Notes

C−C Coupling of the Alkynyl and Alkenyl Fragments of $Os(C_2CO_2CH_3)\{CH=CHC(O)OCH_3\}(CO)(P^iPr_3)_2$ by Action of HCl: The Vinylidene $[Os\{CH=CHC(O)OCH_3\}(C=CHCO_2CH_3)(CO)(P^iPr_3)_2]BF_4$ as Intermediate

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Summary: The alkynyl−alkenyl complex $Os(C_2CO_2CH_3)\{CH=CHC(O)OCH_3\}(CO)(P^iPr_3)_2$ (2) reacts with HCl to give the butadienyl derivative $Os\{C(CH=CHCO_2CH_3)=CHC(O)OCH_3\}Cl(CO)(P^iPr_3)_2$ (3), which can be also obtained by protonation of 2 with $HBF_4 \cdot OEt_2$ to give $[Os\{CH=CHC(O)CH_3\}(C=CHCO_2CH_3)(CO)(P^iPr_3)_2]BF_4$ (4) and subsequent treatment of 4 with NaCl. The protonation of 3 with $HBF_4 \cdot OEt_2$ affords the α,β-unsaturated carbene complex $[Os\{C(CH=CHCO_2CH_3)CH_2C(O)OCH_3\}Cl(CO)(P^iPr_3)_2]BF_4$ (5).
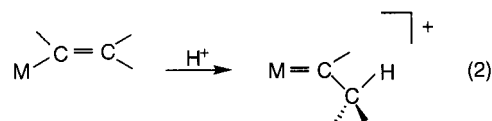
Electronic structures and reactivity of organic fragments change, often dramatically, when they coordinate to late transition metals to form organometallic complexes.[1]

Coordination of $[RC\equiv C]^-$ to a metal center transfers the nucleophilicity from the α-carbon atom to the β-carbon atom. Thus, the addition of electrophiles to the electron-rich C_β of metal alkynyl derivatives has been described on many occasions and is the best known entry into the synthesis of vinylidene compounds (eq 1).[2]

$$M-C\equiv C-R \xrightarrow{H^+} M=C=C\begin{smallmatrix}H\\R\end{smallmatrix}\ \rceil^+ \qquad (1)$$
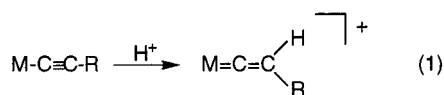
Theoretical studies on vinylidene complexes have identified the electron deficiency of the vinylidene ligand at the α-carbon atom.[3] Thus, the reactions with nucleophiles generally result in the formation of alkenyl derivatives.[2] X-ray diffraction and reactivity studies on

alkenyl complexes indicate that for an adequate description of the bonding situation in this type of compounds a second zwitterionic resonance form (b, Scheme 1) must be considered. As a result of the significant contribution of the zwitterionic resonance form, the C_β atoms of the alkenyl ligands, in a manner similar to the C_β atoms of the vinylidene ligands, have a strong nucleophilic character, and their reactions with electrophilic reagents afford carbene derivatives (eq 2).[4]

$$M\begin{smallmatrix}\\C=C\\\end{smallmatrix} \xrightarrow{H^+} M=C\begin{smallmatrix}\\H\\C\end{smallmatrix}\ \rceil^+ \qquad (2)$$

We have previously reported that the dihydride−dihydrogen complex $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (1)[5] reacts with 2 equiv of methylpropiolate to give the alkynyl−alkenyl derivative $Os(C_2CO_2CH_3)\{CH=CHC(O)OCH_3\}(CO)(P^iPr_3)_2$ (2, eq 3). In agreement with Scheme 1, the molecular structure of this compound determined by X-ray diffraction analysis reveals a significant contribution of the resonance form b to the

