Synthesis and Characterization of Ruthenium−Osmium Complexes Containing μ-Bisalkenyl, μ-Alkenylvinylidene, and μ-Alkenylcarbene Bridge Ligands

Maria L. Buil and Miguel A. Esteruelas*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

Received December 15, 1998

Summary: The metaloalkyne complex Ru{(E)-CH═CH−$(CH_2)_4$-C≡CH}Cl(CO)$(P^iPr_3)_2$ reacts with OsHCl(CO)-$(P^iPr_3)_2$ to give the heterodinuclear-μ-bisalkenyl derivative $(P^iPr_3)_2$(CO)ClRu{(E)-CH═CH−$(CH_2)_4$-CH═CH-(E)}OsCl(CO)$(P^iPr_3)_2$ via the hydrido-vinylidene intermediate $(P^iPr_3)_2$(CO)ClRu{(E)-CH═CH−$(CH_2)_4$-CH═C}-OsHCl(CO)$(P^iPr_3)_2$. The reaction of the heterodinuclear-μ-bisalkenyl complex with HCl selectively affords $(P^iPr_3)_2$(CO)ClRu{(E)-CH═CH−$(CH_2)_5$−CH}$OsCl_2$(CO)-$(P^iPr_3)_2$.

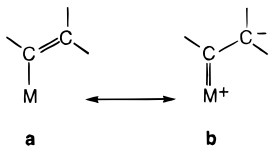
Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on March 27, 1999 on http://pubs.acs.org | doi: 10.1021/om9810192

Reactions between transition-metal hydrido complexes and terminal alkynes to afford alkenyl derivatives are an elemental step of many catalytic cycles.[1] From a mechanistic point of view, these reactions can proceed via either π-alkyne or vinylidene intermediates.[2]

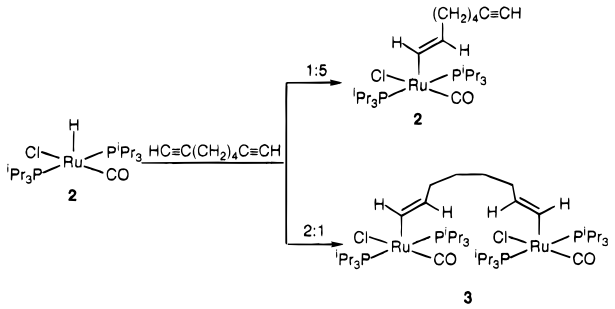
X-ray diffraction and reactivity studies on alkenyl complexes indicate that for an adequate description of the bonding situation in this type of compound a second zwitterionic resonance form (**b**, Scheme 1) must be considered. As a result of the significant contribution of the zwitterionic resonace form, the C_β atoms of the alkenyl ligands have a strong nucleophilic character, and their reactions with electrophilic reagents afford carbene derivatives.[3]

Reactions between transition-metal hydrido complexes and terminal diynes, to prepare μ-bisalkenyl derivatives, have received much less attention than those involving terminal alkynes. In 1995, we reported the synthesis of the homo-dinuclear complex $(P^iPr_3)_2$-(CO)ClOs{(*E*)-CH═CH−$(CH_2)_4$-CH═CH-(*E*)}OsCl(CO)-$(P^iPr_3)_2$, by reaction of OsHCl(CO)$(P^iPr_3)_2$ with 1,7-octadiyne in a 2:1 molar ratio.[3g] Recently, Jia *et al.* have described the preparation of the dimeric ruthenium derivatives $(PPh_3)_2$(CO)ClRu{(*E*)-CH═CH−R−CH═CH-(*E*)}RuCl(CO)$(PPh_3)_2$ (R = C_6H_4, *p*-C_6H_4−C_6H_4) by treatment of RuHCl(CO)$(PPh_3)_3$ with the corresponding diyne.[4] As far as we know, heterodinuclear compounds containing μ-bisalkenyl linkages have not previously been reported.

