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Formation of Cationic Half-Sandwich Osmium−Vinylidene Complexes from $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ and Terminal Alkynes

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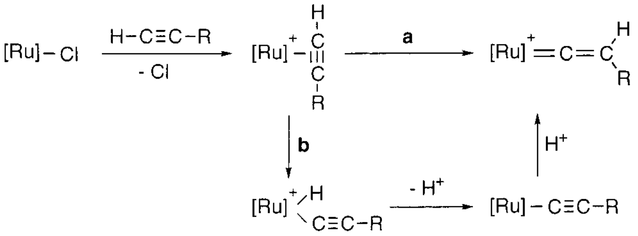
*Summary: Ab initio calculations on the model complexes $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]^+$ (**1**), $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$ (**2**), and $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CH_2)(PH_3)_2]^+$ (**3**) indicate that the thermodynamic stability of these compounds decreases according to the sequence **3** > **1** > **2**. According to this, the vinylidene complexes $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CHR)(P^iPr_3)_2]PF_6$ (R = Cy (**8**), Ph (**9**)) are prepared by deprotonation of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Cy (**4**), Ph (**5**)) with KOH in methanol and subsequent protonation of the resulting alkynyl derivatives $Os(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2$ (R = Cy (**6**), Ph (**7**)). The X-ray structure of $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CHPh)(P^iPr_3)_2]PF_6$ (**9**) is also reported.*

Cationic half-sandwich osmium vinylidene complexes are very scarce. The compounds of this type previously reported include $[Os(\eta^5\text{-}C_5Me_5)({=}C{=}CHR)(CO)(PPh_3)]PF_6$ (R = ^{t}Bu, Ph),[1] $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CHR)(CO)(P^iPr_3)]BF_4$ (R = Ph, $\overline{C{=}CH(CH_2)_3CH_2}$),[2] and $[Os(\eta^5\text{-}C_9H_7)({=}C{=}CHR)(PPh_3)_2]PF_6$ (R = H, $(CH_2)_3CH_2OH$, ^{t}Bu, $\overline{C{=}CH(CH_2)_nCH_2}$).[3] In contrast to osmium, the ruthenium analogues are well known and have attracted increasing attention in recent years, due to their connection with important stoichiometric and catalytic reactions of utility in organic synthesis.[4]

The procedure widely used in the preparation of cationic half-sandwich ruthenium vinylidene complexes involves the treatment of chloro starting materials with terminal alkynes in the presence of NH_4PF_6, $NaBPh_4$, or related salts.[5] From a mechanistic point of view, it has been proposed that these reactions proceed via π-alkyne intermediates followed by tautomerization. The isomerization of the π-alkynes into vinylidenes appears to occur by two alternative pathways (**a** and **b** in Scheme 1), via either intramolecular 1,2-hydrogen migration or hydride−alkynyl species.[6] It is taken for granted that once the π-alkyne intermediates are formed, the pathways **a** and **b** are competitive and the choice of one or the other is determined by the electron density of the metallic fragment. Basic metallic fragments favor pathway **b**. Thus, it has been observed that $Ru(\eta^5\text{-}C_5Me_5)Cl(^iPr_2PCH_2CH_2P^iPr_2)$ reacts with terminal alkynes in the presence of $NaBPh_4$ to give vinylidene derivatives via hydride−alkynyl−ruthenium(IV) intermediates, while under the same conditions the formation of the analogous vinylidene complexes containing the less basic $[Ru(\eta^5\text{-}C_5H_5)(^iPr_2PCH_2CH_2P^iPr_2)]^+$ unit proceeds through 1,2-hydrogen migration.[5c,f]

Scheme 1



On the other hand, for osmium, we have observed that in the presence of terminal alkynes the $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ unit affords vinylidene compounds, via π-alkyne intermediates by 1,2-hydrogen shift,[7] while the less basic $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metallic fragment gives the hydride−alkynyl−osmium(IV) derivatives $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$;[8] i.e., the metallic fragment with higher basicity favors pathway **a**.

To understand the behavior of the osmium systems, we have carried out ab initio calculations on the model complexes $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]^+$ (**1**), $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$ (**2**), and $[Os(\eta^5\text{-}C_5H_5)$-

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[1] Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.

[2] Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878.

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[4] (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313. (c) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599. (d) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193−195*, 977. (e) Bruneau, C.; Dixneauf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (f) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309.

