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From Tetrahydroborate− to Aminoborylvinylidene−Osmium Complexes via Alkynyl−Aminoboryl Intermediates

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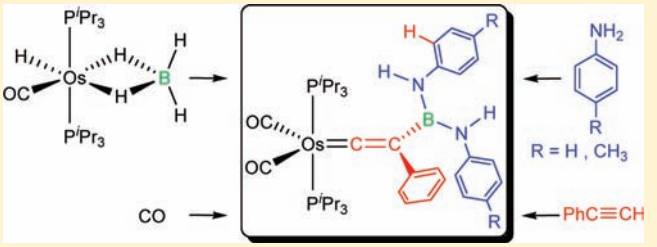
Supporting Information

ABSTRACT: The tetrahydroborate $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**1**) reacts with aniline and *p*-toluidine to give the aminoboryl derivatives $Os\{B(NHC_6H_4R)NHCCHCHC(R)CHC\}(CO)(P^iPr_3)_2$ (R = H (**2**), CH_3 (**3**)) and four H_2 molecules. Treatment of **2** and **3** with phenylacetylene gives $Os\{B(NHC_6H_4R)_2\}(C{\equiv}CPh)(CO)(P^iPr_3)_2$ (R=H (**4**), CH_3 (**5**)), which react with HBF_4 to afford the amino(fluoro)boryl species $Os\{BF(NHC_6H_4R)\}(C{\equiv}CPh)(CO)(P^iPr_3)_2$ (R = H (**6**), CH_3 (**7**)). In contrast to HBF_4, the addition of acetic acid to **4** and **5** induces the release of phenylacetylene and the formation of the six-coordinate derivatives $Os\{B(NHC_6H_4R)_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2$ (R = H (**8**), CH_3 (**9**)). The coordination number six for **4** and **5** can be also achieved by addition of CO. Under this gas $Os\{B(NHC_6H_4R)_2\}(C{\equiv}CPh)(CO)_2(P^iPr_3)_2$ (R = H (**10**), CH_3 (**11**)) are formed. In toluene, these alkynyl−aminoboryl compounds evolve into the aminoborylvinylidenes $Os\{{=}C{=}C(Ph)B(NHC_6H_4R)_2\}(CO)_2(P^iPr_3)_2$ (R = H (**12**), CH_3 (**13**)) via a unimolecular 1,3-boryl migration from the metal to the C_β atom of the alkynyl ligand. Similarly to **4** and **5**, complexes **6** and **7** coordinate CO to give $Os\{BF(NHC_6H_4R)\}(C{\equiv}CPh)(CO)_2(P^iPr_3)_2$ (R = H (**15**), CH_3 (**16**)), which evolve to $Os\{{=}C{=}C(Ph)BF(NHC_6H_4R)\}(CO)_2(P^iPr_3)_2$ (R = H (**17**), CH_3 (**18**)).



INTRODUCTION

The chemistry of transition metal complexes of boron is a field of great current interest[1] for its transversal implications including the functionalization of organic molecules,[2] the preparation of new oligomers and polymers,[3] and the reversible dehydrocoupling of amineboranes and related compounds.[3a,4]

Boryl complexes, $M-BR_2$, are the subclass of compounds with metal−boron bonds exhibiting the strongest potential for the functionalization of hydrocarbons.[5] They allow highly selective introduction of boryl moieties into organic substrates, which in turn can be converted into a whole series of other functionalities.[6] These species, featuring an electron precise bond ($2c,2e^-$) between the transition metal and the boron element,[7] are commonly prepared by oxidative addition of B−H, B−B, and B−E bonds (E = main group element) to low-valent transition metal complexes. Salt elimination reactions between anionic transition metal compounds and haloboranes or halodiboranes represent an important alternative synthetic pathway.[8] The use of catecholborane and its derivatives has given access to a large number of boryl complexes. More recently, boranes with boron−nitrogen bonds have also served as starting compounds for a few aminoboryl derivatives.[9]

Transition metal−vinylidene complexes[10] are intermediates in a number of synthetically important transformations of terminal alkynes.[11] The alkyne−vinylidene tautomerization (Scheme 1) has been considered to occur by 1,2-hydrogen shift on η^2-coordinated alkynes[12] (**a**) and through oxidative addition via hydride−alkynyl intermediates evolving either unimolecular 1,3-hydrogen shift[13] (**b**) or deprotonation of the metal center and subsequent protonation of the alkynyl ligand at C_β[14] (**c**). A fourth pathway (**d**) that may afford vinylidene ligands involves an α-elimination reaction of a metal−alkenyl group, which may be obtained through insertion of the alkyne into a metal−hydride bond.[15] Remarkable findings in recent years have shown that disubstituted vinylidene can be prepared from internal alkynes through a 1,2-shift similar to that observed in the case of terminal alkynes. They include heteroatom-substituted alkynes such a silyl-,[16] stannyl-,[17] thio-,[18] and iodoalkynes[19] as well as acylalkynes.[20] Ishii and co-workers have demonstrated that, under appropiate conditions, it is also possible to form vinylidenes from unfunctionalized internal alkynes.[21] Both allenes[22] and alkylidenecyclopropanes[23] have been recently employed to prepare ruthenium− and osmium−vinylidene complexes, respectively.

