Synthesis and Second-Order NLO Properties of Donor−Acceptor σ-Alkenyl Ruthenium Complexes

Ping Yuan,[†] Jun Yin,[†] Guang-ao Yu,[†] Quanyuan Hu,*[,‡] and Sheng Hua Liu*[,†,§]

Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China, Ministry-of-Education, Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan 430062, People's Republic of China, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

Received June 29, 2006

The compounds p-R−C_6H_4−CH═CH−C≡C−TMS (R = NO_2, $N(CH_3)_2$, OCH_3) were obtained from Wittig olefination of TMS−C≡C−CH_2PPh_3Br with p-R−C_6H_4−CHO in THF, which can be desilylated to give p-R−C_6H_4−CH═CH−C≡C−H. Treatment of $RuHCl(CO)(PPh_3)_3$ with p-R−C_6H_4−CH═CH−C≡C−H produced $RuCl(CO)(PPh_3)_2$(CH═CH−CH═CH−C_6H_4−R-p). The later complexes reacted with 4-phenylpyridine (PhPy), 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP), and KTp (Tp = hydridotris(pyrazolyl)borate) to give $RuCl(CO)(PhPy)(PPh_3)_2$ (CH═CH−CH═CH−C_6H_4−R-p), RuCl(CO)(PMP)(CH═CH−CH═CH−C_6H_4−R-p), and $RuTp(CO)(PPh_3)$ (CH═CH−CH═CH−C_6H_4−R-p), respectively. The structure of $RuTp(CO)(PPh_3)$(CH═CH−CH═CH−C_6H_4−R-p) (R = $N(CH_3)_2$, **7b**) has been confirmed by X-ray diffraction. The NLO properties (hyper-Rayleigh scattering measurements) of the complexes **5**, **6**, and **7** reveal that changes induced in the ligands of ruthenium (**5a**−**7a** or **5b**,**6b**) have a large impact on the hyperpolarizability.

Introduction

Synthesis of new organic and organometallic "push−pull" molecules with NLO properties has been intensively pursued in resent years due to their potential applications in optoelectronics, telecommunications, and optical storage devices.[1] Metal (organometallic and coordination) complexes are attracting considerable interest.[2,3] Compared to organic molecules, they offer a larger variety of molecular structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the coordinated metal center.[4] Among them, metallocenyl and σ-alkynyl complexes command the most attention. Compared with metallocenyl complexes, σ-multiple-bond complexes incorporate the metal in the same plane as the π-conjugated system, which has been suggested to enhance the NLO response.[5,6] Although alkenes tend to be more hyperpolarizable than alkynes, as already stated for the solvochromicities, previously reported examples of "push−pull" σ-alkenyl complexes are limited,[7] maybe because of synthesis difficulties.

In this paper, we report some novel σ-alkenyl complexes with NLO properties, in which the ruthenium end-group and donor- or acceptor-substituted phenyl are connected by a CH═CH−CH═CH bridge. The ruthenium end-group behaves more like an electron-rich group due to the coordinated P's or N's lone electron pairs, though this effect is weakened by the strong π-acceptor CO. As a result, when R = NO_2 on the other end of the conjugated bridge, β_0 is much larger than when R = $N(CH_3)_2$ or OCH_3. The present study focuses on the synthesis, structural characterization, and NLO properties of these complexes.

Results and Discussion

Synthesis of Metal Complexes. The general synthetic route for the preparation of "push−pull" σ-alkenyl complexes is outlined in Scheme 1. The compounds p-R−C_6H_4−CH═CH−C≡C−TMS (R = NO_2, $N(CH_3)_2$, OCH_3) (**2**) were obtained from Wittig olefination of TMS−C≡C−CH_2PPh_3Br with p-R−C_6H_4−CHO in THF. Like most Wittig reactions, the product was obtained as a mixture of *E* and *Z* isomers, which could not be completely separated by chromatography. Treatment of **2** with *n*-Bu_4NF in THF produced compounds p-R−C_6H_4−CH═CH−C≡C−H (R = NO_2, $N(CH_3)_2$, OCH_3) (**3**), which were purified by recrystallization. Compounds **3** were characterized by NMR spectroscopy.

---

* Corresponding authors. E-mail: chshliu@mail.ccnu.edu.cn.

[†] Central China Normal University.

[‡] Hubei University.

[§] Fujian Institute of Research on the Structure of Matter.

(1) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley-Interscience: New York, 1991. (b) Boyd, R. W. *Nonlinear Optics*; Academic Press: San Diego, CA, 1992. (c) Zyss, J. *Molecular Nonlinear Optics*; Academic Press: New York, 1994.

(2) (a) Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349. (b) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: New York, 1992; p 116. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 291.

(3) Bella, S. D. *Chem. Soc. Rev.* **2001**, *30*, 355, and references therein.

(4) (a) Bella, S. D.; Fragalà, I.; Ledoux, I.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 9481. (b) Bella, S. D.; Fragalà, I.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 12747. (c) Bella, S. D.; Fragalà, I.; Ledoux, I.; Diaz-Garcia, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 9550. (d) Coe, B. J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Oxford, U.K., 2004; Vol. 9, pp 621−687.