[5] See for example: (a) Lagadec, R. L.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030. (b) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1757. (c) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (e) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 950. (f) Bustelo, E., Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563.

[6] Theoretical studies support both mechanisms. See for example: (a) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. (b) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (c) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. (d) Stegman, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089.

[7] Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657.

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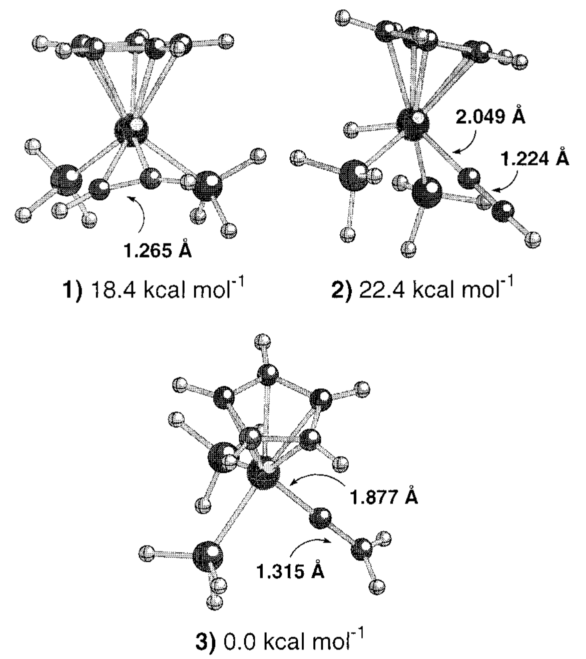
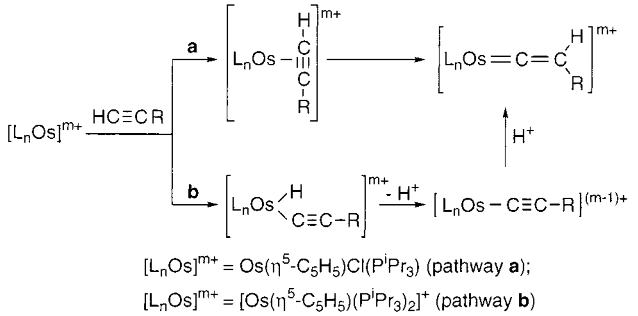


Figure 1. Optimized structures and relative energies (kcal·mol^{-1}) of $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]^+$ (**1**), $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$ (**2**), and $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CH_2)(PH_3)_2]^+$ (**3**) obtained by ab initio calculations at the DFT/B3LYP level using the LANL2DZ basis set and ECP for Os and 6-31G for the rest of the atoms.

$({=}C{=}CH_2)(PH_3)_2]^+$ (**3**). Figure 1 shows their optimized structures and relative energies at the DFT/B3LYP level.[9] The results show that the π-alkyne model complex **1** is 4.0 kcal·mol^{-1} more stable than the hydride–alkynyl model compound **2**; that is, the π-alkyne species $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CR)(PR'_3)_2]^+$ cannot be intermediates in the formation of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(PR'_3)_2]^+$, since they appear to be thermodynamically more stable than the products of the oxidative addition. The fact that the reactions of $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ with terminal alkynes afford selectively $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$ must be rationalized assuming that the oxidative addition of the H–C(sp) bond of the alkyne is a kinetically favored process with regard to the coordination of the carbon–carbon triple bond.[10] So, for osmium, pathways **a** and **b** are not competitive processes on a common intermediate but independent reactions without any common intermediate (Scheme 2).

Scheme 2



The theoretical calculations also indicate that the vinylidene model complex **3** is 22.4 kcal·mol^{-1} more stable than **2**. However, the complexes $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$ do not evolve into the corresponding vinylidenes in the solid state or in solution, in contrast to that observed for the related hydride–alkynyl–ruthenium(IV) compounds.[5c,e,f]

It has been proposed, according to Schemes 1 and 2, that once the hydride–alkynyl intermediates are formed, the hydride dissociates as a proton, yielding alkynyl species. Protonation of these intermediates at the C_β atom affords the vinylidene derivatives. As a consequence of the common ion effect, it has been experimentally proved that the addition of strong acids inhibits the formation of the vinylidenes.[5c] The different behavior observed for the hydride–alkynyl–ruthenium(IV) and –osmium(IV) suggests that the basicity of the osmium species $Os(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2$ is higher than that of the related ruthenium one. This agrees with the well-known increase of the basicity of transition metal complexes as the metal is replaced by successively heavier metals from the same group.[12] As a consequence of the high basicity of the $Os(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2$ species, the necessary energy for the dissociation of H^+ from $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$ imposes a high activation barrier for the isomerization of the hydride–alkynyl–osmium(IV) complexes into the corresponding vinylidene derivatives.