Complexes containing a tetrahydroborate ligand attached to the metal through two bridging hydrogen atoms are known for most of the transition metals.[24] NMR studies have provided evidence of fluxional motion involving the tetrahydroborate ligand. In the majority of cases, the exchange is simply between bridging and terminal hydrogen atoms within the

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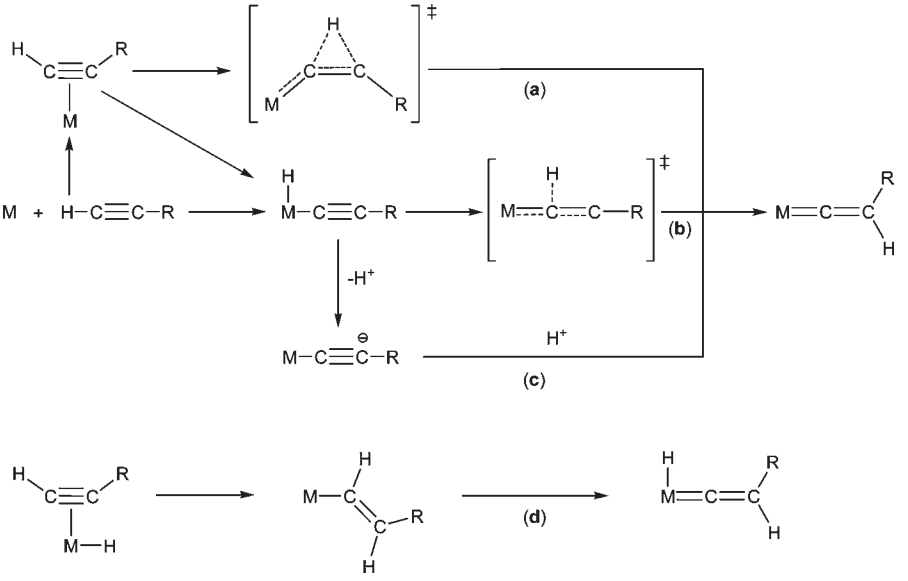
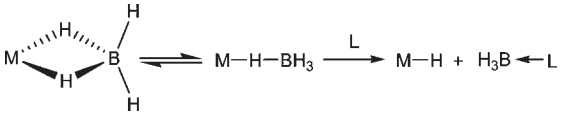
Scheme 1



Scheme 2



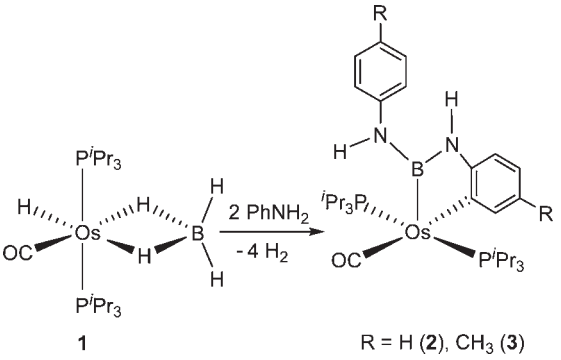
tetrahydroborate ligand. The most generally accepted mechanism involves the initial breaking of an M−H−B bridge.[24e,24f,24h,25] Molecular orbital calculations have indicated that this is the preferred pathway for exchange of bridging and terminal hydrogens in the tetrahydroborate ligand in $OsH_3(\eta^2\text{-}H_2BH_2)(P^iPr_3)_2$.[26] In agreement with this, most commonly BH_3 has been abstracted from the ligand if the reaction mixture contains any nucleophile L capable of forming an adduct $H_3B{\leftarrow}L$ (Scheme 2).[24i,27]

Complex $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ is a perfect example of a transition metal tetrahydroborate,[28] which strictly follows the behavior previously metioned.[29] As a part of our recent research program on new insights in transition metal complexes of boron,[30] we have studied its behavior toward anilines and have discovered that it is an excellent material to generate aminoboryl derivatives. Interestingly, the formed ligands facilitate the entry of an alkynyl group into the metal center. The resulting alkynyl−aminoboryl intermediates evolve to afford unprecedented aminoborylvinylidene complexes.