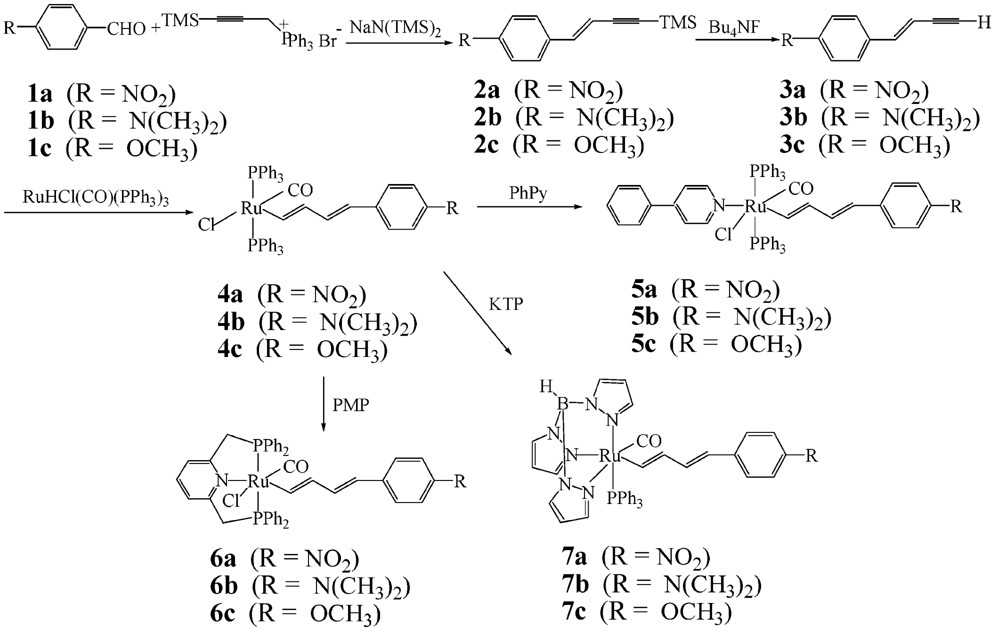
(5) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

(6) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1999**, *18*, 582.

(7) (a) Muller, T. J. J.; Netz, A.; Ansorge, M. *Organometallics* **1998**, *18*, 5066. (b) Xia, H.−P.; Wen, T. B.; Hu, Q. Y.; Wang, X.; Chen, X.-G.; Shek, L. Y.; Williams, I. D.; Wong, K. S.; Wong, G. K. L.; Jia, G.-C. *Organometallics* **2005**, *24*, 562. (c) Humphrey, P. A.; Turner, P. A.; Masters, F.; Field, L. D.; Cifuentes, M. P.; Humphrey, M. G.; Asselberghs, I.; Persoons, A.; Samoc, M. *Inorg. Chim. Acta* **2005**, *358*, 1663.

10.1021/om0605736 CCC: $37.00

Scheme 1



Compounds **3** reacted with $RuHCl(CO)(PPh_3)_3$ to give the insertion products $RuCl(CO)(PPh_3)_2(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}R\text{-}p)$ (R = NO_2, $N(CH_3)_2$, OCH_3) (**4**), which could be isolated as a solid (**4a**, purple; **4b**, brown; **4c**, red). These compounds have been characterized by NMR. The ^{31}P NMR spectrum in CD_2Cl_2 of complex **4a** showed a singlet at 31.23 ppm, which is slightly downfield from that for complexes **4b** (30.94 ppm) and **4c** (30.98 ppm) due to the electron acceptance effect of NO_2. These are typical for $RuCl((E)\text{-}CH{=}CHR)(CO)(PPh_3)_2$.[8] The ^1H NMR spectrum in CD_2Cl_2 of complex **4a** displayed the Ru−CH signal at 8.60 ppm (**4b**, 7.90; **4c**, 7.76), the chemical shift of which is similar to those of complexes $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}(CH{=}CH)_n)$[9] and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}Ar{-}CH{=}CH)$,[10] and the five-coordinated complexes **4** are air-sensitive especially in solution.