In agreement with the theoretical results and the pathway **b** of Scheme 2, the vinylidene compounds of the type $[Os(\eta^5\text{-}C_5H_5)({=}C{=}CHR)(P^iPr_3)_2]^+$ can be prepared by deprotonation of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$ with strong bases and subsequent protonation of the resulting alkynyl–osmium(II) intermediates (Scheme 3).

Treatment of the previously reported compounds $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Cy (**4**), Ph (**5**)) with a 1:10 excess of KOH in methanol affords the alkynyl derivatives $Os(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2$ (R = Cy (**6**), Ph (**7**)) in good yield, after 1 h at room temperature. In the IR spectra of these compounds in Nujol, the most noticeable feature is the presence of the ν(C≡C) vibrations, which appear at 2069 (**6**) and 2074 (**7**) cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectra, the OsC(sp) resonances are observed as triplets at 65.5 (**6**) and 93.1 (**7**) ppm with C–P coupling constants of about 18 Hz, whereas the

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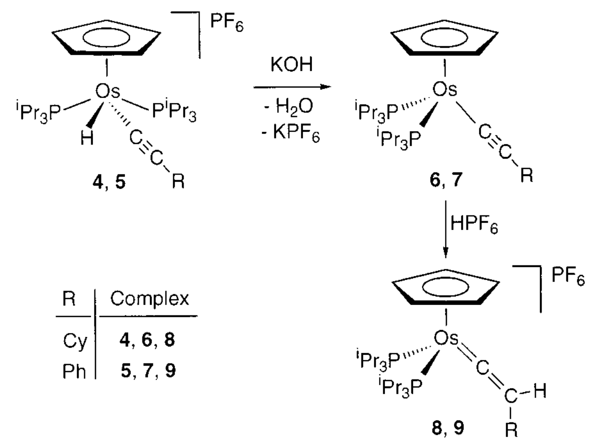
[9] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[10] We have previously reached the same conclusion in an intuitive manner.[8] In this context, it should be noted that the coordination of the alkyne requires a parallel approach of the carbon–carbon triple bond to the phosphorous–phosphorous vector, while the oxidative addition of the alkyne should take place via a perpendicular approach of the H–C(sp) bond to the P–P vector. Furthermore, a heterolytic H–C activation of the alkyne cannot be discarded, due to the well-known acidic character of the H–C(sp) hydrogen of the alkynes.[11]

[11] See for example: Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 3486.

[12] (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (b) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155.

Scheme 3



C_β(sp) resonances appear as singlets at about 109 ppm. The $^{31}P\{^1H\}$ NMR spectra show singlets at about 4 ppm.

According to Scheme 3, the addition of 1.0 equiv of HPF_6 in water to diethyl ether solutions of **6** and **7** leads to the vinylidenes $[Os(\eta^5\text{-}C_5H_5)(=C=CHR)(P^iPr_3)_2]PF_6$ (R = Cy (**8**) Ph (**9**)) in high yields. The ^1H NMR spectra of these compounds show the =CH resonances of the vinylidene ligands at 2.54 (**8**) and 2.79 (**9**) ppm. In the $^{13}C\{^1H\}$ NMR spectra the C_α atoms of the vinylidenes display triplets at 300.6 (**8**) and 307.1 (**9**) ppm with coupling constants of 10.9 (**8**) and 12.0 (**9**) Hz, whereas the resonances corresponding to the C_β atoms appear as singlets at 119.3 (**8**) and 117.0 (**9**) ppm. The $^{31}P\{^1H\}$ NMR spectra show singlets at 8.6 (**8**) and 9.3 (**9**) ppm.