This paper reports (i) the preparation of aminoboryl complexes from a transition metal−tetrahydroborate prototype, (ii) their conversion into alkynyl−aminoboryl species, (iii) the transformation of the latter to aminoborylvinylidene derivatives, and (iv) a mechanistic proposal for the isomerization on the basis of a kinetic study and DFT calculations.

RESULTS AND DISCUSSION

1. Formation of the Aminoboryl Ligands. Arylamines show a behavior significantly different from that previously observed for other Lewis bases. In contrast to phosphines, phosphites, and carbon monoxide, which produce the abstraction of BH_3 from the metal center of $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$[28] (**1**), the treatment of toluene solutions of this compound with 2.1 equiv of aniline and *p*-toluidine leads, after 15 h under reflux, to the aminoboryl derivatives $Os\{B(NHC_6H_4R)NHCCHCHC(R)CHC\}(CO)(P^iPr_3)_2$ (R = H (**2**), CH_3 (**3**)), according to eq 1.



(1)

These reactions, in addition to the formation of the aminoboryl ligands in the coordination sphere of osmium, produce four hydrogen molecules per equivalent of starting complex. Five hydrogen atoms come from **1**, the BH_4 group, and the hydride ligand. The amines contribute with one NH-hydrogen atom each. Furthermore, one of them undergoes *ortho*-metalation of the phenyl group and gives an *ortho*-CH-hydrogen atom. Complexes **2** and **3** are notable not only for the unprecedented synthetic procedure leading to them but also for the unsaturated character of the metal center. Most osmium compounds containing two phosphine ligands are saturated and resist becoming unsaturated. The presence of at least one π-donor ligand makes such unsaturated species achievable.[29e] Complexes **2** and **3** are rare examples of unsaturated compounds of this type that do not

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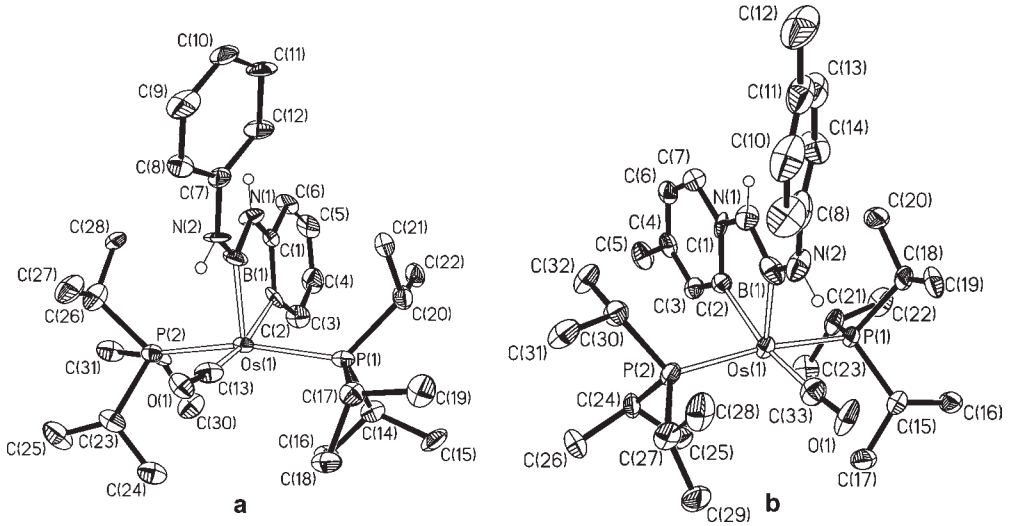


