 g, 3.15 mmol) in CH₂Cl₂ (80 mL) was slowly (in 20 min) added 1,3,5-triethynylbenzene (0.190 g, 1.27 mmol in 10 mL of CH₂Cl₂). 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 C₁₂₃H₉₉Cl₃O₃P₆Ru₃: C, 66.53; H, 4.79. Found: C, 66.70; H, 4.61. ³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ 29.9 (s). ¹H NMR (C₆D₆, 300.13 MHz): δ 6.20 (d, *J*(HH) = 13.2 Hz, 3 H, RuCH=CH), 6.72 (s, 3 H, CH of C₆H₃), 7.25 (m, 54 H, PPh₃), 8.03 (m, 36 H, PPh₃), 8.84 (d, *J*(HH) = 13.2 Hz, 3 H, RuCH). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz): δ 118.5 (s, CH of C₆H₃), 127.3–134.5 (m, PPh₃), 137.2 (s, RuCH=CH), 139.1 (s, C of C₆H₃), 146.7 (t, *J*(PC) = 8.3 Hz, RuCH), 202.4 (t, *J*(PC) = 13.7 Hz, CO).

1,3,5-[Cl(CO)(PMe₃)₂RuCH=CH]₃C₆H₃ (4). To a Schlenk flask containing 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ (1.20 g, 0.540 mmol) was added a THF solution of PMe₃ (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 C₄₂H₉₀Cl₃O₃P₆Ru₃: C, 37.89; H, 6.81. Found: C, 37.91; H, 6.64. ³¹P{¹H} NMR (CD₂Cl₂, 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, PMe₃), 1.57 (d, *J*(PH) = 6.8 Hz, 27 H, PMe₃), 6.65 (ddt, *J*(HH) = 17.8 Hz, *J*(PH) = 6.3, 2.6 Hz, 3 H, RuCH=CH), 7.02 (s, 3 H, CH of C₆H₃), 8.13 (ddt, *J*(HH) = 17.8 Hz, *J*(PH) = 7.9, 3.4 Hz, 3 H, RuCH). ¹³C{¹H} NMR (CD₂Cl₂, 100.40 MHz): δ 16.9 (t, *J*(PC) = 15.5 Hz, PMe₃), 20.3 (d, *J*(PC) = 20.6 Hz, PMe₃), 117.3 (s, CH of C₆H₃), 135.9 (t, *J*(PC) = 5.1 Hz, RuCH=CH), 141.7 (d, *J*(PC) = 6.4 Hz, C of C₆H₃), 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)(PPh₃)₂RuCH=CH]₃C₆H₃ (5). A mixture of [Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ (0.200 g, 0.09 mmol) and pyridine (0.2 mL) in CH₂Cl₂ (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 C₁₃₈H₁₁₄Cl₃N₃O₃P₆Ru₃: C, 67.39; H, 4.68. Found: C, 67.58; H, 4.57. ³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ 26.1 (s). ¹H NMR (C₆D₆, 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=CH), 6.61 (t, *J*(HH) = 7.0 Hz, 3 H, *p*-H of Py), 6.87 (s, 3 H, CH of C₆H₃), 7.0–7.8 (m, 90 H, PPh₃), 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)(PPh₃)₂RuCH=CH]₃C₆H₃ (6). A mixture of 1,3,5-[Cl(CO)(PPh₃)₂RuCH=CH]₃C₆H₃ (0.500 g, 0.225 mmol) and 4-phenylpyridine (0.300 g, 1.93 mmol) in CH₂Cl₂

(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 C₁₅₆H₁₂₆Cl₃N₃O₃P₆Ru₃: C, 69.75; H, 4.73. Found: C, 69.82; H, 4.85. ³¹P{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=CH), 6.39 (s, 3 H, CH of C₆H₃), 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). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 121.5 (s, CH of C₆H₃), 126.7 (s, *m*-C of Py), 137.5 (s, C of C₆H₃), 140.2 (RuCH=CH), 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)(PPh₃)₃ (8a). To a solution of OsHCl(CO)(PPh₃)₃ (0.50 g, 0.48 mmol) in CH₂Cl₂ (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 C₆₃H₅₂ClO₃Os: C, 66.16; H, 4.58. Found: C, 66.03; H, 4.70. ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 298 K): δ -11.6 (br), -22.7 (br) (with an integration ratio of ca. 2:1). ¹H NMR (300.13 MHz, CDCl₃, 298 K): δ 6.28 (d br, *J*(HH) = 17.5 Hz, 1 H, =CHPh), 6.66–7.49 (m, 50 H, PPh₃, Ph), 7.78 (d br, *J*(HH) = 17.5 Hz, 1 H, OsCH). ³¹P{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, =CHPh, PPh₃), 8.32 (d br, *J*(HH) = 14.0 Hz, 1 H, OsCH). ¹³C{¹H} NMR (100.40 MHz, CDCl₃, 298 K): δ 123.9–142.3 (m, PPh₃, Ph), 135.5 (br, =CHPh, confirmed by a ¹H–¹³C COSY NMR experiment), 147.7 (br, OsCH, confirmed by a ¹H–¹³C COSY NMR experiment), 182.3 (t, *J*(PC) = 8.4 Hz, CO).

OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)₃ (8b). To a solution of OsHCl(CO)(PPh₃)₃ (0.45 g, 0.43 mmol) in CH₂Cl₂ (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 C₆₄H₅₄ClO₃Os: C, 66.40; H, 4.70. Found: C, 66.30; H, 4.90. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 298 K): δ -11.1 (br), -22.7 (br) (with an integration in a ratio of ca. 2:1). ¹H NMR (300.13 MHz, CD₂Cl₂, 298 K): δ 2.24 (s, 3 H, CH₃), 6.10 (d br, *J*(HH) = 17.2 Hz, 1 H, =CH(*p*-tolyl)), 6.48–7.36 (m, 49 H, PPh₃, *p*-tolyl), 7.63 (d br, *J*(HH) = 17.5 Hz, 1 H, OsCH). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 200 K): δ -10.9 (d, *J*(PP) = 11.4 Hz), -23.1 (t, *J*(PP) = 11.4 Hz). ¹H NMR (300.13 MHz, CD₂Cl₂, 200 K): δ 2.21 (s, 3 H, CH₃), 6.12 (d br, *J*(HH) = 13.2 Hz, 1 H, CH(*p*-tolyl)), 6.56–7.70 (m, 50 H, PPh₃, *p*-tolyl, OsCH). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 298 K): δ 21.0 (s, CH₃), 124.8–139.6 (m, other PPh₃, C₆H₄), 135.8 (br, =CH(*p*-tolyl), confirmed by a ¹H–¹³C COSY NMR experiment), 144.4 (br, OsCH, confirmed by a ¹H–¹³C COSY NMR experiment), 182.2 (t, *J*(PC) = 8.1 Hz, CO).

1-HC≡C-3,5-[Cl(CO)(PPh₃)₂OsCH=CH]₂C₆H₃ (9). To a CH₂Cl₂ solution (20 mL) of OsHCl(CO)(PPh₃)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 CH₂Cl₂). 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 C₁₂₂H₉₈Cl₂O₂P₆Os₂: C, 65.61; H, 4.42.

Found: C, 65.79; H, 4.85. $^{31}\text{P}\{^1\text{H}\}$ 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=CH), 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)(PPh₃)₂(PMe₃)OsCH=CH]₂C₆H₃ (10).

To a Schlenk flask containing 1-HC≡C-3,5-[Cl(CO)(PPh₃)₂-OsCH=CH]₂C₆H₃ (0.50 g, 0.22 mmol) was added a THF solution of PMe₃ (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 $\text{C}_{92}\text{H}_{86}\text{Cl}_2\text{O}_2\text{P}_6\text{Os}_2$: C, 59.38; H, 4.66. Found: C, 59.57; H, 4.73. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz): δ -55.8 (t, $J(\text{PP}) = 12.9$ Hz, PMe₃), -12.4 (d, $J(\text{PP}) = 12.9$ Hz, PPh₃). ^1H NMR (C_6D_6 , 300.13 MHz): δ 1.26 (d, $J(\text{PH}) = 7.4$ Hz, PMe₃), 2.85 (s, 1 H, ≡CH), 6.25 (dm, $J(\text{HH}) = 13.5$ Hz, 2 H, OsCH=CH), 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, PPh₃), 8.75 (ddt, $J(\text{HH}) = 13.5$ Hz, $J(\text{PH}) = 7.5$, 2.2 Hz, 2 H, OsCH). $^{13}\text{C}\{^1\text{H}\}$ 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, PPh₃), 142.2 (d, $J(\text{PC}) = 6.0$ Hz, OsCH=CH), 148.5 (dt, $J(\text{PC}) = 62.4$, 14.2 Hz, OsCH), 203.6 (q, $J(\text{PC}) = 9.2$ 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 K α radiation ($\lambda = 0.71073$ 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 PPh₃ 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

Acknowledgment. The authors acknowledge financial support from the Hong Kong Research Grants Council (HKUST6187/00P).

Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for 1,3,5-[Cl(CO)(Py)(PPh₃)₂RuCH=CH]₃C₆H₃ (**5**) and OsCl(CH=CH(*p*-tolyl))(CO)(PPh₃)₃ (**8b**). The materials are available free of charge via the Internet at <http://pubs.acs.org>.

OM0496939

(36) Sheldrick, G. M. *SADABS*, Empirical Absorption Correction Program; University of Göttingen, Germany, 1996.

(37) Bruker. *SHELXTL* Reference Manual (Version 5.1); Bruker Analytical X-Ray Systems Inc.: Madison, WI, 1997.

(38) Hsu, C. C.; Huang, T. H.; Zang, Y. L.; Lin, J. L.; Cheng, Y. Y.; Lin, J. T.; Wu, H. H.; Wang, C. H.; Kuo, C. T.; Chen, C. H. *J. Appl. Phys.* **1996**, 80 (10), 5996.

(39) (a) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, 63, 3285. (b) Houbrechts, S.; Clays, K.; Persoons, A.; Pikramenou, Z.; Lehn, J.-M. *Chem. Phys. Lett.* **1996**, 258, 485.