Scheme 1



Scheme 2



Now, we have observed that the five-coordinate ruthenium complex RuHCl(CO)$(P^iPr_3)_2$ (**1**) reacts with 1,7-octadiyne in a 1:5 molar ratio to give Ru{(*E*)-CH═CH−$(CH_2)_4$C═CH}Cl(CO)$(P^iPr_3)_2$ (**2**). When the reaction is carried out in a 2:1 molar ratio the binuclear compound $(P^iPr_3)_2$(CO)ClRu{(*E*)-CH═CH−$(CH_2)_4$−CH═CH−(*E*)}RuCl(CO)$(P^iPr_3)_2$ (**3**) is obtained according to Scheme 2.

The presence in these compounds of the alkenyl units with an *E* stereochemistry is strongly supported by the resonances of the vinylic protons of the carbon-donor ligands, in the ^{1}H NMR spectra. The values of the coupling constants between these protons, 12.6 (**2**) and 13.1 (**3**) Hz, are characteristic for this arrangement.[5] The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra agree well with those previously reported for the related compounds M{(*E*)-CH═CHR}Cl(CO)$(P^iPr_3)_2$ (M = Ru, Os), where

(1) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(2) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988. (c) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (d) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M. P.; Oliván, M.; Oñate, E.; Ruiz N. *Organometallics* **1998**, *17*, 4500.

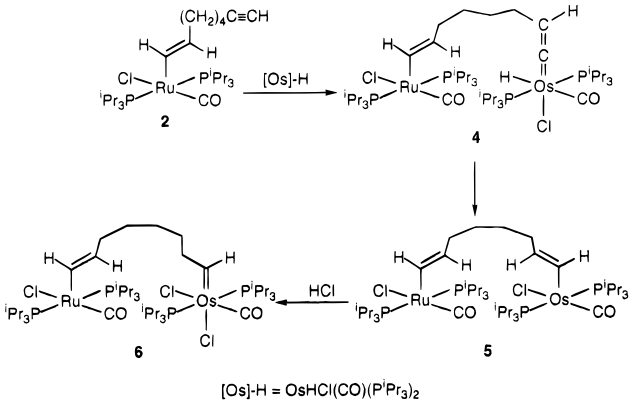
(3) (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455. (c) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (d) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (e) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (f) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669. (g) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (h) Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Sola E.; Zeier, B. *J. Chem. Soc., Dalton Trans.* **1997**, 181. (i) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169.

(4) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. P. *J. Organomet. Chem.* **1997**, *539*, 53

(5) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748.

10.1021/om9810192 CCC: $18.00 © 1999 American Chemical Society
Publication on Web 03/27/1999

Scheme 3



the square-pyramidal coordination of the metal atom has been proven by a single X-ray diffraction study on Os{(*E*)-CH=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$.[6] The resonances corresponding to the C_α atoms of the alkenyl groups appear in the $^{13}C\{^1H\}$ NMR spectra at 139.73 (**2**) and 137.72 (**3**) ppm as triplets with a C−P coupling constant of 10.6 Hz, for both compounds, while the resonances due to the C_β atoms are observed at 134.00 (**2**) and 134.46 (**3**) ppm, also as triplets but with a C−P coupling constant of 3.2 Hz. The $^{31}P\{^1H\}$ NMR spectra show singlets at 38.1 (**2**) and 38.0 (**3**) ppm.

At room temperature, complex **2** reacts with OsHCl(CO)(P^{i}Pr$_3$)$_2$ to give initially the hydrido−vinylidene derivative (P^{i}Pr$_3$)$_2$(CO)ClRu{(*E*)-CH=CH−(CH$_2$)$_4$−CH=C}OsHCl(CO)(P^{i}Pr$_3$)$_2$ (**4**), which evolves in toluene into the heterodinuclear-μ-bisalkenyl complex (P^{i}Pr$_3$)$_2$(CO)ClRu{(*E*)-CH=CH−(CH$_2$)$_4$−CH=CH-(*E*)}OsCl(CO)(P^{i}Pr$_3$)$_2$ (**5**) according to Scheme 3. This isomerization was followed by $^{31}P\{^1H\}$NMR spectroscopy by measuring the disappearance of the Os−P resonance of **4** as a function of time. In this way, first-order rate constants k_{obs} were obtained between 303 and 343 K, which yield values for the activation parameters of $\Delta H^{\ddagger} = 22.1 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.1 \pm 2.3$ cal K^{-1} mol^{-1}, according to an Eyring analysis. The slightly negative value of the activation entropy suggests that the insertion of the vinylidene ligand into the Os−H bond of **4** is an intramolecular process, which occurs by a concerted mechanism with a geometrically highly oriented transition state.