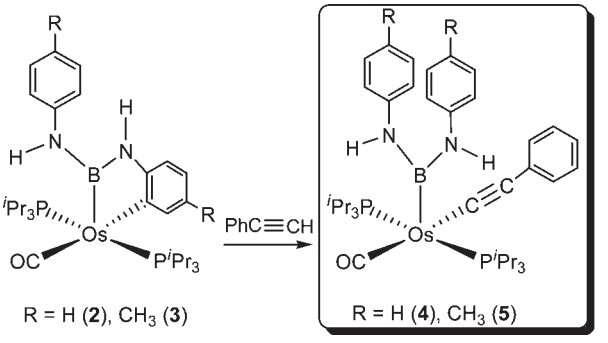
Figure 1. Molecular diagram of **2** (a) and **3** (b). Selected bond lengths (Å) and angles (deg): (a) Os(1)−B(1) 2.072(13), 2.046(16), 2.036(14), and 2.078(14); Os(1)−C(2) 2.161(12), 2.126(12), 2.127(12), and 2.157(11); P(1)−Os(1)−P(2) 165.74(10), 167.49(10), 166.11(11), and 167.73(11); C(2)−Os−C(13) 167.5(5), 168.5(6), 169.5(5), and 168.9(5). (b) Os(1)−B(1) 2.071(11), 2.038(10), 2.087(11), 2.055(10), 2.055(10), 2.067(11), 2.073(10), and 2.061(11); Os(1)−C(2) 2.154(10), 2.156(9), 2.162(9), 2.161(9), 2.146(9), 2.151(9), 2.146(9), and 2.161(10); P(1)−Os(1)−P(2) 167.97(9), 167.94(8), 168.29(9), 167.08(8), 169.77(8), 167.63(8), 168.53(8), and 167.46(9); C(2)−Os−C(33) 167.8(4), 168.6(4), 170.0(4), 169.5(4), 171.7(3), 170.3(4), 170.3(4), and 168.8(4).

have any π-donor ligand. We note that the reaction of OsCl(Bcat)(CO)$(PPh_3)_2$ (Bcat = catecholboryl) with *o*-tolyllithium leads to Os(*o*-tolyl)(Bcat)(CO)$(PPh_3)_2$. However, attempts to prepare the phenyl and *p*-tolyl analogues were not successful. Thus, the steric protection afforded by the bulkier *o*-tolyl group was argued in order to rationalize the stability of this unsaturated species.[31] The alkenyl−alkynyl−carbyne complex Os{(E)-CH=CHPh}(C≡CPh)(≡CCH_2Ph)$(P^iPr_3)_2$ is other rare case of an unsaturated osmium−bisphosphine derivative that does not contain any π-donor ligand. In contrast to **2** and **3**, it is unstable at temperatures higher than −30 °C, evolving into a complex mixture of unidentified products.[32]

Complexes **2** and **3** were isolated as orange solids in 91 and 93% yield, respectively, and characterized by X-ray diffraction analysis. The structure of **2** has four chemically equivalent but crystallographically independent molecules in the asymmetric unit, whereas the structure of **3** has eight molecules of the same type. Figure 1 shows a drawing of a molecule of each complex. The geometries around the osmium atoms can be rationalized as square pyramids with the boron atoms in the apex and *trans* phosphines (167.73(11)−165.74(10)° for **2** and 169.77(8)−167.08(8)° for **3**).[33] The Os−B distances of between 2.078(14) and 2.036(14) Å (**2**) and 2.087(11) and 2.038(10) Å (**3**) support the osmium−boryl formulation,[34] whereas the Os−phenyl bond lengths of between 2.161(2) and 2.126(12) Å (**2**) and 2.161(9) and 2.146(9) Å (**3**) are typical for Os−C_{aryl} single bonds.[35] According to the sp^2 hybridization at the boron, the angles around this atom are between 130.8(12) and 111.6(9)° (**2**) and 130.6(7) and 111.9(7)° (**3**).

The ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{11}B NMR spectra of these compounds in THF-d_8 at room temperature are consistent with the structures shown in Figure 1. In the ^{1}H NMR spectra, the most noticeable resonances are two singlets at 5.79 and 5.14 ppm (**2**) and 5.60 and 5.00 ppm (**3**), corresponding to the inequivalent NH-hydrogen atoms. The $^{13}C\{^1H\}$ NMR spectra show the Os−C_{phenyl} resonances at 168.5 (**2**) and 168.6 (**3**) ppm as triplets with C−P coupling constants of 11.2 and 11.5 Hz, respectively. In agreement with the *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectra contain singlets at 29.4 (**2**) and 29.5 (**3**) ppm. The chemical shift for the boron resonances in the ^{11}B NMR spectra, 29 ppm for both compounds, is the expected one for five-coordinate square pyramidal osmium−boryl derivatives with the boryl ligand *trans* disposed to the coordination vacancy.[34c,34g]

2. Introduction of the Alkynyl Group: Formation of Alkynyl−Aminoboryl Derivatives. In spite of the chelate character of the aminoboryls of **2** and **3**, the metalated phenyl group of these ligands undergoes a σ-bond metathesis reaction with phenylacetylene. Thus, the treatment of toluene solutions of **2** and **3** with 1.5 equiv of the alkyne for 4 h at room temperature leads to the alkynyl−aminoboryl derivatives Os{$B(NHC_6H_4$-R)$_2$}(C≡CPh)(CO)$(P^iPr_3)_2$ (R = H (**4**), CH_3 (**5**)), as a result of the addition of the C(sp)−H bond of the alkyne to the Os−C_{aryl} bonds of **2** and **3**. Complexes **4** and **5** were isolated as orange (**4**) and red (**5**) solids in 68% and 72% yield, respectively, according to eq 2.