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(2) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.
(3) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(4) (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7768. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455. (c) Cavey, 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. I.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (e) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, F. C.; Georgious, 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. (j) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798.
(5) (a) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (b) Gusev, D. G.; Kunlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775.
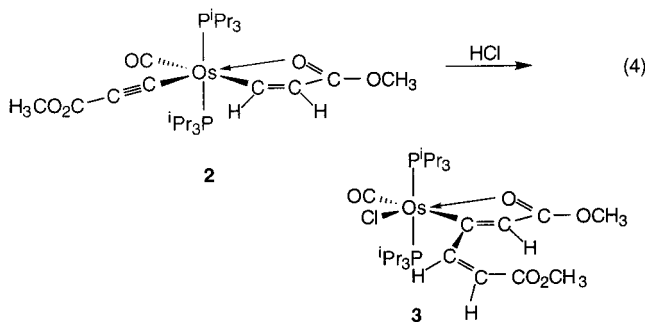
Scheme 1
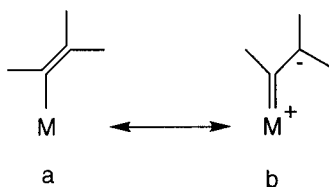
osmium–alkenyl bond, which is improved by the presence of the carboxyl substituent.[6]
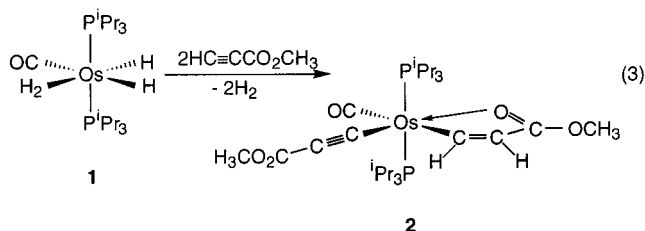
Now, we have observed that the reaction of **2** with HCl in toluene at room temperature produces the C–C coupling of the alkenyl and alkynyl fragments to give the butadienyl derivative Os{C(CH=CHCO₂CH₃)=CHC-(O)OCH₃}Cl(CO)(P^{i}Pr₃)₂ (**3**), as a violet solid in 75% yield, according to eq 4.

The presence of the butadienyl ligand in **3** is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound. In the ^{1}H NMR spectrum the most noticeable resonances are a singlet at 7.44 ppm, corresponding to the =CH proton of the heterometallacycle, and two doublets at 9.65 and 5.69 ppm due to the =CH protons of the CH=CHCO₂CH₃ unit. The *cis* disposition of these hydrogen atoms at the C–C double bond was inferred on the basis of the value of the H–H coupling constant, 11.25 Hz, which is characteristic for this arrangement. In the ^{13}C{^{1}H} NMR spectrum the Os–C resonance appears at 169.9 ppm as a triplet with a C–P coupling constant of 7.0 Hz, whereas the =CH resonances are observed at 155.8, 135.0, and 114.2 ppm as singlets.

The reaction shown in eq 4 suggests that although the C$_\beta$ carbon atoms of both the alkynyl ligand and the alkenyl fragment are nucleophilic centers, the nucleophilicity of the C$_\beta$ carbon atom of the alkynyl ligand is stronger than that of the C$_\beta$ carbon atom of the alkenyl fragment. Thus, the formation of the butadienyl ligand of **3** can be rationalized as the selective

(6) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663.
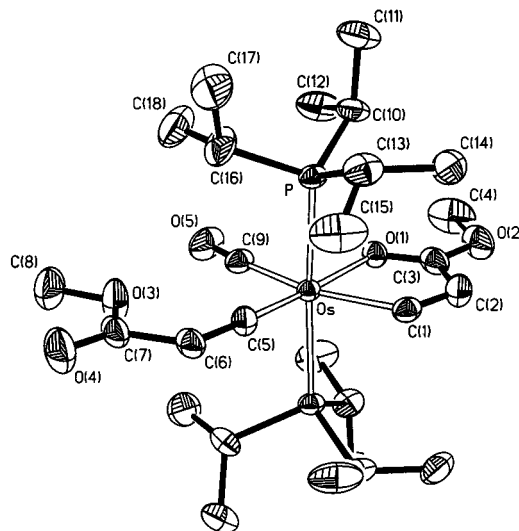

