Formation of an Asymmetric Acyclic Osmium−Dienylcarbene Complex

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*Summary: The styryl-allenylidene complex [Os{(E)-CH═CHPh}(═C═C═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**2**) reacts with HBF$_4$ to give the styryl-alkenylcarbyne [Os{(E)-CH═CHPh}(≡CCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ (**3**), which in acetonitrile evolves into the dienylcarbene derivative [Os{═C[(E)-CH═CHPh]-CH═CPh$_2$}(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ (**4**) by means of the concerted migration of the styryl ligand from the metal center to the carbyne C$_\alpha$ atom. A kinetic study and DFT calculations on the transformation of **3** into **4** are reported.*

Asymmetric dienyl ketones (**Ia** in Chart 1) are important intermediates in the synthesis of a wide variety of organic compounds. They not only are Michael acceptors but also undergo the Nazarov reaction to provide an efficient route to cyclopentenones.[1] Transition metal dienylcarbene complexes (**Ib** in Chart 1) are a class of compound analogues in which the oxygen atom has been formally replaced by a transition metal and its associated ligands.

Dienylcarbene complexes are very scarce. A few compounds containing a cyclic dienylcarbene ligand have been reported.[2] Some [P,C,P]-pincer derivatives with a ligand skeleton formed by a symmetrical acyclic dienylcarbene moiety have also been described.[3] However, as far as we know, simple **Ib** structures are unknown.

Osmium is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds.[4] A clear example is the hydride-carbyne complexes OsHCl$_2$(≡CR)(PR′$_3$)$_2$, which are oxidized isomers of the unknown compounds OsCl$_2$(═CHR)(PR′$_3$)$_2$.[5] However, it should also be taken into account that the kinetics and thermodynamics of the redox equilibria depend critically on the electronic properties of the ligands of the complexes, and therefore, both are easily governable.[6] The equilibrium between hydride-carbyne and carbene species is not an exception. The sequential substitution of the chloride ligands in OsHCl$_2$(≡CCH═CPh$_2$)(P^{i}Pr$_3$)$_2$ by acetonitrile molecules produces a sequential decrease of the activation energy for the hydride migration from the metal center to the carbyne carbon atom, as a consequence of the gradual decrease of the electron richness of the metal center.[7] The tendency of osmium to afford the oxidized isomers along with our ability to control the redox equilibria facilitates the assembly of organic fragments, which allows the preparation of osmium−dienylcarbene derivatives with the **Ib** skeleton (Scheme 1).

Chart 1

Ia **Ib**

We have recently shown that the treatment at 243 K of acetonitrile solutions of the dicationic hydride-alkenylcarbyne complex [OsH(≡CCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ with ^{t}BuOK produces the selective abstraction of the C$_\beta$-H hydrogen atom of the alkenylcarbyne ligand. The deprotonation leads to the hydride-allenylidene derivative [OsH(═C═C═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**1**), which reacts with phenylacetylene to give the styryl-allenylidene compound [Os{(*E*)-CH═CHPh}(═C═C═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**2**), as a result of the insertion of the carbon−carbon triple bond of the alkyne into the Os−H bond.[8] Now we have observed that, similarly to **1**, complex **2** has the typical behavior of Lewis base transition metal complexes. Thus, as expected for an electron-rich species,[6a,9] it reacts with HBF$_4$. The addition at 243 K of 2.0 equiv of this acid to an acetonitrile solution of **2** leads to the

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(1) See for example: (a) Pellisier, H. *Tetrahedron* **2005**, *61*, 6479. (b) Frontier, A. J.; Collison, C. *Tetrahedron* **2005**, *61*, 7577.