Complex **9** has been further characterized by an X-ray crystallographic study. The structure has two chemical equivalent but crystallographically independent molecules of complex **9** in the asymmetric unit. A drawing of one of them is shown in Figure 2. The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The P(1)–Os–C(1) and P(2)–Os–C(1) angles are 96.3(2)° and 95.5(2)° and 89.0(3)° and 93.7(2)°, respectively, while the P(1)–Os–P(2) angle (102.52(7)° and 101.54(7)°) strongly deviates from the ideal value of 90°. This is due to the large steric hindrance experienced by the triisopropylphosphine groups, as a consequence of their large cone angle (160°).[13] Similar values (between 102.7(1)° and 106.72(4)°) have been found in other transition-metal compounds containing two bulky phosphines mutually *cis* disposed.[8,14]

The vinylidene ligand is bound to the osmium in a nearly linear fashion with Os–C(1)–C(2) angles of 166.7(7)° and 171.1(7)°. The Os–C(1) (1.793(8) and 1.794(8) Å) and C(1)–C(2) (1.337(10) and 1.346(10) Å) bond lengths compare well with those found in other osmium–vinylidene complexes[15] and support the vinylidene formulation.

The structural parameters of the model complex **3** are in agreement with those obtained from the X-ray diffraction analysis for **9**. The main difference between the structures of **3** and **9** is the P–Os–P angle. The calculated value (92.7°) is significantly lower than that obtained from the X-ray diffraction analysis. This indicates that, in fact, the deviation observed from the ideal value of 90° in **9** is mainly due to the large steric hindrance experienced by the triisopropylphosphine groups. The same relationship has been previously observed between the structures of the carbyne compounds $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH=CH_2)(PH_3)_2]^{2+}$ and $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH=CPh_2)(P^iPr_3)_2]^{2+}$.[8]

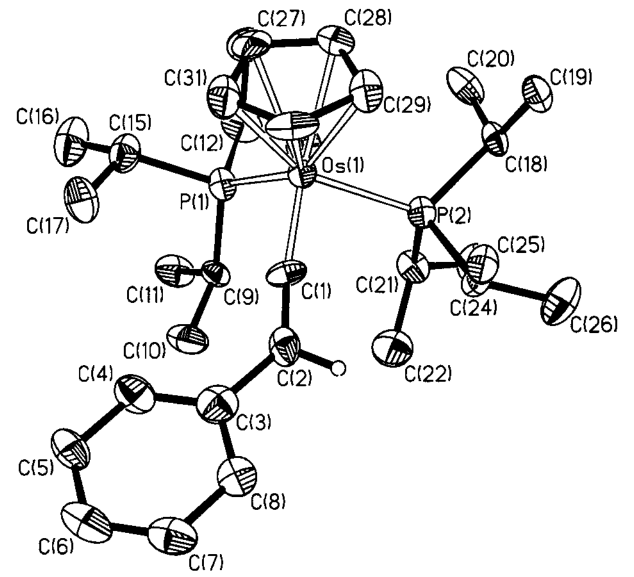


Figure 2. Molecular diagram for the cation of $[Os(\eta^5\text{-}C_5H_5)(=C=CHPh)(P^iPr_3)_2]PF_6$ (**9**). Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (deg): Os(1)–C(1) 1.793(8) and 1.794(8), C(1)–C(2) 1.337(10) and 1.346(10); P(1)–Os(1)–P(2) 102.52(7) and 101.54(7), P(1)–Os(1)–C(1) 96.3(2) and 95.5(2), P(2)–Os(1)–C(1) 89.0(3) and 93.7(2), Os(1)–C(1)–C(2) 166.7(7) and 171.1(7), C(1)–C(2)–C(3) 134.8(8) and 126.9(8).

In summary, although similarly to ruthenium,[5d] the cationic half-sandwich osmium vinylidene complexes $[Os(\eta^5\text{-}C_5H_5)(=C=CHR)(P^iPr_3)_2]^+$ are the thermodynamically favored products from the reactions of $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ with terminal alkynes, they cannot be obtained in a one-pot synthesis reaction because (i) the oxidative addition of the H–C(sp) bond of the alkyne is kinetically favored with regard to the coordination of the carbon–carbon triple bond, and (ii) the high basicity of the alkynyl intermediates $Os(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2$ imposes a high energy for the dissociation of H^+ from $[OsH(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2]^+$, which is the rate-determining step for the transformation of the hydride–alkynyls into vinylidenes. Thus, the formation of the vinylidenes $[Os(\eta^5\text{-}C_5H_5)(=C=CHR)(P^iPr_3)_2]^+$ from $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ and terminal alkynes requires a three-step procedure involving (i) oxidative addition of the H–C(sp) bond of the alkyne to the metallic center of the starting complex, (ii) deprotonation of the resulting hydride–alkynyl derivatives $[OsH(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2]^+$ with strong bases, and (iii) protonation of the resulting alkynyls $Os(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2$.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by known

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[13] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[14] (a) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27. (b) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L.; Steinert, P.; Werner, H. *Organometallics* **1997**, *16*, 6010. (c) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184.