(2)

Complex **5** has been characterized by X-ray diffraction analysis. The structure (Figure 2) proves the displacement of the

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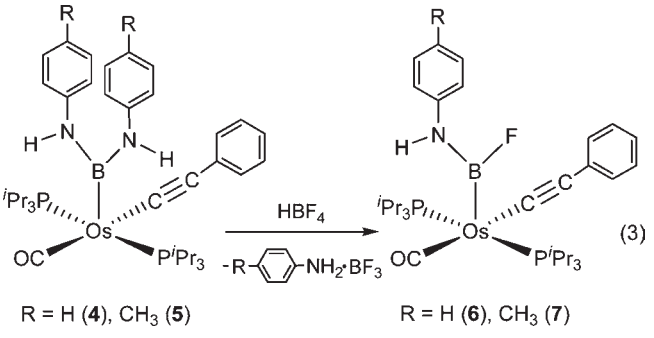
metalated phenyl group from the coordination sphere of the metal by an alkynyl ligand. The geometry around the osmium atom can be rationalized as a square pyramid, similar to those of **2** and **3**, with the boron in the apex, *trans* phosphines (P(1)−Os−P(2) = 165.95(5)°),[33] and the alkynyl ligand *trans* to the carbonyl group (C(1)−Os−C(23) = 173.7(2)°) occupying the position of the metalated phenyl. The Os−C(1) bond length of 2.082(5) Å supports an Os−C(sp) single bond[14e,35b,36] and indicates a low degree of metal-to-ligand back-bonding.[37] The C(1)−C(2) distance and the Os−C(1)−C(2) and C(1)−C(2)−C(3) angles are 1.223(7) Å and 176.7(5) and 178.6(7)°, respectively. The Os−B bond length of 2.076(6) Å agrees well with those of **2** and **3**. The angles around the boron atom, 118.3(5) (N(1)−B−N(2)), 125.7(4) (N(1)−B−Os), and 115.9(4)° (N(2)−B−Os), are consistent with the sp^2 hybridization at this atom.

The ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra of **4** and **5** in benzene-d_6 at room temperature are consistent with the structure shown in Figure 2. In the ^{1}H NMR spectra, the NH-hydrogen atoms display broad resonances at about 5.5 ppm for both compounds. The ^{13}C{^{1}H} NMR spectra show at 141.8 (**4**) and 142.0 (**5**) ppm triplets with a C−P coupling constant of 15.4 Hz and at 128.5 (**4**) and 128.4 (**5**) ppm singlets corresponding to the OsC_α and C_β carbon atoms of the alkynyl ligand. The ^{31}P{^{1}H}NMR spectra contain singlets at 32.8 (**4**) and 33.9 (**5**) ppm. In agreement with **2** and **3**, in the ^{11}B NMR spectra the boron resonances appear at 31 ppm (**4** and **5**).

One of the amido substituents of the aminoboryl ligands of **4** and **5** can be replaced by fluoride to afford amino(fluoro)boryl derivatives. Treatment of toluene solutions of **4** and **5** with 1.05 equiv of $HBF_4 \cdot OEt_2$ for 3 h at room temperature leads to the alkynyl−amino(halo)boryl complexes Os{BF(NHC$_6$H$_4$R)}(C≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (R = H (**6**), CH_3 (**7**)), which were isolated as orange solids in 62% (**6**) and 56% (**7**) yield, according to eq 3.



(3)

The presence of the fluorine substituent at the boron atom of **6** and **7** is strongly supported by the ^{1}H and ^{19}F NMR spectra of these compounds in benzene-d_6 at room temperature. The ^{1}H NMR spectra show at 6.62 (**6**) and 6.52 (**7**) ppm doublets, with a H−F coupling constant of 21.9 Hz, whereas the ^{19}F NMR spectra contain fluoride resonances at −35.7 (**6**) and −36.5 (**7**) ppm. The ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra agree well with those of **4** and **5** and are consistent with the structure shown in Figure 2. The ^{13}C{^{1}H} NMR spectra show at 144.0 (**6**) and 144.1 (**7**) ppm triplets with a C−P coupling constant of 14.7 Hz and at 128.4 (**6**) and 128.3 (**7**) ppm singlets due to the C_α and