(2) (a) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2458. (b) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982**, *21*, 1321. (c) Wadepohl, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 127. (d) Wadepohl, H.; Galm, W.; Pritzow, H.; Wolf, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1459. (e) Edwards, A. J.; Gallop, M. A.; Johnson, B. F. G.; Köhler, J. U.; Lewis, J.; Raithby, P. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1093. (f) Wadepohl, H.; Galm, W.; Pritzkow, H.; Wolf, A. *Chem.−Eur. J.* **1996**, *2*, 1453. (g) Klosin, J.; Jones, W. M.; Abboud, K. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 1101. (h) Cave, G. W. V.; Hallett, A. J.; Errington, W.; Rourke, J. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 3270. (i) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959. (j) Aime, S.; Arce, A. J.; Giusti, D.; Gobetto, R.; Steed, J. W. *J. Chem. Soc., Dalton Trans.* **2000**, 2215. (k) Albrecht, M.; Stoeckli-Evans, H. *Chem. Commun.* **2005**, 4705. (l) Schuster, O.; Raubenheimer, H. G. *Inorg. Chem.* **2006**, *45*, 7997. (m) Schneider, S. K.; Roembke, P.; Julius, G. R.; Raubenheimer, H. G.; Herrmann, W. A. *Adv. Synth. Catal.* **2006**, *348*, 1862.

(3) (a) Weng, W.; Parkin, S.; Ozerov, O. Y. *Organometallics* **2006**, *25*, 5345. (b) Weng, W.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 3315.

(4) (a) Caulton, K. G. *J. Organomet. Chem.* **2001**, *56*, 617–618. (b) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1. (c) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (d) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (e) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.

(5) (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (b) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999. (c) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951.

(6) See for example: (a) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2037. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129.

(7) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184.

(8) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965.

(9) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2007**, *129*, 8850.

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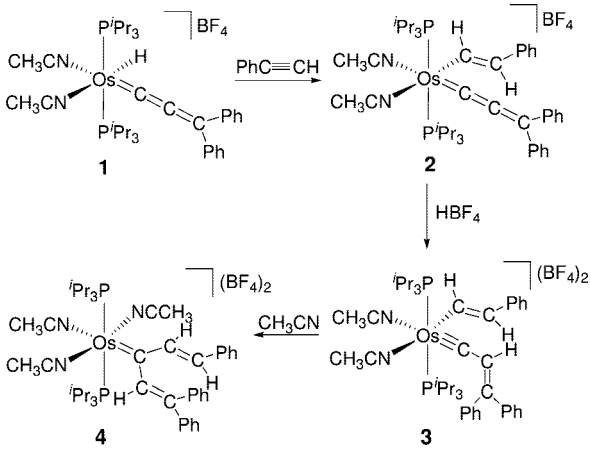
Scheme 1



dicationic styryl-alkenylcarbyne derivative [Os{(*E*)-CH═CHPh}-(≡CCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ (**3**), as a consequence of the selective protonation of the C$_\beta$ atom of the allenylidene ligand[10] in the presence of the nucleophilic C$_\beta$ atom of the styryl group.[11] Attempts to obtain **3** directly by reaction of the hydride-carbyne [OsH(≡CCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ with phenylacetylene were unsuccessful. At room temperature in 1,2-dichloroethane, reaction is not observed, while under reflux hydride migration from the metal center to the carbyne carbon atom takes place. Because the insertion of the alkyne requires the previous dissociation of the coordinated acetonitrile molecule *trans* disposed to the C-donor ligand, this suggests that a diphenylallenylidene ligand has a *trans* effect higher than an alkenylcarbyne group.

Complex **3** is isolated as a green solid in almost quantitative yield (97%). In the ^{1}H NMR spectrum in acetonitrile-d_3 at 243 K the vinyl C$_\beta$−H resonance of the alkenyl ligand appears at 8.60 ppm, whereas the C$_\alpha$−H signal is observed at 6.41 ppm. In accordance with the *E* stereochemistry at the carbon−carbon double bond, the value of the H$_\alpha$−H$_\beta$ coupling constant is 16.8 Hz. The C$_\beta$-H proton of the carbyne gives rise to a singlet at 5.88 ppm. As expected for the structure proposed in Scheme 1, the coordinated acetonitrile molecules display two singlets at 2.97 and 2.73 ppm. Characteristic resonances of the carbyne ligand in the ^{13}C{^{1}H} NMR spectrum are a triplet at 283.4 ppm, with a C−P coupling constant of 7.7 Hz, and two singlets at 169.4 (CPh$_2$) and 131.6 (CH). The alkenyl ligand generates two triplets at 140.8 (C$_\beta$) and 139.6 (C$_\alpha$) with C−P coupling constants of 1.9 and 3.4 Hz, respectively. In agreement with the *trans* disposition of the phosphine ligands, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 10.6 ppm.