Figure 1. Molecular diagram of complex **4**. Selected distances (Å) and angles (deg): Os–P, 2.4479(8); Os–O(1), 2.187(3); Os–C(1), 2.078(5); Os–C(5), 1.815(6); Os–C(9), 1.953(6); O(1)–C(3), 1.265(6); O(2)–C(3), 1.314(7); O(2)–C(4), 1.436(7); O(3)–C(8), 1.425(7); O(3)–C(7) 1.338(7); O(4)–C(7), 1.210(7); O(5)–C(9), 1.144(6); C(1)–C(2), 1.341-(7); C(2)–C(3), 1.422(8); C(5)–C(6), 1.325(7); C(6)–C(7), 1.445(8); P–Os–P′, 172.44(5); O(1)–Os–C(1), 75.5(2); O(1)–Os–C(5), 176.5(2); O(1)–Os–C(9), 84.4(2); C(1)–Os–C(5), 108.0(2); C(1)–Os–C(9), 159.8(2); C(5)–Os-C(9), 92.2(2); Os–C(5)–C(6), 174.2(5); C(5)–C(6)-C(7), 121.2(6).

protonation of the C$_\beta$ carbon atom of the alkynyl ligand, followed by the migratory insertion of the resulting vinylidene into the Os–CH bond of the heterometallacycle. The insertion should be promoted by the entry of a chloro ligand into the coordination sphere of the osmium atom. In agreement with this, we have also observed that the addition of 1 equiv of HBF₄·OEt₂ to diethyl ether solutions of **2** affords the alkenyl–vinylidene complex [Os{CH=CHC(O)OCH₃}(C=CHCO₂-CH₃)(CO)(P^{i}Pr₃)₂]BF₄ (**4**), as a yellow solid in 65% yield (eq 5), and that the treatment of **4** with NaCl gives **3** in 91% yield.
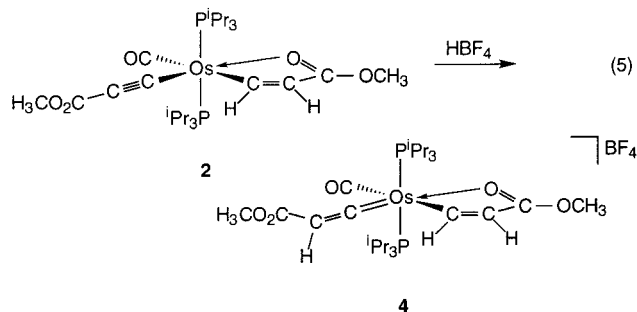
A view of the molecular geometry of **4** is shown in Figure 1. The coordination geometry around the osmium center can be rationalized as a distorted octahedron with the two phosphorus atoms occupying opposite positions [P–Os–P′ = 172.44(5)°]. An ideal equatorial plane is formed by the atoms C(1) and O(1) of the chelating alkenyl ligand—defining with the osmium atom a five-membered ring [O(1)–Os–C(1) = 75.5(2)°]—the atom C(5) of the vinylidene group disposed *trans* to O(1) [O(1)–Os–C(5) = 176.5(2)°], and the CO ligand located *trans* to C(1) [C(1)–Os–C(9) = 159.8(2)°].

The vinilydene ligand is bound to the metal in a nearly linear fashion with an Os−C(5)−C(6) angle of 174.2(5)°. The Os−C(5) [1.815(6) Å] and C(5)−C(6) [1.325(7) Å] bond lengths compare well with the ones found in other osmium−vinylidene complexes[7] and support the vinylidene formulation. The structural parameters within the heterometallacycle agree well with those found in the starting material complex.