Several related six-coordinated complexes were prepared from complex **4**. Reaction of **4** with 4-phenylpyridine (PhPy), 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP), and KTp (Tp = hydridotris(pyrazolyl) borate) gave the corresponding six-coordinated complexes $RuCl(CO)(PhPy)(PPh_3)_2(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}R\text{-}p)$ (R = NO_2, $N(CH_3)_2$, OCH_3) (**5**), $RuCl(CO)(PMP)(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}R\text{-}p)$ (R = NO_2, $N(CH_3)_2$, OCH_3) (**6**), and $RuTp(CO)(PPh_3)(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}R\text{-}p)$ (R = NO_2, $N(CH_3)_2$, OCH_3) (**7**), respectively. These complexes have been characterized by NMR spectroscopy. Closely related mononuclear complexes $RuCl(CH{=}CHR)(L)(CO)(PPh_3)_2$ (L = 2e nitrogen donor ligands) have been previously prepared from the reaction of $HC{\equiv}CR$ with $RuHCl(L)(CO)(PPh_3)_2$.[11] A few ruthenium PMP complexes, for example $RuCl_2(PPh_3)(PMP)$ and $RuHX(PPh_3)(PMP)$ (X = Cl, OAc),[12] have also been reported. Homonuclear bimetallic complexes $[RuCl(PhPy)(CO)(PPh_3)_2]_2(\mu\text{-}(CH{=}CH)_n)$ (n = 3, 4), $[RuCl(CO)(PMP)]_2(\mu\text{-}(CH{=}CH)_n)$ (n = 3, 4),[9b,c] and $[RuTp(CO)(PPh_3)]_2(\mu\text{-}(CH{=}CH)_2\text{-}C_6H_4\text{-}(CH{=}CH)_2)$[13] and heteronuclear bimetallic complexes $Fc(CH{=}CH)_3RuCl(CO)(PhPy)(PPh_3)_2$, $Fc(CH{=}CH)_3RuCl(CO)(PMP)$, and $Fc(CH{=}CH)_3RuTp(CO)(PPh_3)$[14] were also reported. The structure of **7b** has been confirmed by X-ray diffraction study (Figure 1).

Crystal Structure of Complex $RuTp(CO)(PPh_3)(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}N(CH_3)_2\text{-}p)$ (7b). The molecular structure of $RuTp(CO)(PPh_3)(CH{=}CH{-}CH{=}CH{-}C_6H_4{-}N(CH_3)_2\text{-}p)$ (**7b**) is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The ruthenium center is a distorted octahedron with Tp occupying three coordinational points. It is worth noting that the vinyl groups are essentially coplanar with Ru−CO. Thus Ru(1), C(40), O(1), C(1), and C(2) form a plane with maximum deviation from the least-squares plane of 0.0105 Å for C(1). This coplanar phenomenon of the vinyl group and CO is expected due to the strong π-interaction between CO and vinyl with metal centers in such a conformation.[15] The Ru−N(1) bond (2.194(3) Å) of complex **7b** is slightly longer than the Ru−N(2) bond (2.125(3) Å) and Ru−N(3) bond (2.154 Å), due to the strong trans influence of the vinyl ligand.[16] The $(CH)_4$ unit

---

[8] Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem* **1986**, *309*, 169.

[9] (a) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1998**, *17*, 4762. (b) Liu, S. H.; Xia, H. P.; Wen, T. B.; Zhou, Z. Y.; Jia, G. *Organometallics* **2003**, *22*, 737. (c) Liu, S. H.; Chen, Y. H.; Wan, K. L.; Wen, T. B.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Organometallics* **2002**, *21*, 4984. (d) Liu, S. H.; Hu, Q. Y.; Xue, P.; Wen, T. B.; Williams, I. D.; Jia, G. *Organometallics* **2005**, *24*, 769.

[10] (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.

[11] (a) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169. (b) Santos, A.; López, J.; Galán, A.; González, J. J.; Tinono, P.; Echavarren, A. M. *Organometallics* **1997**, *16*, 3482. (c) Romereo, A.; Santos, A.; López, J.; Echavarren, A. M. *J. Organomet. Chem.* **1990**, *391*, 219.

[12] (a) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chem, Y. *Organometallics* **1997**, *16*, 3941. (b) Rahmouni, N.; Osborn, J. A.; Decian, A.; Fischer, J.; Ezzamarty, A. *Organometallics* **1998**, *17*, 2470, and references therein.

[13] Liu, S. H.; Xia, H. P.; Wan, K. L.; Yeung, R. C. Y.; Hu, Q. Y.; Jia, G. *J. Organomet. Chem.* **2003**, *683*, 331.

[14] Yuan, P.; Liu, S. H.; Xiong, W.; Yin, J.; Yu, G.; Sung, H. Y.; Williams, I. D.; Jia, G. *Organometallics* **2005**, *24*, 1452.

[15] Choi, S. H.; Bytheway, I.; Lin, Z.; Jia, G. *Organometallics* **1998**, *17*, 3974.

[16] Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5.

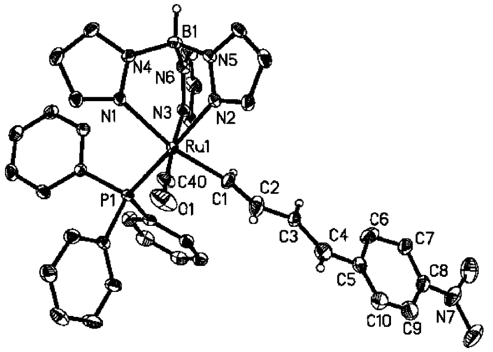


Figure 1. Molecular structure of RuTp(CO)(PPh$_3$)(CH═CH−CH═CH−C$_6$H$_4$−N(CH$_3$)$_2$) (**7b**).