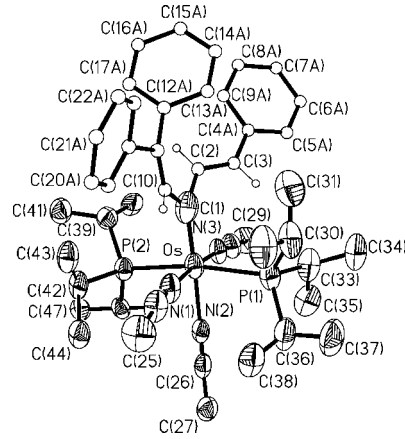


Figure 1. Molecular diagram of the cation of **4**. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.855(14), C(1)−C(2) 1.523(18), C(1)−C(10) 1.458(18), C(2)−C(3) 1.317(16), P(1)−Os−P(2) 170.31(12), N(1)−Os−N(3) 174.0(4), C(1)−Os−N(2) 177.4(5).

Complex **3** is unstable in acetonitrile. At room temperature the styryl ligand migrates from the metal center to the carbyne carbon atom to afford the osmium−dienylcarbene compound [Os{═C[(*E*)-CH═CHPh]CH═CPh$_2$}(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$](BF$_4$)$_2$ (**4**), which is isolated as a brown solid in 82% yield.

Figure 1 shows a view of the structure of the cation of this species. The geometry around the osmium atom can be described as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying *trans* positions (P(1)−Os−P(2) = 170.31(12)°). The perpendicular plane is formed by the acetonitrile molecules *mer* disposed (N(1)−Os−N(3) = 174.0(4)°) and the carbene group *trans* disposed to N(2) (C(1)−Os−N(2) = 177.4(5)°). The structure proves the formation of the dienylcarbene ligand. Its most conspicuous feature is the Os−C(1) bond length of 1.855(14) Å, which supports the Os═C double bond formulation.[7,9,12]

The substituents of C(1) lie in the plane containing the nitrogen atoms. As a result, the acetonitrile molecules *cis* disposed to the dienylcarbene ligand are chemically inequivalent. In agreement with this, the ^{1}H NMR spectrum of **4** in dichlomethane-d_2 at 203 K contains three resonances for the acetonitrile methyl groups at 2.94 and 2.92 ppm (*cis* to C(1)) and 2.86 (*trans* to C(1)). On raising the temperature, the *cis* acetonitrile methyl resonances coalesce, until finally only one resonance is observed at 228 K. This behavior can be understood as the result of the rotation of the dienylcarbene ligand around the Os−C(1) bond. The value of $\Delta G^{\ddagger}_{228}$ is 12.1 kcal·mol^{-1}, which agrees well with the values reported for transition metal carbene complexes.[7,13] The most noticeable resonances of the dienylcarbene ligand are a singlet at 7.99 ppm, due to the vinylic proton of the CH═CPh$_2$ unit, and two doublets at 7.35 and 6.86

(10) EHT-MO calculations indicate that the HOMO orbital of allenylidene complexes is mainly located at the C$_\beta$ atom of the allenylidene ligand. See: (a) Berke, H.; Huttner, G.; Von Seyerl, J. Z. *Naturforsch. B* **1981**, *36*, 1277. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (c) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A.; Schrickel, J. *Organometallics* **1996**, *15*, 3556. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (e) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434. (f) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585.