The C_β carbon atom of the OsC=CH unit of the butadienyl ligand of **3** also shows nucleophilic character. Thus, the reaction of **3** with 1 equiv of HBF$_4$·OEt$_2$ in diethyl ether at room temperature affords the α,β-unsaturated carbene derivative [Os{C(CH=CHCO$_2$-CH$_3$)CH$_2$C(O)CH$_3$}Cl(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**), which was isolated as a brown solid in 63% yield (eq 6).
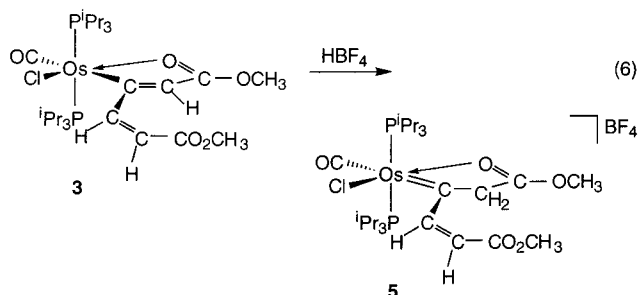
The presence of an α,β-unsaturated carbene ligand in **5** is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound. In the ^{1}H NMR spectrum the most noticeable resonances are a singlet at 4.10 ppm, corresponding to the CH$_2$ protons of the heterometallacycle, and at 7.90 and 7.50 ppm two doublets with a H−H coupling constant of 10.80 Hz, due to the olefinic hydrogen atoms of the alkenyl unit. In the ^{13}C{^{1}H} NMR spectrum the Os=C carbon atom gives rise to a triplet with a C−P coupling constant of 6.0 Hz, at 266.9 ppm, whereas the carbon atoms of the alkenyl unit and the CH$_2$ carbon atom of the heterometallacycle display singlets at 157.7, 118.2, and 68.8 ppm, respectively.

In conclusion, the addition of a toluene solution of HCl to toluene solutions of the alkynyl−alkenyl complex Os-(C$_2$CO$_2$CH$_3$){CH=CHC(O)OCH$_3$}(CO)(P^{i}Pr$_3$)$_2$ produces the C−C coupling of the alkynyl and alkenyl fragments to give selectively the butadienyl derivative Os{C(CH=CHCO$_2$CH$_3$)=CHC(O)OCH$_3$}Cl(CO)(P^{i}Pr$_3$)$_2$. The reaction proceeds by protonation of the C_β carbon atom of the alkynyl ligand and subsequent migratory insertion of the resulting vinylidene into the Os−alkenyl bond. The insertion is promoted by the entry of chloride into the coordination sphere of the osmium. The selective protonation of the alkynyl group in the presence of the alkenyl ligand elegantly proves that under the same conditions the C_β atom of an alkynyl ligand has a stronger nucleophilic character than the C_β atom of an alkenyl ligand.

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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 material Os(C$_2$CO$_2$CH$_3$){CH=CHC(O)OCH$_3$}(CO)(P^i-Pr$_3$)$_2$ was prepared by a published method.[6]