The hydrido−vinylidene complex **4** was isolated as a dark pink solid in 68% yield. The presence of a hydrido ligand in this complex was inferred from the ^1H and $^{31}P\{^1H\}$ NMR spectra. In agreement with the mutually *trans* disposition of the hydrido and carbonyl ligands, in the ^1H NMR spectrum in benzene-d_6, the hydrido resonance appears at −4.67 ppm. A similar chemical shift has been found in other *trans*-hydrido−carbonyl−osmium compounds.[7] The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 38.4 (P−Ru) and 45.3 (P−Os) ppm. Under off-resonance conditions, the second one splits into a doublet. The vinylidene group was characterized in the ^1H NMR spectrum by a double triplet at 3.18 ppm with H−H and H−P coupling constants of 1.2 and 4.2 Hz, respectively, and in the $^{13}C\{^1H\}$ NMR spectrum by two broad resonances at 336.80 (C_α) and 115.72 (C_β) ppm.

The presence in complex **5** of a μ-bisalkenyl ligand with an *E* stereochemistry at both carbon−carbon double bonds is strongly supported by the ^1H NMR spectrum. The values of the coupling constants between the vinylic protons of these groups, 12.6 (RuCH=CH) and 12.0 (OsCH=CH) Hz, agree well with those observed for **2** and **3**. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α atoms of the alkenyl units give rise to triplets at 139.11 (RuC_α) and 108.08 (OsC_α) ppm with C−P coupling constants of 6.8 and 4.6 Hz, respectively, whereas the resonances corresponding to the C_β atoms are observed at 134.79 (Ru) and 133.88 (Os) ppm, as singlets. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 38.4 (Ru−P) and 22.8 (Os−P) ppm.

In agreement with the nucleophilic character of the C_β atom of an alkenyl ligand, complex **5** reacts with HCl. However, interestingly, only the C_β atom of the Os−alkenyl unit is attacked. Thus, the treatment of **5** with the stoichiometric amount of a toluene HCl solution selectively affords (P^{i}Pr$_3$)$_2$(CO)ClRu{(*E*)-CH=CH−(CH$_2$)$_5$-CH}OsCl$_2$(CO)(P^{i}Pr$_3$)$_2$ (**6**). This fact elegantly proves that under the same conditions, the C_β atom of the alkenyl ligands of the osmium−alkenyl complexes has a stronger nucleophilic character than the C_β atom of the alkenyl ligands on ruthenium−alkenyl compounds.

The selective attack at the C_β atom of the Os−alkenyl unit of **5** is strongly suported by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **6**, which for the ligands bonded to the ruthenium atom show spectroscopic data similar to those found in **5**, while the spectroscopic data of the ligands bonded to the osmium of **6** undergo significant changes with regard to those of **5**. In the ^1H NMR spectrum the most noticeable changes are the presence of a triplet at 18.98 ppm with a H−H coupling constant of 6.6 Hz, corresponding to the Os=CH proton, and the absence of osmium−alkenyl resonances. Similarly, the $^{13}C\{^1H\}$ NMR spectrum shows the Os=C resonance at 301.85 ppm and does not contain osmium−alkenyl signals. In the $^{31}P\{^1H\}$ NMR spectrum the Os−P resonance appears at 12.3 ppm, shifted 10.5 ppm to higher field in comparison with that of **5**, while the Ru−P resonances of **5** and **6** are observed at the same chemical shift, 38.4 ppm.