Table 1. Crystal Data and Structure Refinement for Compound 7b

formula	$C_{40}H_{39}BN_7OPRu$
fw	776.63
temperature, K	293(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2(1)/c$
a, Å	13.4803(9)
b, Å	14.9598(9)
c, Å	18.767(1)
α, deg	90
β, deg	98.342(1)
γ, deg	90
V, Å^3	3744.6(4)
Z	4
d_{calc}, g cm^{-3}	1.378
θ range, deg	1.75 to 25.50
abs coeff, mm^{-1}	0.503
F(000)	1600
index ranges, deg	$-10 \leq h \leq 16$, $-18 \leq k \leq 17$, $-22 \leq l \leq 22$
no. of reflns	3876
no. of ind reflns	19 169/6928 [R(int) = 3.23%]
no. of data/restraints/params	6928/0/464
final R indices [$I > 2\sigma(I)$]	R1 = 0.0497, wR2 = 0.1202
goodness of fit	1.047
largest diff peak, e Å^{-3}	0.990
largest diff hole, e Å^{-3}	−0.436

shows a single/double alternation pattern of carbon−carbon bonds. Both of the olefinic double bonds are in trans geometry. The Ru−C(1) bond is 2.049(4) Å, and the bond length of C−C in the C(1)−C(2)−C(3)−C(4)−C(5) chain is 1.209(7), 1.449(6), 1.361(7), and 1.538(8) Å in turn, which shows that in complex **7b** the length of single bonds and double bonds all increase with the increasing of their distance from the ruthenium center.

NLO Properties of Metal Complexes. The molecular second-order nonlinearities for complexes **5**−**7** as determined by the hyper-Rayleigh scattering (HRS) technique are given in Table 3. The HRS experiments were carried out in chloroform solutions of the complexes at 1500 nm fundamental wavelength. Some of them, such as **7b**, **5c**, **6c**, and **7c**, are absent in this table, since their signals are too weak to be examined. Changes of the ligands of the ruthenium end-group leads to no obviously change in λ_{max}, but replacing the other end-group from NO$_2$ to N(CH$_3$)$_2$ in proceeding from **5a** to **5b** or **6a** to **6b** results in a blue-shift in λ_{max}.

The second-order nonlinearities for complexes **5a**, **6a**, and **7a** are larger than related metallocenyl complexes since the in-plane MLCT transition is more efficient than the out-plane MLCT transition.[5,17] Within the series studied, changes induced in the ligands of ruthenium (**5a**−**7a** or **5b**,**6b**) have a large impact on the hyperpolarizability, and introduction of an acceptor group, such as NO$_2$, results in an increase in β and β_0. For this series of complexes, increasing β is not correlated with a red-shift in λ_{max}.

Table 2. Selected Bond Lengths and Bond Angles of Complex 7b

	Bond Lengths (Å)		
Ru(1)−C(40)	1.817(5)	B(1)−N(4)	1.538(6)
Ru(1)−C(1)	2.049(4)	B(1)−H(1)	1.04(4)
Ru(1)−N(2)	2.125(3)	O(1)−C(40)	1.139(5)
Ru(1)−N(3)	2.154(3)	C(1)−C(2)	1.209(7)
Ru(1)−N(1)	2.194(3)	C(2)−C(3)	1.449(6)
Ru(1)−P(1)	2.3455(9)	C(3)−C(4)	1.361(7)
B(1)−N(5)	1.521(6)	C(4)−C(5)	1.538(8)
B(1)−N(6)	1.528(6)		
	Bond Angles (deg)		
C(40)−Ru(1)−C(1)	92.7(2)	C(40)−Ru(1)−N(2)	90.33(16)
C(1)−Ru(1)−N(2)	87.33(15)	C(40)−Ru(1)−N(3)	175.18(15)
C(1)−Ru(1)−N(3)	86.2(2)	N(2)−Ru(1)−N(3)	84.93(12)
C(40)−Ru(1)−N(1)	95.71(18)	C(1)−Ru(1)−N(1)	167.50(18)
N(2)−Ru(1)−N(1)	83.44(11)	N(3)−Ru(1)−N(1)	84.64(11)
C(40)−Ru(1)−P(1)	92.26(13)	C(1)−Ru(1)−P(1)	93.95(13)
N(2)−Ru(1)−P(1)	177.05(9)	N(3)−Ru(1)−P(1)	92.50(9)
N(1)−Ru(1)−P(1)	94.90(8)	O(1)−C(40)−Ru(1)	176.6(4)
C(1)−C(2)−C(3)	131.2(7)	C(4)−C(3)−C(2)	130.1(6)
C(3)−C(4)−C(5)	128.3(6)	C(10)−C(5)−C(4)	122.2(6)
C(6)−C(5)−C(4)	114.7(5)		

Table 3. HRS Results at a Wavelength of 1500 nm for Complexes 5−**7**[a]

complex	λ_{max} (nm)	ϵ ($\times 10^4$ M^{-1} cm^{-1})	β(1500) ($\times 10^{-30}$ esu)	β_0 ($\times 10^{-30}$ esu)
5a	463	5.13	689	386
6a	472	4.70	860	469
7a	472	3.17	698	380
5b	346	2.01	84	63
6b	348	5.22	40	29

[a] Using external reference method (ERM) to calculate the β_{1500} values. Disperse Red 1 as reference, β_{1500}(DR1) = 30.2 × 10^{-30} esu. HRS experiments were operated according to the literature, except that the RG715 filter was replaced by a RG9 filter before collecting the HRS signals. The value of β_0 was extrapolated from the value of β_{1500} according to the two-level model. References: see HRS experiment.