(11) X-ray diffraction and reactivity studies on osmium−alkenyl complexes indicate that for an adquate description of the bonding situation in this type of compounds a zwitterionic resonance form must also be considered. As a result of a significant contribution of the latter, the C$_\beta$ atoms of the alkenyl ligands have a strong nucleophilic character. See for example: (a) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798. (b) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. (c) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332. (d) Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2007**, *26*, 3260.

(12) See for example: (a) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858. (b) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (d) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (e) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129. (f) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 3082. (g) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 5140.

(13) See for example: (a) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (b) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 370.

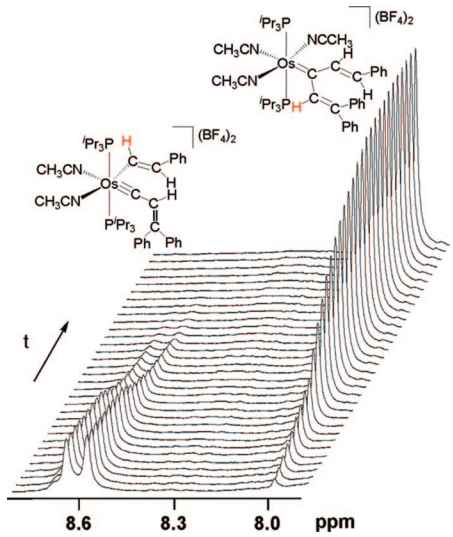


Figure 2. Stacked ^{1}H NMR spectra illustrating the transformation of **3** into **4** in CD_3CN at 313 K.

Table 1. Rate Constants for the Transformation of 3 into 4

T (K)	solvent	[CH_3CN]	k_{obs} (10^5 s^{-1})
295	CD_3CN		5.5 ± 1.5
295	CD_2Cl_2	11.20	6.8 ± 0.5
295	CD_2Cl_2	2.29	5.8 ± 0.9
295	CD_2Cl_2	0.23	7.0 ± 0.4
303	CD_3CN		15.5 ± 0.9
313	CD_3CN		44.1 ± 1.8
323	CD_3CN		102.3 ± 0.6
333	CD_3CN		248.8 ± 2.2
343	CD_3CN		550.3 ± 1.4

ppm corresponding to the styryl moiety. The value of the H−H coupling constants of 15.8 Hz strongly supports the *E* stereochemistry at the C═C double bond of the latter. In the $^{13}C\{^1H\}$ NMR spectrum the Os−C_α resonance is observed at 272.9 ppm as a triplet with a C−P coupling constant of 5.2 Hz. In agreement with the *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at −8.5 ppm.

The formation of **4** was followed by ^{1}H NMR spectroscopy by measuring the disappearance of the C_α−H resonance of the styryl ligand of **3** and the appearance of the vinyl resonance of the CH═CPh_2 unit of the dienylcarbene ligand of **4**. As shown in Figure 2, in acetonitrile-d_3, the decrease of **3** and the corresponding increase of **4** are exponential functions of the time, in agreement with a pseudo-first-order process.