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procedures and distilled under argon prior to use. The starting materials [OsH(η^5-C_5H_5)(C≡CR)(P^iPr_3)$_2$]PF_6 (R = Cy (**4**), Ph (**5**)) were prepared as previously reported.[8]

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).

Preparation of Os(η^5-C_5H_5)(C≡CCy)(P^iPr_3)$_2$ (6). A suspension of **4** (105 mg, 0.13 mmol) in MeOH (10 mL) was treated with an excess of KOH (70 mg, 1.25 mmol). After the mixture was stirred for 2 h at room temperature, the resulting solution was evaporated to dryness. The residue was extracted with 10 mL of toluene, and the filtrate was vacuum-dried. The pale yellow oil was treated with 1 mL of cold pentane to afford a white solid, which was dried in a vacuum. Yield: 44.6 mg (52%). Anal. Calcd for $C_{31}H_{58}OsP_2$: C, 55.00; H, 7.74. Found: C, 54.90; H, 7.41. IR (Nujol, cm^{-1}): ν(C≡C) 2069 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.76 (s, 5 H, Cp), 2.94 (br t, 1 H, $^3J_{HP}$ = 10.2 Hz, Os=C=CH), 2.39 (m, 6 H, PCH), 2.10−0.90 (11 H, Cy), 1.26 (dvt, 18 H, $^3J_{HH}$ = 7.5 Hz, N = 12.0 Hz, PCHCH_3); 1.16 (dvt, 18 H, $^3J_{HH}$ = 7.5 Hz, N = 12.0 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K): δ 109.1 (s, ≡*C*Cy); 74.6 (s, Cp), 65.5 (t, $^2J_{CP}$ = 18.4 Hz, OsC≡), 36.4, 33.8, 26.9, 26.2 (all s, Cy), 30.6 (second-order system, PCH), 21.6, 21.0 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 3.9 (s). MS (FAB$^+$): m/z 685 (M$^+$), 523 (M$^+$ − P^iPr_3).

Preparation of Os(η^5-C_5H_5)(C≡CPh)(P^iPr_3)$_2$ (7). Complex **7** was prepared analogously as described for **6** starting from **5** (110 mg, 0.13 mmol). Yield: 80 mg (75%). Anal. Calcd for $C_{31}H_{52}OsP_2$: C, 55.01; H, 7.71. Found: C, 54.79; H, 7.53. IR (Nujol, cm^{-1}): ν(C≡C) 2074 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.60−6.90 (5 H, Ph); 4.79 (s, 5 H, Cp), 2.36 (m, 6 H, PCH), 1.23 (dvt, 18 H, $^3J_{HH}$ = 7.1 Hz, N = 11.7 Hz, PCHCH_3), 1.11 (dvt, 18 H, $^3J_{HH}$ = 7.1 Hz, N = 11.7 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K): δ 132.2, (s, C_{ipso} Ph), 131.3 (s, C_{para} Ph), 128.1, 122.7 (s, C_{ortho}, C_{meta} Ph), 109.9 (s, ≡*C*Ph), 93.1 (t, $^2J_{CP}$ = 18.5 Hz, OsC≡), 75.1 (s, Cp), 30.4 (second-order system, PCH), 21.2, 20.8 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 4.6 (s). MS (FAB$^+$): m/z 679 (M$^+$ + H).