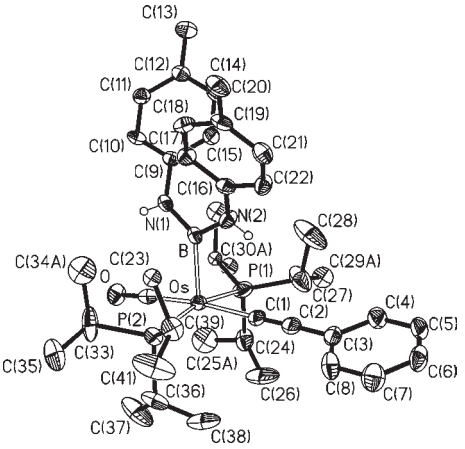


Figure 2. Molecular diagram of **5**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.082(5), C(1)−C(2) 1.223(7), Os−B 2.076(6), B−N(1) 1.434(7), B−N(2) 1.467(7); Os−C(1)−C(2) 176.7(5), C(1)−C(2)−C(3) 178.6(7), P(1)−Os−P(2) 165.95(5), C(1)−Os−C(23) 173.7(2), N(1)−B−N(2) 118.3(5), N(1)−B−Os 125.7(4), N(2)−B−Os 115.9(4).

C_β carbon atoms of the alkynyl ligand. The ^{31}P{^{1}H}NMR spectra contain singlets at 35.6 (**6**) and 35.5 (**7**) ppm, whereas the boron resonances in the ^{11}B NMR spectra are observed at 28 (**6**) and 30 (**7**) ppm.

The formation of **6** and **7** involves the addition of HF to one of the B−N bonds of **4** and **5**. In addition to **6** and **7**, the process generates aniline and *p*-toluidine that are trapped by BF_3 to form the corresponding $RNH_2 \cdot BF_3$ adducts (R = Ph, *p*-tolyl; $\delta_{^{11}B}$, 22; $\delta_{^{19}F}$, −32). Amino(halo)boryl complexes are very scarce.[9] Salt elimination reactions represent the route of choice to prepare the greater part of this type of compounds.[38] Two exceptions are the osmium derivative Os{BC1(NHC$_5$H$_4$N)}C1(CO)(PPh$_3$)$_2$, which is obtained by reaction of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ with 2-aminopyridine,[34d] and the bis(boryl) complex *cis*-[(Ph$_3$P)$_2$Pt{BCl(NMe$_2$)}$_2$], resulting from the oxidative addition of the B−B bond of the diborane to Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$.[39] Asymmetric fluoroboryl compounds are particularly rare. Complex Os{BF(OC$_5$H$_4$N)}C1(CO)(PPh$_3$)$_2$[34e] and Fe(η^5-C$_5$H$_5$){BF[Si(SiMe$_3$)$_3$]}(CO)$_2$[40] have been prepared by halide metathesis starting from the corresponding chloride counterparts, whereas the paramagnetic species [Ir{BF(C$_{12}$H$_8$)}Cl(PMe$_3$)$_3$]$^+$ has been synthesized by reaction of IrCl(C$_{12}$H$_8$)(PMe$_3$)$_3$ with $NOBF_4$ through the formal insertion of BF into a Ir−C bond.[41]

Alkynyl groups coordinated to late transition metals show a high nucleophilicity at the C_β atom. Thus, the addition of HBF_4 to alkynyl complexes is a known entry into the synthesis of vinylidene compounds.[10] In this context, the selective preparation of **6** and **7**, according to eq 3, should be pointed out. The driving force for their formation instead of cationic vinylidene species appears to be the trend of the $[BF_4]^-$ anion to release fluoride in the presence of neutral Lewis bases[42] and the high formation energy of a B−F bond. In agreement with this, in contrast to HBF_4, the addition of acetic acid to toluene solutions of **4** and **5** affords the six-coordinate derivatives Os{B(NHC$_6$H$_4$R)$_2$}(κ^2-O$_2$CCH$_3$)(CO)(P^{i}Pr$_3$)$_2$ (R = H (**8**), CH_3 (**9**)), as a result of the protonation of the alkynyl ligand and its subsequent displacement by the carboxylate group. These

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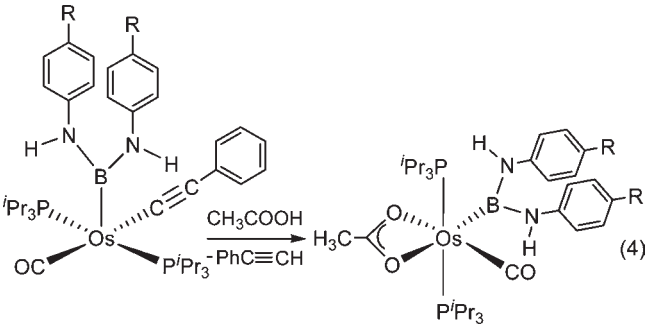
complexes were isolated as light orange (**8**) and yellow (**9**) oils in 86% and 90% yield, respectively, according to eq 4.