Preparation of Os{C(CH=CHCO$_2$CH$_3$)=CHC(O)OCH$_3$}-Cl(CO)(P^{i}Pr$_3$)$_2$ (3). A solution of **2** (101 mg, 0.18 mmol) in 8 mL of toluene was treated with a toluene HCl solution (0.09 M) (2.2 mL, 0.20 mmol). The yellow solution changed immediately to deep violet. After the mixture was stirred for 30 min, the solvent was removed in vacuo. The violet residue was washed twice with 2 mL of cold pentane and dried in vacuo. The product is a violet solid. Yield: 100 mg (75%). Anal. Calcd for C$_{27}$H$_{51}$ClO$_5$OsP$_2$ (%): C, 43.63; H, 6.91. Found: C, 43.25; H, 7.38. IR (Nujol, cm^{-1}): ν(C≡O) 1899(s), ν(C=O) 1673(m) and 1640(m), ν(C=C) 1588(m) and 1557(m). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ, 9.65 [d, 1H, J(HH) = 11.25 Hz, =CHCO$_2$], 7.44 (s, 1H, OsC=CH), 5.69 [d, 1H, J(HH) = 11.25 Hz, OsCCH=], 3.53 (s, 3H, CO$_2$CH$_3$), 3.47 (s, 3H, CO$_2$H$_3$), 2.60 (m, 6H, PCH), 1.38 [dvt, 18H, N = 14.00 Hz, J(HH) = 7.00 Hz, PCCH$_3$], 1.07 [dvt, 18H, N = 12.40 Hz, J(HH) = 6.60 Hz, PCCH$_3$]. ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$): δ, 5.6 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$): δ, 187.2 (t, J(CP) = 9.8 Hz, C≡O), 170.4 (s, CO$_2$), 169.9 [t, J(CP) = 7.0 Hz, OsC], 165.8 (2×) (s, CO$_2$), 155.8, 135.0 and 114.2 (all s, C=), 53.9 and 50.3 (both s, OCH$_3$), 23.4 (dvt, N = 23.7 Hz, PCH), 20.6 and 19.1 (both s, PCHCH$_3$).

Reaction of 2 with HBF$_4$: Preparation of [Os{CH=CHC(O)OCH$_3$}(C=CHCO$_2$CH$_3$)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (4). A yellow solution of **2** (330 mg, 0.47 mmol) in 10 mL of diethyl ether was treated dropwise with HBF$_4$·OEt$_2$ (7.31 M) (76 μL, 0.56 mmol), and a yellow solid was formed. After 30 min the suspension was concentrated to 3 mL, and the yellow solid was filtered off, washed with 2 mL of cold diethyl ether, and dried in vacuo. The product is a yellow solid. Yield: 240 mg (65%). Anal. Calcd for C$_{27}$H$_{51}$BF$_4$O$_5$OsP$_2$ (%): C, 40.81; H, 6.47. Found: C, 40.62; H, 6.46. IR (Nujol, cm^{-1}): ν(C≡O) 2040(s), ν(C=O) 1700(m) and 1610(m), ν(C=C) 1570(m), ν(B−F) 1050-(br). ^{1}H NMR (300 MHz, CDCl$_3$): δ, 10.74 [d, 1H, J(HH) = 9.30 Hz, OsCH=], 7.06 [dt, 1H, J(HH) = 9.30 Hz, J(HP) = 2.20 Hz, =CH], 4.08 (s, 3H, CO$_2$CH$_3$), 3.66 (s, 3H, CO$_2$CH$_3$), 2.77 (br s, 1H, CHCO$_2$CH$_3$), 2.53 (m, 6H, PCH), 1.32 [dvt, 18H, N = 14.55 Hz, J(HH) = 7.14 Hz, PCHCH$_3$], 1.28 [dvt, 18H, N = 14.3 Hz, J(HH) = 7.14 Hz, PCHCH$_3$]. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ, 17.3 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ, 311.1 [t, J(CP) = 9.4 Hz, Os=C], 202.8 [t, J(CP) = 8.3 Hz, OsCH=], 188.1 [t, J(CP) = 7.4 Hz, C≡O], 185.2 and 160.6 (both s, CO$_2$), 125.1 and 105.1 (both s, =CH−), 55.5 and 51.4 (both s, OCH$_3$), 24.9 [vt, N = 26.6 Hz, PCH], 19.6 and 19.1 (both s, PCHCH$_3$).