To determine the role of acetonitrile during the reaction, we have also studied the formation of **4** in dichloromethane-d_2 as solvent and in the presence of acetonitrile concentrations between 0.23 and 11.20 M. Interestingly, at 295 K, the value of k_{obs} for the reaction carried out in acetonitrile as solvent, 5.5×10^{-5} s^{-1}, is similar to those found for the reactions carried out in dichloromethane-d_2 and in the presence of acetonitrile, between 5.8×10^{-5} and 7.0×10^{-5} s^{-1}. This result clearly shows that the formation rate of **4** is independent of the acetonitrile amount in the reaction medium. So, acetonitrile does not play any role in the formation of the dienylcarbene ligand. Its function is to trap the five-coordinated intermediate [Os{═C[(*E*)-CH═CHPh]CH═CPh_2}$(CH_3CN)_2(P^iPr_3)_2](BF_4)_2$ (**5**), which is generated as a result of the 1,2-shift of the styryl group from the metal center to the carbyne carbon atom. The values obtained for k_{obs} in the temperature range studied are collected in Table 1. The activation parameters obtained from the Eyring analysis are $\Delta H^{\ddagger} = 18.5 \pm 0.1$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -15.0 \pm 1.9$ cal·mol^{-1}·K^{-1}. The negative value of the activation entropy suggests that the migration of the styryl group to the carbyne carbon atom occurs by a concerted mechanism with a geometrically highly oriented transition state. To obtain information about its nature, we have performed DFT calculations (B3PW91) on the formation of **4** using PH_3, CCH═CH_2, and CH═CH_2 as a model of P^iPr_3, CCH═CPh_2, and CH═CHPh, respectively. The changes in free energy (ΔG) have been computed at 298.15 K and $P = 1$ atm. Figure 3 shows the energy profile, the optimized structures, and selected structural parameters.

The migration of the vinyl ligand of [Os(CH═CH_2)(≡CCH═CH_2)$(CH_3CN)_2(PH_3)_2]^{2+}$ (**3t**) to the carbyne carbon atom C_3 takes place through the transition state **TS**, which lies 13.4 kcal·mol^{-1} above **3t**. It results from the approach of the α-carbon atom C_1 of the vinyl group to C_3, until a C_1-C_3 distance of 1.946 Å. As a consequence of this, the C_1-Os-C_3 angle decreases from 94.2° in **3t** to 57.7° in **TS**.

The formation of the C_1-C_3 bond, with the corresponding rupture of the Os−C_1 bond (2.180 Å) of **TS**, generates the dienylcarbene derivative [Os{═$C(CH═CH_2)_2$}$(CH_3CN)_2(PH_3)_2]^{2+}$ (**5t**). The coordination sphere of the metal center of this species, which lies 18.3 kcal·mol^{-1} below **3t**, is completed with the C_1-C_2 double bond of the dienylcarbene ligand. The osmium−olefin coordination exhibits Os−C distances of 2.180 Å (Os−C_1) and 2.298 Å (Os−C_2), which agree well with those found in other osmium−olefin complexes (2.13−2.28 Å).[14] The displacement of the C_1-C_2 double bond by an acetonitrile molecule leads to [Os{═$C(CH═CH_2)_2$}$(CH_3CN)_3(PH_3)_2]^{2+}$ (**4t**). The process is exothermic by 24.8 kcal·mol^{-1}.

The formation of **4** is a process similar to the formation of the alkenylcarbene complex [Os(═CHCH═CPh_2)$(CH_3CN)_3(P^iPr_3)_2](BF_4)_2$ from the hydride carbyne [OsH(≡CCH═CPh_2)$(CH_3CN)_2(P^iPr_3)_2](BF_4)_2$.[7] The comparison of the results of the kinetic studies and the theoretical calculations on both processes indicates that the 1,2-hydrogen shift has an activation energy greater by 6.0 kcal·mol^{-1} than the migration of the alkenyl group. At first glance, one could think that this is surprising, since an s orbital is less directional than the sp^2 hybrids and, therefore, the s orbitals can have more multicentered bonding at the transition state, which should lead to lower activation energy. In this context, it should be noted that, according to the molecular orbital describing the forming bond at the isocontour level of 0.04 au (**TS**, HOMO−3; Figure 3), it appears to be clear that the interaction between the alkenyl and alkenylcarbyne ligands takes place through the p orbitals at the α-carbon atoms of both groups.

(14) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. (c) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (d) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141. (e) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (f) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, *19*, 3260. (g) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681. (h) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (i) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomás, J. *Organometallics* **2003**, *22*, 2087. (j) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (k) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416. (l) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (m) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 2030. (n) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 5180. (o) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Inorg. Chem.* **2006**, *45*, 10162.