R = H (**4**), CH_3 (**5**) R = H (**8**), CH_3 (**9**)

The six-coordinate nature of **8** and **9** is strongly supported by their IR and ^{11}B NMR spectra. The IR spectra in dichloromethane show the ν_{asym}(OCO) bands at 1601 (**8**) and 1613 (**9**) cm^{-1} and the ν_{sym}(OCO) bands at 1497 (**8**) and 1514 (**9**) cm^{-1}. The values of $\Delta\nu$ ($\Delta\nu = \nu_{asym}(OCO) - \nu_{sym}(OCO)$) of 104 (**8**) and 99 (**9**) cm^{-1} are consistent with the bidentate coordination mode of the acetate group.[43] As expected for six-coordinate osmium−boryl compounds,[34c] the boron resonances in the ^{11}B NMR spectra in benzene-d_6, 37 ppm for **8** and **9**, appear significantly shifted toward lower field (by about 10 ppm) with regard to those of the related five-coordinate derivatives. A singlet at 25.2 ppm in the ^{31}P{^{1}H} NMR spectra is also characteristic of these complexes.

3. Alkynyl−Aminoboryl to Aminoborylvinylidene Transformation. Complexes **4** and **5** are also new examples of five-coordinate unsaturated complexes that do not contain any π-donor ligand. The coordination number six for both compounds can be achieved by coordination of carbon monoxide. Under an atmosphere of this gas, the toluene solutions of **4** and **5** afford the *cis*-dicarbonyl derivatives Os{B(NHC$_6$H$_4$R)$_2$}(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (R = H (**10**), CH_3 (**11**)), which were isolated as white solids in 86% (**10**) and 93% (**11**) yield, according to Scheme 3.

Figure 3 shows a view of the X-ray structure of **11**. The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying *trans* positions (P(1)−Os−P(2) = 177.59(3)°). The perpendicular plane is formed by the carbonyl groups *cis* disposed (C(23)−Os−C(24) = 99.30(13)°), the boryl *trans* disposed to C(24) (B−Os−C(24) = 169.65(12)°), and the alkynyl *trans* disposed to C(23) (C(1)−Os−C(23) = 167.88(12)°). The Os−B bond length of 2.256(4) Å is about 0.2 Å longer than those of **2**, **3**, and **5**. This is consistent with a decrease of the π-donation from the metal base frontier orbitals into the empty boron p orbital, as a consequence of the *trans* coordination of other π-acidic ligands like carbon monoxide, which weakens the Os−B bond. According to the sp^2 hybridization, the angles around the boron atom are between 117.9(2) and 123.4(2)°. The Os−C(1) distance of 2.087(3) Å is statistically identical with the separation between the metal center and the alkynyl ligand in **5**. In agreement with the latter, the C(1)−C(2) bond length and Os−C(1)−C(2) and C(1)−C(2)−C(3) angles are 1.211(4) Å and 174.1(3) and 178.8(3)°, respectively. As expected for a π-acidic character of the boryl ligand higher than that of the alkynyl group, the separation between the metal center and the carbonyl ligand *trans* disposed to the first of them (Os−C(24) = 1.922(3) Å) is longer (about 0.05 Å) than that between the metal center and the carbonyl ligand *trans* disposed to the second one (Os−C(23) = 1.873(3) Å).