In conclusion, the carbon−carbon triple bonds of 1,7-octadiyne can be inserted in a sequential manner into the M−H bonds of the complexes MHCl(CO)(P^{i}Pr$_3$)$_2$ (M = Ru, Os) to give the heterodinuclear-μ-bisalkenyl derivative (P^{i}Pr$_3$)$_2$(CO)ClRu{(*E*)-CH=CH−(CH$_2$)$_4$-CH=CH-(*E*)}OsCl(CO)(P^{i}Pr$_3$)$_2$. The insertion in the Os−H bond proceeds via a hydrido−vinylidene intermediate through a geometrically highly oriented transition state. In the heterobinuclear-μ-bisalkenyl complex, the C_β atom of the Os−alkenyl unit has a stronger nucleophilic character than the C_β atom of the Ru−alkenyl fragment, as is proven by the reaction of this compound with HCl, which selectively affords (P^{i}Pr$_3$)$_2$(CO)ClRu{(*E*)-CH=CH−(CH$_2$)$_5$−CH}OsCl$_2$(CO)(P^{i}Pr$_3$)$_2$.

(6) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(7) (a) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221. (b) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (c) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on March 27, 1999 on http://pubs.acs.org | doi: 10.1021/om9810192

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on March 27, 1999 on http://pubs.acs.org | doi: 10.1021/om9810192

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os) were prepared by published methods.[7a]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(PH) + J(P'H)$ for ^1H and $N = J(PC) + J(P'C)$ for $^{13}C\{^1H\}$) are given in hertz.

Preparation of Ru{(*E*)-CH=CH−$(CH_2)_4$C≡CH}Cl(CO)-$(P^iPr_3)_2$ (2). A solution of $RuHCl(CO)(P^iPr_3)_2$ (150 mg, 0.31 mmol) in 6 mL of toluene was treated with 1,7-octadiyne (208 μL, 1.55 mmol). After stirring for 3 h at 333 K, the solution was cooled to room temperature, filtered through Kieselguhr, and concentrated in vacuo to ca. 0.5 mL. Addition of 5 mL of methanol gave a pink solid, which was stirred for 15 min at −78 °C. The solution was decanted, and the resulting pink solid was washed with methanol and dried in vacuo. Yield: 137 mg (70%). Anal. Calcd for $C_{27}H_{53}ClOP_2Ru$ (%): C, 54.76; H, 9.02. Found: C, 54.97; H, 9.36. IR (Nujol, cm^{-1}): ν(C≡C) 2030, ν(CO) 1908, ν(C=C) 1588. ^1H NMR (300 MHz, C_6D_6): δ 7.45 (dt, 1H, J(HH) = 12.6 Hz, J(HP) = 0.9 Hz, RuCH=), 5.21 (dtt, 1H, J(HH) = 12.6 Hz, J(HH) = 6.6 Hz, J(HP) = 2.1 Hz, =CH), 2.76 (m, 8H, PCH and $-CH_2-$), 2.23 (m, 2H, $-CH_2-$), 2.07 (m, 2H, $-CH_2-$), 1.89 (t, 1H, J(HH) = 2.7 Hz, ≡CH), 1.50 (m, 2H, $-CH_2-$), 1.31 (dvt, 18H, J(HH) = 5.7 Hz, N = 13.2 Hz, PCHCH_3), 1.30 (dvt, 18H, J(HH) = 6.0 Hz, N = 13.2 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 203.83 (t, J(CP) = 13.0 Hz, Ru−CO), 139.73 (t, J(CP) = 10.6 Hz, RuCH=), 134.00 (t, J(CP) = 3.2 Hz, =CH), 84.48 (s, −C≡), 68.64 (s, ≡CH), 36.00, 29.82 and 28.46 (all s, $-CH_2-$), 24.30 (vt, N = 29.3 Hz, PCH), 20.01 and 19.88 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 38.1 (s).