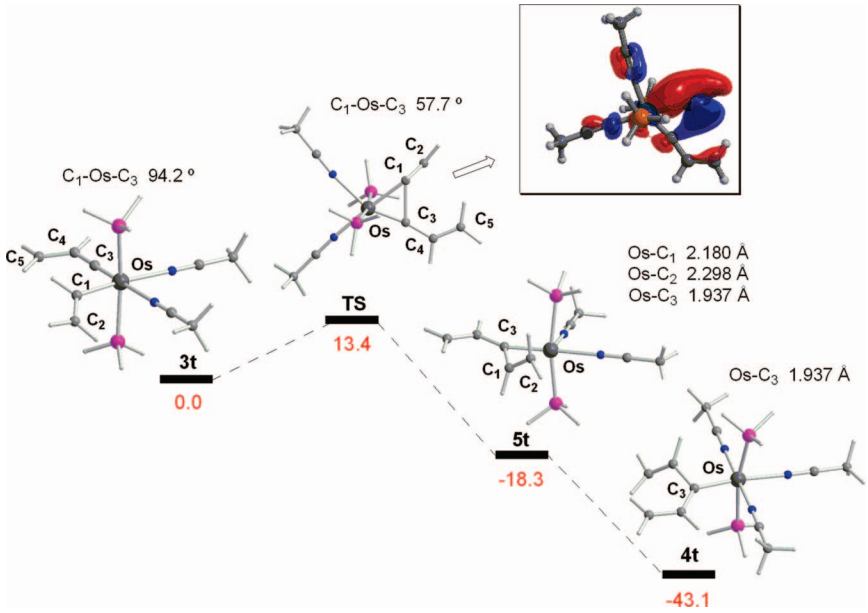


Figure 3. Relative energies (ΔG, 298 K, 1 atm; kcal·mol^{-1}) for the transformation of **3t** into **4t**.

In conclusion, because for osmium the α-substituent migration equilibrium in carbon donor ligands can be shifted toward the oxidized or reduced forms, regulating the electron richness of the metal center with the coligands of the complexes, dienylcarbene derivatives can be obtained by formal insertion of alkynes into the C_α−H bond of alkenylcarbene ligands. Thus, starting from an equilibrium between species alkenylcarbene and hydride-alkenylcarbyne, we had previously obtained an styryl-allenylidene compound.[7,8] Now, using the latter, we have prepared a novel dicationic osmium−dienylcarbene derivative by protonation of the allenylidene ligand of an styryl-allenylidene complex and subsequent migration of the styryl group from the metal center to the C_α atom of the resulting alkenylcarbyne.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by standard procedures and distilled under argon prior to use. The starting material [Os(*E*)-(CH=CHPh)(=C=C=CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**2**) was prepared by the published method.[8] Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H$_3$PO$_4$ (^{31}P{^{1}H}). Coupling constants, *J* and *N*, are given in hertz.