Summary

We have successfully prepared donor−acceptor σ-alkenyl ruthenium complexes with conjugated side chains by insertion reaction of RuHCl(CO)(PPh$_3$)$_3$ and p-R−C$_6$H$_4$−CH═CH−C≡CH. The structure of RuTp(CO)(PPh$_3$)(CH═CH−CH═CH−C$_6$H$_4$−N(CH$_3$)$_2$-p) (**7b**) has been confirmed by X-ray diffraction. The NLO properties (hyper-Rayleigh scattering measurements) of complexes **5**, **6**, and **7** reveal that changes induced in the ligands of ruthenium (**5a**−**7a** or **5b**,**6b**) have a large impact on the hyperpolarizability.

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

---

(17) (a) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291. (b) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A. *Organometallics* **1996**, *15*, 1935. (c) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175.

hydride (dichloromethane, $CHCl_3$). The starting materials $RuHCl(CO)(PPh_3)_3$,[18] 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP),[19] and KTp[20] were prepared according to literature methods. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ^1H, ^{13}C, and ^{31}P NMR spectra were collected on an American Varian Mercury Plus 400 spectrometer (400 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

General Synthesis of Compounds p-R−C_6H_4−CH=CHC≡CTMS (2). To a slurry of (3-trimethylsilyl-2-propyl)triphenylphosphonium bromide (2.20 g, 5.0 mmol) in THF (50 mL) was added a 2 M THF solution of $NaN(SiMe_3)_2$ (2.5 mL, 5.0 mmol). The mixture was stirred for 30 min, and then a solution of the aldehyde p-R−C_6H_4−CHO (**1**) (4.7 mmol) in THF (20 mL) was added slowly. The resulting solution was stirred for another 30 min, and then water (50 mL) was added. The layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (2 × 20 mL) and dried over $MgSO_4$, filtered, and then concentrated under rotary evaporation. The crude product was purified by column chromatography (silica gel, eluent: ether/petroleum ether = 5/95) to give a yellow solid.

2a: Yield: 0.51 g, 45%. Anal. Calcd for $C_{13}H_{15}NO_2Si$: C, 63.64; H, 6.16; N, 5.71. Found: C, 63.28; H, 6.21; N, 5.56. ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 9H, $SiMe_3$), 6.33 (d, J(HH) = 16.0 Hz, 1H, $=CHC\equiv$), 7.02 (d, J(HH) = 15.6 Hz, 1H, $C_6H_4-CH=$), 7.50 (d, J(HH) = 8.0 Hz, 2H, $O_2NCC_2H_2C_2H_2C$), 8.19 (d, J(HH) = 8.8 Hz, 2H, $O_2NCC_2H_2C_2H_2C$).

2b: Yield: 0.55 g, 48%. Anal. Calcd for $C_{15}H_{21}NSi$: C, 74.01; H, 8.70; N, 5.75. Found: C, 73.89; H, 8.88; N, 5.60. ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 9H, $SiMe_3$), 3.00 (s, 6H, $N(CH_3)_2$), 5.98 (d, J(HH) = 16.0 Hz, 1H, $=CHC\equiv$), 6.66 (d, J(HH) = 8.0 Hz, 2H, $(CH_3)_2NCC_2H_2C_2H_2C$), 6.96 (d, J(HH) = 16.0 Hz, 1H, $C_6H_4-CH=$), 7.28 (m, 2H, $(CH_3)_2NCC_2H_2C_2H_2C$).

2c: Yield: 0.45 g, 42%. Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 72.62; H, 8.03. ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 9H, $SiMe_3$), 3.82 (s, 3H, OCH_3), 6.05 (d, J(HH) = 16.0 Hz, 1H, $=CHC\equiv$), 6.88 (m, 2H, $CH_3OCC_2H_2C_2H_2C$), 6.97 (d, J(HH) = 16.0 Hz, 1H, $C_6H_4-CH=$), 7.33 (m, 2H, $CH_3OCC_2H_2C_2H_2C$).

General Synthesis of Compounds p-R−C_6H_4−CH=CHC≡CH (3). To a solution of complex **2** (2.0 mmol) in THF (10 mL) was slowly added a 1 M THF solution of n-$Bu_4N^+F^-$ (2.0 mL, 1 M in THF with 5% water) with stirring. After 2 h, the solvent was removed. The crude product was purified to give a yellow solid.

3a: Yield: 0.31 g, 90%. Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.50; H, 4.21; N, 8.01. ^1H NMR (400 MHz, $CDCl_3$): δ 3.21 (d, J(HH) = 2.4 Hz, 1H, $\equiv CH$), 6.30 (q, J(HH) = 2.2, 16.6 Hz, 1H, $=CHC\equiv$), 7.08 (d, J(HH) = 16.0 Hz, 1H, $C_6H_4-CH=$), 7.53 (d, J(HH) = 8.8 Hz, 2H, $O_2NCC_2H_2C_2H_2C$), 8.20 (d, J(HH) = 8.8 Hz, 2H, $O_2NCC_2H_2C_2H_2C$).