Preparation of $(P^iPr_3)_2$(CO)ClRu{(E)-CH=CH−$(CH_2)_4$−CH=CH-(E)}RuCl(CO)$(P^iPr_3)_2$ (3). A solution of **1** (117 mg, 0.24 mmol) in 10 mL of toluene was treated with 1,7-octadiyne (16 μL, 0.12 mmol). After stirring for 3 h at 60 °C, the solution was cooled to room temperature and filtered and the solvent removed. The residue was washed repeatedly with cold methanol, yielding a pink solid, which was dried in vacuo. Yield: 108 mg (83%). Anal. Calcd for $C_{46}H_{96}Cl_2O_2P_4Ru_2$ (%): C, 51.24; H, 8.97. Found: C, 51.35; H, 8.78. IR (Nujol, cm^{-1}): ν(CO) 1903, ν(C=C) 1585. ^1H NMR (300 MHz, C_6D_6): δ 7.40 (d, 2H, J(HH) = 13.1 Hz, RuCH=), 5.24 (m, 2H, =CH), 2.68 (m, 12H, PCH), 2.33 and 1.52 (both m, 4H, $-CH_2-$), 1.27 (dvt, 36H, J(HH) = 5.7 Hz, N = 12.9 Hz, PCHCH_3), 1.26 (dvt, 36H, J(HH) = 6.0 Hz, N = 12.9 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 203.27 (t, J(CP) = 13.8 Hz, Ru−CO), 137.72 (t, J(CP) = 10.6 Hz, RuCH=), 134.46 (t, J(CP) = 3.2 Hz, =CH), 36.10 and 30.14 (both s, $-CH_2-$), 24.30 (vt, N = 18.8 Hz, PCH), 19.89 and 19.79 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 38.0 (s).

Preparation of $(P^iPr_3)_2$(CO)ClRu{(*E*)-CH=CH−$(CH_2)_4$-CH=C} OsHCl(CO)$(P^iPr_3)_2$ (4). A solution of **2** (130 mg, 0.22 mmol) in 6 mL of toluene was treated with $OsHCl(CO)(P^iPr_3)_2$ (122 mg, 0.22 mmol). After stirring for 15 min at 218 K, the solution was concentrated to ca. 0.5 mL. Addition of 5 mL of methanol gave a dark pink solid. The solution was decanted, and the resulting solid was washed with methanol and dried in vacuo. Yield: 171 mg (68%). Anal. Calcd for $C_{46}H_{96}Cl_2O_2OsP_4Ru$ (%): C, 47.24; H, 8.28. Found: C, 47.68; H, 8.46. IR (Nujol, cm^{-1}): ν(Os−H) 2030, ν(CO) 1905, 1883, ν(Os=C=C) 1666, ν(C=C) 1589. ^1H NMR (300 MHz, C_6D_6): δ 7.40 (d, 1H, J(HH) = 11.7 Hz, RuCH=), 5.20 (m, 1H, RuCH=CH), 3.18 (dt, 1H, J(HH) = 1.2 Hz, J(HP) = 4.2 Hz, =C=CH), 2.80 (m, 2H, $-CH_2-$), 2.66 (m, 8H, PCH and $-CH_2-$), 2.58 (m, 8H, PCH and $-CH_2-$), 2.28 (m, 2H, $-CH_2-$), 1.26 and 1.23 (both dvt, each 36H, J(HH) = 6.9 Hz, N = 13.2 Hz, PCHCH_3), −4.67 (t, 1H, J(HP) = 28.5 Hz, Os−H). $^{13}C\{^1H\}$ NMR (75.43 MHz, toluene-d_8, 223 K): δ 336.80 (br, Os=C), 203.7 (br, Ru−CO), 179.84 (br, Os−CO), 139.65 (br, RuCH=), 134.80 (br, RuCH=*C*), 115.72 (br, Os=C=*C*), 37.26 and 31.84 (both s, $-CH_2-$), 24.35 (vt, N = 18.2 Hz, PCH), 19.80, 19.75 and 19.69 (all s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 45.3 (s, Os−P); 38.4 (s, Ru−P).