Reaction of 4 with NaCl. A solution of **4** (70 mg, 0.09 mmol) in 5 mL of tetrahydrofuran at room temperature was treated with an excess of sodium chloride (26 mg, 0.44 mmol) for 2 h. The color turned from yellow to deep violet, and the solvent was removed in vacuo. A 15 mL portion of dichloromethane was added, and the mixture was filtered to eliminate the excess of sodium chloride and sodium tetrafluoroborate. The solution was concentrated to ca. 1 mL, and 2 mL of cold pentane were added. The deep violet precipitate was filtered off and dried in vacuo. Yield: 60 mg (91%). The solid was characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy as complex **3**.

Preparation of Os{C(CH=CHCO$_2$CH$_3$)CH$_2$C(O)OCH$_3$}-Cl(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (5). A violet solution of **3** (100 mg, 0.13 mmol) in 8 mL of diethyl ether was treated with HBF$_4$·OEt$_2$ (7.31 M) (22 μL, 0.16 mmol). The violet solution immediately formed a brown suspension. After the mixture was stirred for

2 h, the solvent was filtered off, and the brown solid was dissolved in 1 mL of dichloromethane. Then, hexane was added dropwise until the mixture turned cloudy. The mixture was kept for 3 days at -20 °C, and a brown precipitate was obtained, which was filtered off and dried in vacuo. The product is a brown solid. Yield: 70 mg (63%). Anal. Calcd for $C_{27}H_{52}ClBF_4O_5OsP_2$ (%): C, 39.02; H, 6.31. Found: C, 38.90; H, 6.15. IR (Nujol, cm^{-1}): ν(C≡O) 1953(s), ν(C=O) 1750(m) and 1630(m), ν(C=C) 1588(m). ^{1}H NMR (300 MHz, CDCl$_3$): δ, 7.90 [d, 1H, J(HH) = 10.80 Hz, CH=], 7.50 [d, 1H, J(HH) = 10.80 Hz], 4.27 (s, 3H, CO$_2$CH$_3$), 4.10 (s, 2H, CH$_2$), 3.80 (s, 3H, CO$_2$CH$_3$), 2.60 (m, 6H, PCH), 1.30 [dvt, 18H, N = 15.00 Hz, J(HH) = 7.23 Hz, PCHCH_3], 1.24 [dvt, 18H, N = 14.20 Hz, J(HH) = 7.10 Hz, PCHCH_3]. ^{31}P{^{1}H} NMR (121.4 CDCl$_3$): δ, 17.4 (s). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): δ, 266.9 [t, J(CP) = 6.0 Hz, Os=C], 179.7 [t, J(CP) = 9.0 Hz, C≡O], 175.2 (s, CO$_2$), 167.2 [br t, J(CP) < 1 Hz, CO$_2$], 157.7 and 118.2 (both s, CH=), 68.8 (s, CH$_2$), 56.6 and 52.9 (both s, OCH$_3$). 26.1 [dvt, N = 25.1 Hz, PCH], 18.8 and 19.9 (both s, PCHCH_3). MS (FAB$^+$): m/z = 745(M$^+$).

X-ray Structure Analysis of Complex [Os{CH=CHC-(O)OCH$_3$}(C=CHCO$_2$CH$_3$)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (4). A crystal suitable for X-ray diffraction analysis (0.31 × 0.29 × 0.11 mm) was mounted onto a glass fibber and transferred to a Siemens-P4 automatic diffractometer (T = 200.0(2) K, Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 50 high-angle reflec-tions (orthorhombic, space group *Pnam*, a = 27.643(2) Å, b = 12.965(1) Å, c = 9.407(1) Å, V = 3371.4(5) Å^3, Z = 4). Data were collected by the ω scan method over a θ range of 1.5–27.7°. Corrections for decay and absorption (semiempirical method) were applied. The structure was solved by Patterson (Os atom) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93). The osmium atom was observed in a crystallographic mirror plane that divides the molecule. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. The refinement converged to R1(F) = 0.0271 [F^2 > $2\sigma(F^2)$], and wR2($F2$) = 0.0682 [all data], with weighting parameters x = 0.0160 and y = 0.

Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9905759