3b: Yield: 0.30 g, 88%. Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.02; H, 7.81; N, 7.95. ^1H NMR (400 MHz, $CDCl_3$): δ 2.98 (bs, 7H, $N(CH_3)_2$, $\equiv CH$), 5.90 (q, J(HH) = 2.0, 16.0 Hz, 1H, $=CHC\equiv$), 6.65 (d, J(HH) = 8.8 Hz, 2H, $(CH_3)_2NCC_2H_2C_2H_2C$), 6.96 (d, J(HH) = 16.0 Hz, 1H, $C_6H_4-CH=$), 7.28 (d, J(HH) = 8.8 Hz, 2H, $(CH_3)_2NCC_2H_2C_2H_2C$).

3c: Yield: 0.29 g, 92%. Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.63; H, 6.50. ^1H NMR (400 MHz, $CDCl_3$): δ 3.02 (d, J(HH) = 2.4 Hz, 1H, $\equiv CH$), 3.82 (s, 3H, OCH_3), 5.99 (q, J(HH) = 2.4, 16.4 Hz, 1H, $=CHC\equiv$), 6.87 (m, 2H, $CH_3OCC_2H_2C_2H_2C$), 7.00 (d, J(HH) = 16.0 Hz, 1H, $Ph-CH=$), 7.33 (m, 2H, $CH_3OCC_2H_2C_2H_2C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.20 (s, OCH_3), 78.40 (s, $C\equiv CH$), 83.23 (s, $C\equiv CH$), 104.44 (s, $=C-C\equiv$), 114.08 (s, 2C, $CH_3OCC_2H_2C_2H_2C$), 127.63 (s, 2C, $CH_3OCC_2H_2C_2H_2C$), 128.60 (s, $CH_3OCC_2H_2C_2H_2C$), 142.58 (s, $C_6H_4-CH=$), 160.18 (s, $CH_3OCC_2H_2C_2H_2C$).

General Synthesis of Complexes $RuCl(CO)(PPh_3)_2$(CH=CHCH=CH−C_6H_4−R-p) (4). To a suspension of $RuHCl(CO)(PPh_3)_3$ (0.57 g, 0.60 mmol) in CH_2Cl_2 (20 mL) was slowly added a solution of **3** (0.63 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 30 min to give a red solution. The reaction mixture was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (50 mL) to the residue produced a solid (**4a**, purple; **4b**, brown; **4c**, red), which was collected by filtration, washed with hexane, and dried under vacuum.

4a: Yield: 0.25 g, 48.3%. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 31.23 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 5.62 (m, 1H, $C_6H_4-CH=CH$), 5.74 (d, J(HH) = 15.6 Hz, 1H, $Ph-CH=$), 6.68 (q, J(HH) = 10.8, 15.2 Hz, 1H, $C_6H_4-CH=CH-CH=$), 7.03−7.99 (m, 34H, Ph, PPh_3), 8.60 (d, J(HH) = 12.8 Hz, 1H, Ru−CH).

4b: Yield: 0.32 g, 62.0%. ^{31}P NMR(160 MHz, CD_2Cl_2): δ 30.94 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.80 (s, 6H, $N(CH_3)_2$), 5.40 (m, 1H, $C_6H_4-CH=CH$), 5.63 (m, 1H, $Ph-CH=$), 6.20−7.80 (m, 35H, $C_6H_4-CH=CH-CH=$, Ph, PPh_3), 7.76 (d, J(HH) = 13.2 Hz, 1H, Ru−H).

4c: Yield: 0.20 g, 39.3%. ^{31}P NMR(160 MHz, CD_2Cl_2): δ 30.98 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.67 (s, 3H, OCH_3), 5.43 (m, 1H, $Ph-CH=CH$), 5.64 (d, J(HH) = 15.2 Hz, 1H, $C_6H_4-CH=$), 6.37 (q, J(HH) = 15.2, 10.0 Hz, 1H, $C_6H_4-CH=CH-CH=$), 6.69 (m, 2H, $CH_3OCC_2H_2C_2H_2C$), 7.10 (m, 2H, $CH_3OCC_2H_2C_2H_2C$), 7.20−7.60 (m, 30H, PPh_3), 7.90 (d, J(HH) = 12.8 Hz, 1H, Ru−H).

General Synthesis of Complexes $RuCl(CO)(PhPy)(PPh_3)_2$(CH=CHCH=CH−C_6H_4−R-p) (5). A mixture of complex **4** (0.12 mmol) and 4-phenylpyridine (0.03 g, 0.19 mmol) in CH_2Cl_2 (20 mL) was stirred for 30 min. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum.

5a: Yield: 0.10 g, 82.0%. Anal. Calcd for $C_{58}H_{47}ClN_2O_3P_2Ru$: C, 68.40; H, 4.65; N, 2.75. Found: C, 68.76; H, 4.82; N, 2.47. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 26.75 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 5.65 (d, J(HH) = 15.6 Hz, 1H, $C_6H_4-CH=$), 5.84 (q, J(HH) = 10.2, 16.2 Hz, 1H, $C_6H_4-CH=CH$), 6.72 (br q, J(HH) = 10.4, 15.2 Hz, 3H, $C_5H_2H_2N$, $C_6H_4-CH=CH-CH=$), 7.04−7.52 (m, 37H, Ph, $O_2NCC_2H_2C_2H_2C$), 7.97 (d, J(HH) = 8.8 Hz, 2H, $O_2NCC_2H_2C_2H_2C$), 8.39 (br, 2H, $C_5H_2H_2N$), 9.00 (d, J(HH) = 15.6 Hz, 1H, Ru−CH).