Preparation of $(P^iPr_3)_2$(CO)ClRu{(*E*)-CH=CH−$(CH_2)_4$−CH=CH-(*E*)}OsCl(CO)$(P^iPr_3)_2$ (5). A solution of **2** (130 mg, 0.22 mmol) in 6 mL of toluene was treated with $OsHCl(CO)(P^iPr_3)_2$ (122 mg, 0.22 mmol). After stirring for 12 h at 60 °C the solution was cooled, filtered through Kieselguhr, and concentrated to ca. 0.5 mL. Addition of 5 mL of methanol gave a violet solid. The solution was decanted, and the solid washed with methanol and dried in vacuo. Yield: 202 mg (80%). Anal. Calcd for $C_{46}H_{96}Cl_2O_2OsP_4Ru$ (%): C, 47.24; H, 8.28. Found: C, 47.70; H, 8.28. IR (Nujol, cm^{-1}): ν(CO) 1905, 1890, ν(C=C) 1593. ^1H NMR (300 MHz, C_6D_6): δ 7.38 (d, 1H, J(HH) = 12.6, RuCH=), 6.81 (d, 1H, J(HH) = 12.0 Hz, OsCH=), 5.24 (m, 1H, RuCH=C*H*), 4.77 (m, 1H, OsCH=C*H*), 2.85 (m, 8H, PCH and $-CH_2-$), 2.47, 2.31 (both m, each 2H, $-CH_2-$), 1.23 (dvt, 72H, J(HH) = 6.6 Hz, N = 12.9 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 204.67 (t, J(CP) = 13.8 Hz, Ru−CO), 183.08 (t, J(CP) = 9.2 Hz, Os−CO), 139.11 (t, J(CP) = 6.8 Hz, RuCH=), 134.79 (s, RuCH=*C*), 133.88 (s, OsCH=*C*), 108.08 (t, J(CP) = 4.6 Hz, OsCH=), 36.71, 31.39 and 30.69 (all s, $-CH_2-$), 24.57 and 24.37 (both vt, N = 24.4 Hz, PCH), 19.83, 19.81 and 19.69 (all s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 38.4 (s, Ru−P); 22.8 (s, Os−P).

Preparation of $(P^iPr_3)_2$(CO)ClRu{(*E*)-CH=CH−$(CH_2)_5$−CH}$OsCl_2$(CO)$(P^iPr_3)_2$ (6). A solution of **5** (150 mg, 0.128 mmol) in 6 mL of toluene was treated with a solution (0.12 M) of HCl in toluene (1.3 mL, 0.154 mmol). The color turned, immediately, from violet to reddish. After stirring for 2 h, the solution was concentrated to ca. 0.5 mL. Addition of 5 mL of pentane gave an orange solid. The solution was decanted and the solid washed with pentane and dried in vacuo. Yield: 131 mg (85%). Anal. Calcd for $C_{46}H_{97}Cl_3O_2OsP_4Ru$ (%): C, 45.90; H, 8.12. Found: C, 45.58; H, 8.47. IR (Nujol, cm^{-1}): ν(CO) 1905, 1885, ν(C=C) 1590. ^1H NMR (300 MHz, C_6D_6): δ 18.98 (t, 1H, J(HH) = 6.6 Hz, Os=CH), 7.44 (d, 1H, J(HH) = 12.6 Hz, RuCH=), 5.17 (m, 1H, RuCH=C*H*), 2.90−2.60 (m, 20H, PCH and $-CH_2-$), 2.25 (m, 2H, $-CH_2-$), 1.38−1.10 (m, 72H, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 301.85 (t, J(CP) = 11.0 Hz, Os=CH), 203.88 (t, J(CP) = 12.9 Hz, Ru−CO), 180.65 (t, J(CP) = 8.7 Hz, Os−CO), 139.86 (t, J(CP) = 10.6 Hz, RuCH=), 133.93 (t, J(CP) = 2.1 Hz, RuCH=*C*H), 61.25, 36.35 and 35.01 (all s, $-CH_2-$), 24.84 (vt, N = 25.3 Hz, PCH), 24.40 (vt, N = 19.3 Hz, PCH), 19.89, 19.86, 19.56 and 19.13 (all s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 38.4 (s, Ru−P), 12.3 (s, Os−P).

Acknowledgment. We thank the DGICYT (Project PB95-0806, Programa de Promoción General del Conocimiento) for financial support.

OM9810192