Preparation of [Os(η^5-C_5H_5)(=C=CHCy)(P^iPr_3)$_2$]PF_6 (8). To a solution of **6** (58 mg, 0.084 mmol) in 6 mL of diethyl ether was added a solution of HPF_6 (12 μL, 75% in water, 0.083 mmol). The resulting suspension was decanted, and the solid was washed with diethyl ether (2 × 4 mL). A pink solid was isolated. Yield: 78 mg (80%). Anal. Calcd for $C_{31}H_{59}F_6OsP_3$: C, 44.91; H, 7.19. Found: C, 44.51; H, 7.12. IR (Nujol, cm^{-1}): ν(C=C) 1651 (s), ν(PF_6) 839 (s). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.68 (s, 5 H, Cp), 2.54 (m, 1 H, Os=C=CH), 2.36 (m, 6 H, PCH), 1.80−0.90 (11 H, Cy), 1.26 (dvt, 18 H, $^3J_{HH}$ = 7.2 Hz, N = 13.2 Hz, PCHCH_3), 1.21 (dvt, 18 H, $^3J_{HH}$ = 7.2 Hz, N = 13.2 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K, plus APT): δ 300.6 (−, t, $^2J_{CP}$ = 10.9 Hz, Os=*C*=C), 119.3 (+, s, Os=C=*C*), 86.5 (+, s, Cp), 37.4, 26.2, 25.4 (−, s, CH_2 in Cy), 31.2 (+, second-order system, PCH), 29.9 (+, s, CH in Cy), 20.3, 20.1 (+, s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 8.6 (s, P^iPr_3), −145.2 (sept, J_{HH} = 714 Hz, PF_6). MS (FAB$^+$): m/z 685 (M$^+$), 523 (M$^+$ − P^iPr_3).

Preparation of [Os(η^5-C_5H_5)(=C=CHPh)(P^iPr_3)$_2$]PF_6 (9). To a solution of **7** (30.8 mg, 0.045 mmol) in 5 mL of diethyl ether was added a solution of HPF_6 (7 μL, 75% in water, 0.046 mmol). The resulting suspension was decanted, and the solid was washed with diethyl ether (2 × 3 mL). A dark pink solid was isolated. Yield: 29 mg (78%). Anal. Calcd for $C_{31}H_{53}F_6OsP_3$: C, 45.25; H, 6.49. Found: C, 45.68; H, 6.58. IR (Nujol, cm^{-1}): ν(C=C) 1622 (s), ν(PF_6) 841 (s). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.40−6.90 (5 H, Ph), 5.83 (s, 5 H, Cp), 2.79 (br s, 1 H, Os=C=CH), 2.42 (m, 6 H, PCH), 1.26 (dvt, 18 H, $^3J_{HH}$ = 7.2 Hz, N = 13.5 Hz, PCHCH_3), 1.22 (dvt, 18 H, $^3J_{HH}$ = 7.2 Hz, N = 13.5 Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K, plus APT): δ 307.1 (−, t, $^2J_{CP}$ = 12.0 Hz, Os=*C*=C), 128.6, 127.8 (+, s, C_{ortho}, C_{meta} Ph), 126.4 (+, s, C_{para} Ph), 125.1 (−, s, C_{ipso} Ph), 117.0 (+, s, Os=C=*C*), 86.8 (+, s, Cp), 31.5 (+, second-order system, PCH), 20.6, 20.4 (+, s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 9.3 (s, P^iPr_3), −144.1 (sept, J_{HH} = 714 Hz, PF_6). MS (FAB$^+$): m/z 679 (M$^+$), 517 (M$^+$ − P^iPr_3).

X-ray Structure Determination of 9. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **9** in dichloromethane. Crystal data for [Os(η^5-C_5H_5)(=C=CHPh)$_2$(P^iPr_3)$_2$]-PF_6 (**9**): $C_{31}H_{53}F_6OsP_3$ (MW = 822.84); triclinic space group, $P\bar{1}$; a = 8.8234(5) Å, b = 19.1665(11) Å, c = 20.1403(11) Å, α = 92.534(1)°, β = 99.327(1)°, γ = 91.696(1)° at 173.0(2); V = 3355.3(3) Å^3; Z = 4. An irregular crystal (0.12 × 0.02 × 0.02 mm) was mounted on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the entire sphere by a combination of four sets. The cell parameters were determined and refined by least-squares fit of 3533 collected reflections. Each frame exposure time was 30 s covering 0.3° in ω (3° ≤ 2θ ≤ 60°, 41 672 reflections, 15 867 unique, merging R factor 0.1136). The first 100 frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[16] The structure was solved by Patterson and Fourier methods using SHELXS.[16] Full matrix least-squares refinement was carried out using SHELXL97[16] minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and goodness of fit (S) are based on F^2, conventional R factors are based on F. Final R_1 [$F^2 > 2\sigma(F^2)$] = 0.0456, wR_2 [all data] = 0.0796, and S [all data] = 0.602.

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Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles for **9**. This material is available via the Internet at http://pubs.acs.org.

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[16] *SAINTPLUS* and *SHELXTL* v. 6.1 software packages; Bruker Analytical X-ray Systems, Madison, WI, 2000.