5b: Yield: 0.10 g, 82.0%. Anal. Calcd for $C_{60}H_{53}ClN_2OP_2Ru$: C, 70.89; H, 5.26; N, 2.76. Found: C, 71.23; H, 5.01; N, 2.70. ^{31}P NMR(160 MHz, CD_2Cl_2): δ 26.55 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.82 (s, 6H, $N(CH_3)_2$), 5.54 (d, J(HH) = 15.6 Hz, 1H, $C_6H_4-CH=$), 5.61 (q, J(HH) = 9.6, 16.0 Hz, 1H, $C_6H_4-CH=CH$), 6.41 (q, J(HH) = 9.8, 15.4 Hz, 1H, $C_6H_4-CH=CH-CH=$), 6.55 (d, J(HH) = 8.4 Hz, 2H, $(CH_3)_2NCC_2H_2C_2H_2C$), 6.70 (br, 2H, $C_5H_2H_2N$), 6.96−7.54 (m, 37H, Ph, $(CH_3)_2NCC_2H_2C_2H_2C$), 8.14 (d, J(HH) = 16.4 Hz, 1H, Ru−CH), 8.40 (br, 2H, $C_5H_2H_2N$).

5c: Yield: 0.09 g, 73.8%. Anal. Calcd for $C_{59}H_{50}ClNO_2P_2Ru$: C, 70.62; H, 5.02; N, 1.40. Found: C, 70.48; H, 5.25; N, 1.28. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 27.27 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.72 (s, 3H, OCH_3), 5.57 (d, J(HH) = 16.0 Hz, 1H, $Ph-CH=$), 5.65 (m, 1H, $C_6H_4-CH=CH$), 6.45 (q, J(HH) = 10.2, 15.4 Hz, 1H, $C_6H_4-CH=CH-CH=$), 6.70 (br d, J(HH) = 8.8 Hz, 4H, $C_5H_2H_2N$, $CH_3OCC_2H_2C_2H_2C$), 6.91−7.46 (m, 37H, Ph, $CH_3OCC_2H_2C_2H_2C$), 8.27 (d, J(HH) = 16.4 Hz, 1H, Ru−CH), 8.40 (br, 2H, $C_5H_2H_2N$).

---

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

[19] Dahlhoff, W. V.; Nelson, S. M. *J. Chem. Soc. (A)* **1971**, 2184.

[20] Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.

General Synthesis of Complexes RuCl(CO)(PMP)(CH═CHCH═CH−C_6H_4−R-p) (6). A mixture of complex **4** (0.12 mmol) and PMP (0.06 g, 0.12 mmol) in CH_2Cl_2 (20 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volumn of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (20 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum.

6a: Yield: 0.09 g, 92.0%. Anal. Calcd for $C_{42}H_{35}ClN_2O_3P_2Ru$: C, 62.00; H, 4.33; N, 3.44. Found: C, 62.31; H, 4.50; N, 3.26. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.16 (s). ^1H NMR (400 MHz,CD_2Cl_2): δ 4.12 (m, 2H, CH*H*(C_5H_3N)CH*H*), 4.51 (m, 2H, C*H*H-(C_5H_3N)C*H*H), 5.34 (d, *J*(HH) = 15.2 Hz, 1H, C_6H_4−C*H*═), 5.60 (m, 1H, C_6H_4−CH═C*H*), 5.72 (m, 1H, C_6H_4−CH═CH−C*H*═), 6.73−8.00 (m, 28H, Ph, C_5H_3N, Ru−CH).

6b: Yield: 0.08 g, 81.8%. Anal. Calcd for $C_{44}H_{41}ClN_2OP_2Ru$: C, 65.06; H, 5.09; N, 3.45. Found: C, 65.34; H, 4.91; N, 3.33. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.85 (s). ^1H NMR (400 MHz,CD_2Cl_2): δ 2.81 (s, 6H, N(CH_3)$_2$), 4.15 (m, 2H, CH*H*(C_5H_3N)CH*H*), 4.53 (m, 2H, C*H*H(C_5H_3N)C*H*H), 5.18−5.33 (m, 2H, C_6H_4−C*H*═, C_6H_4−CH═C*H*), 5.43 (q, *J*(HH) = 9.4, 15.4 Hz, 1H, C_6H_4−CH═CH−C*H*═), 6.00−7.78 (m, 28H, Ph, C_5H_3N, Ru−CH).