Preparation of [Os{(*E*)-CH=CHPh}(≡CCH=CPh$_2$)(CH$_3$CN)$_2$-(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (3). An orange solution of **2** (422 mg, 0.434 mmol) in 7 mL of acetonitrile at 243 K was treated with HBF$_4$·OEt$_2$ (59 μL, 0.868 mmol). Immediately, the reaction mixture became green. After 5 min at 243 K, the resulting mixture was concentrated. The addition of diethyl ether at 243 K gave rise to the formation of a green solid, which was washed with diethyl ether and dried in vacuo. Yield: 446 mg (97%). Anal. Calcd for C$_{45}$H$_{66}$B$_2$F$_8$N$_2$OsP$_2$: C 50.95; H 6.27; N 2.64. Found: C 50.75; H 6.31; N 2.61. IR (Nujol, cm^{-1}): ν(C≡N) 2318 (w), 2288 (w); ν(C=C) 1587 (m); ν(BF) 1058 (vs). ^{1}H NMR (300 MHz, CD$_3$CN, 243 K): δ 8.60 (d, J_{H-H} = 16.8, 1H, =CHPh), 7.8−7.1 (m, 15H, Ph), 6.41 (d, J_{H-H} = 16.8, 1H, OsCH=), 5.88 (s, 1H, −CH=), 2.97 and 2.73 (both s, 6H, CH$_3$CN), 2.81 (m, 6H, PCH), 1.36 (dvt, *N* = 14.4, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), 1.15 (dvt, *N* = 13.9, J_{H-H} = 7.0, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_3$CN, 243 K): δ 10.6 (s). ^{19}F NMR (282.3 MHz, CD$_3$CN, 293 K): δ −150.2 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_3$CN, 243 K): δ 283.4 (t, J_{C-P} = 7.7, Os≡C), 169.4 (s, =CPh$_2$), 140.8 (t, J_{C-P} = 1.9, C$_{ipso}$−Ph$_{vinyl}$), 139.8 (t, J_{C-P} = 3.4, =CHPh), 139.2 and 138.9 (both s, C$_{ipso}$−Ph$_{carbyne}$), 135.6 and 133.0 (s, CN), 131.6 (s, =CH−), 134−126 (all s, CH$_{Ph}$), 126.0 (s, OsCH), 26.9 (vt, *N* = 12.7, PCH), 19.7 and 19.2 (both s, PCH*C*H$_3$), 5.1 and 5.0 (s, *C*H$_3$CN).

Preparation of [Os{=C(CH=CHPh)(CH=CPh$_2$)}(CH$_3$CN)$_3$-(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (4). A green solution of **3** (446 mg, 0.420 mmol) in 10 mL of acetonitrile was stirred for 12 h at room temperature. The resulting mixture was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether afforded a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 379 mg (82%). Anal. Calcd for C$_{47}$H$_{69}$B$_2$F$_8$N$_3$OsP$_2$: C 51.23; H 6.31; N 3.81. Found: C 50.72; H 6.23; N 3.77. IR (Nujol, cm^{-1}): ν(C≡N) 2320 (w), 2273 (w); ν(C=C) 1585 (m), 1566 (m); ν(BF) 1061 (vs). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): δ 7.99 (s, 1H, Os=C(CH=CPh$_2$)), 7.6−7.0 (m, 15H, Ph), 7.35 (d, J_{H-H} = 15.8, 1H, Os=C(C*H*=CHPh)), 6.86 (d, J_{H-H} = 15.8, 1H, Os=C(CH=C*H*Ph)), 2.95 (s, 6H, CH$_3$CN), 2.93 (s, 3H, CH$_3$CN), 2.63 (m, 6H, PCH), 1.39 (dvt, *N* = 13.0, J_{H-H} = 6.6, 18H, PCHC*H*$_3$), 1.37 (dvt, *N* = 13.0, J_{H-H} = 6.6, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ −8.5 (s). ^{19}F NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ −150.2 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.5 MHz, CD$_2$Cl$_2$, 293 K): δ 272.9 (t, J_{C-P} = 5.2, Os=C), 152.8 (s, Os=C(*C*H=CPh$_2$)), 150.2 (s, Os=C(*C*H=CHPh)), 145.0 (s, =CPh$_2$), 141.3 and 140.4 (both s, C$_{ipso}$−Ph), 137.1 (s, CN), 135.9 (s, C$_{ipso}$−Ph$_{vinyl}$), 127.3 (s, =CHPh), 130.0, 129.7, 129.6, 129.5, 129.1, 128.3, 128.1, 127.8, and 127.7 (all s, CH$_{Ph}$), 126.2 and 126.1 (s, CN), 26.2 (vt, *N* = 11.9, PCH), 19.3 and 19.2 (both s, PCH*C*H$_3$), 5.0, 4.9 and 4.0 (s, *C*H$_3$CN).

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Supporting Information Available: X-ray analysis, computational details, kinetic analysis for the styryl-alkenylcarbyne to dienylcarbene transformation, orthogonal coordinates of theoretical structures, and crystal structure determination, including a CIF file giving crystal data for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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