6c: Yield: 0.08 g, 83.4%. Anal. Calcd for $C_{43}H_{38}ClNO_2P_2Ru$: C, 64.62; H, 4.79; N, 1.75. Found: C, 64.37; H, 4.95; N, 1.87. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.42 (s). ^1H NMR (400 MHz,CD_2Cl_2): δ 3.63 (s, 3H, OCH_3), 4.14 (m, 2H, CH*H*(C_5H_3N)CH*H*), 4.50 (m, 2H, C*H*H(C_5H_3N)C*H*H), 5.21 (d, *J*(HH) = 15.4 Hz, 1H, C_6H_4−C*H*═), 5.35 (q, *J*(HH) = 9.8, 15.4 Hz, 1H, C_6H_4−CH═C*H*), 5.46 (q, *J*(HH) = 9.8, 15.0 Hz, 1H, C_6H_4−CH═CH−C*H*═), 6.11−7.80 (m, 28H, Ph, C_5H_3N, Ru−CH).

General Synthesis of Complexes RuTp(CO)(PPh_3) (CH═CHCH═CH−C_6H_4−R-p) (7). A mixture of complex **4** (0.12 mmol) and KTp (0.03 g, 0.13 mmol) in CH_2Cl_2 (20 mL) was stirred for 2 h. The solution was filtered through a column of Celite to remove the KCl. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (20 mL) to the residue produced a solid, which was collected by filtration, washed with hexane, and dried over vacuum.

7a: Yield: 0.08 g, 87.0%. Anal. Calcd for $C_{38}H_{33}BN_7O_3PRu$: C, 58.62; H, 4.27; N, 12.59. Found: C, 58.25; H, 4.12; N, 12.75. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 48.92 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 5.84−8.00 (m, 32H, PPh_3, C*H*═, Tp), 8.37 (d, *J*(HH) = 16.0 Hz, 1H, Ru−CH).

7b: Yield: 0.08 g, 87.0%. Anal. Calcd for $C_{40}H_{39}BN_7OPRu$: C, 61.86; H, 5.06; N, 12.62. Found: C, 61.58; H, 5.18; N, 12.28. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.49 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.81 (s, 6H, N(CH_3)$_2$), 5.80−7.67 (m, 33H, PPh_3, CH═, Tp).

7c: Yield: 0.08 g, 88.0%. Anal. Calcd for $C_{39}H_{36}BN_6O_2PRu$: C, 61.34; H, 4.75; N, 11.01. Found: C, 61.66; H, 4.58; N, 10.86. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.48 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.79 (s, 3H, OCH_3), 5.80−7.82 (m, 32H, PPh_3, CH═, Tp), 7.80 (d, *J*(HH) = 16.0 Hz, 1H, Ru−CH).

Crystallographic Analysis for RuTp(CO)(PPh_3)(CH═CH−CH═CH−C_6H_4−N(CH_3)$_2$-p) (7b). Crystals suitable for X-ray diffraction were grown from a dichloromethane solution layered with hexane. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4K diffractometer with graphite-monochromatized M*o* Kα radiation (λ = 0.71073 Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. All non-hydrogen atoms were refined anisotropically. All hydrogens were included in their idealized positions and refined using a riding model. Further crystallographic details are summarized in Table 2, and selected bond distances and angles are given in Table 3.

Hyper-Rayleigh Scattering (HRS) Measurement. Details for the experiment are similar to the setup described in ref 21. A high-energy picosecond Nd:YAG laser (Continuum Leopard) provides 35 ps wide pulses of 60 mJ vertically polarized 355 nm radiation at 10 Hz. The beam was pumped into the optical parameter amplification (OPA) apparatus and generated a 2−3 mJ idler wave at 1500 nm. All measurements were carried out in chloroform with sample concentrations of 10^{-4} M. Disperse Red 1 (DR1) was used as reference with a value of β_{1500}(DR1) = 74 × 10^{-30} esu.[21] DR1 was synthesized and recrystallized from methanol, and the purity is proved by ^1H and ^{13}C NMR. Solutions were filtered through a 0.2 μm Teflon filter to remove macroscopic particles that may introduce spurious signals in HRS experiments.

Assuming that the scattering contribution from the solvent is negligibly small, an external reference method (ERM)[22] is used to calculate the β values of chromophores according to eq 1:

$$\beta_c = \sqrt{{\beta_c}^2} = \sqrt{\frac{S_c}{S_{ref}}}\sqrt{{\beta_{ref}}^2} \qquad (1)$$

where *S* is the slope of the appropriate $\mathbf{I}_{2\omega}$versus concentration plot and β_{ref} is the orientational average of the first hyperpolarizability of the reference sample.

Acknowledgment. The authors acknowledge financial support from National Natural Science Foundation of China (Nos. 20472023, 20572029), New Century Excellent Talents in University (NCET-04-0743), the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 705039), the National Key Project for Basic Research of China (No. 2004CCA00100), and Program for Excellent Research Group of Hubei Province (No. 2004ABC002).

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM0605736

---

[21] Stadler, S.; Dietrich, R.; Bourhill, G.; Bräuchle, C.; Pawlik, A.; Grahn, W. *Chem. Phys. Lett.* **1995**, *247*, 271.

[22] Lequan, M.; Branger, C.; Simon, J.; Thami, T.; Chauchard, E.; Persoons, A. *Chem. Phys. Lett.* **1994**, *229*, 101.