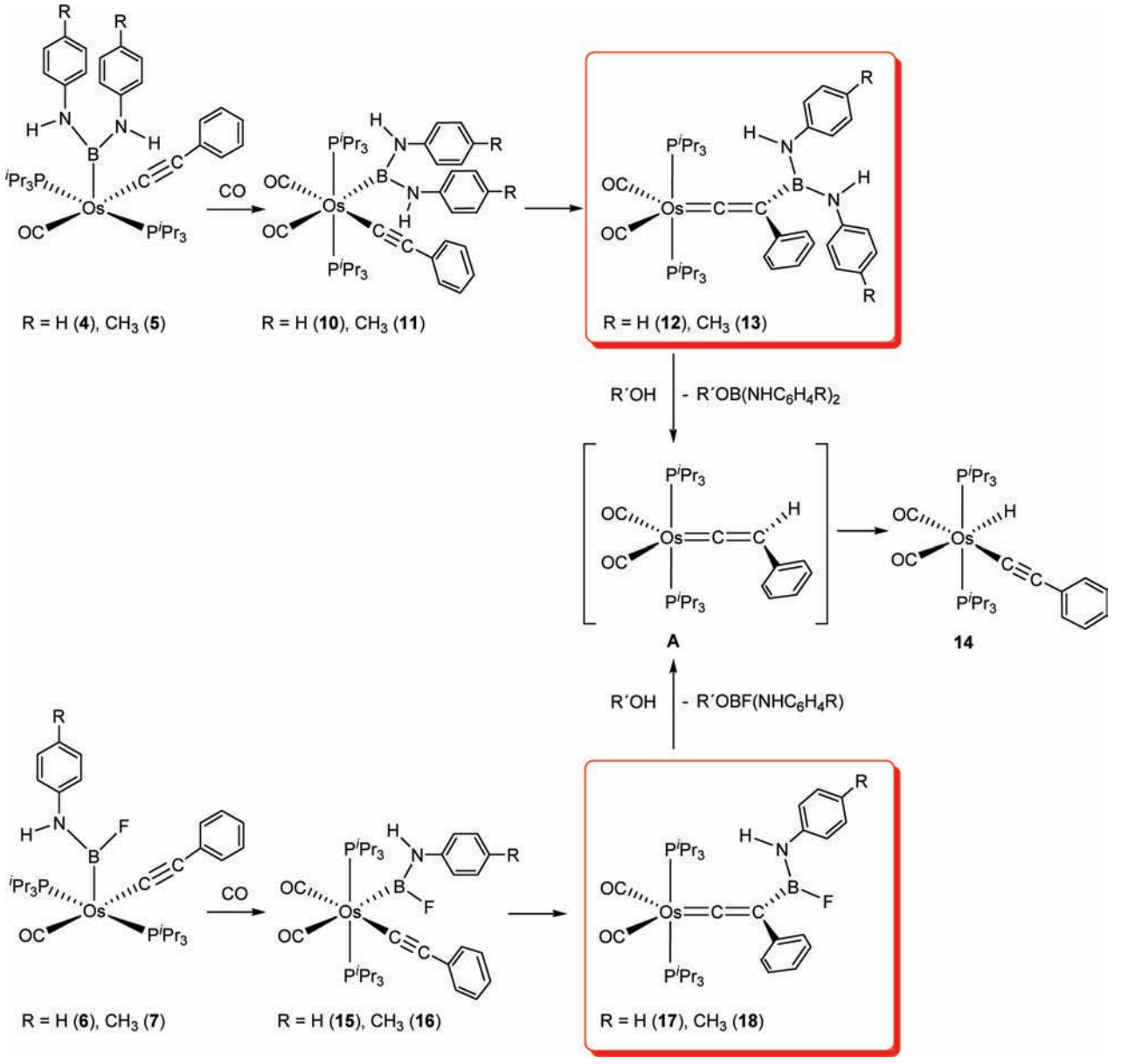
The IR, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra of **10** and **11** are consistent with the structure shown in Figure 3. In agreement with the *cis* disposition of the carbonyl groups, the IR spectra in dichloromethane show two ν(CO) bands at 1979 and 1913 cm^{-1} (**10**) and 1978 and 1910 cm^{-1} (**11**). The ^{1}H NMR spectra in benzene-d_6 at room temperature contain two NH resonances at 8.09 and 5.94 ppm (**10**) and 8.02 and 5.89 ppm (**11**), revealing that in solution the boryl ligands do not rotate around the Os−B bond and the nitrogen atoms of their substituents lie in the plane perpendicular to the P−Os−P direction. In the ^{13}C{^{1}H} NMR spectra, the OsC$_\alpha$ resonances of the alkynyl ligands are observed at 104.9 (**10**) and 105.1 (**11**) ppm as triplets with C−P coupling constants of 16.0 and 16.1 Hz, respectively, whereas the C$_\beta$ signals appear at 114.5 ppm for both compounds. In agreement with equivalent *trans* phosphines, the ^{31}P{^{1}H} NMR spectra contain singlets at 4.6 (**10**) and 4.4 (**11**) ppm. In the ^{11}B NMR spectra the boron resonances appear at 44 (**10**) and 43 (**11**) ppm, shifted by 13 (**10**) and 12 (**11**) ppm to lower field with regard to those of **4** and **5**. This is consistent with the π-donation decrease from the metal to the boron, as a consequence of the carbonyl coordination, which is not compensated by the amido substituents. In this context, it should be mentioned that the B−N distances in **11** of 1.433(4) Å (B−N(1)) and 1.446(4) Å (B−N(2)) are statistically identical to those of **5** (B−N(1) = 1.434(7) Å and B−N(2) = 1.467(7) Å).

Complexes **10** and **11** are moderately stable in solution. In toluene at 80 °C, they evolve into the aminoborylvinylidene derivatives Os{=C=C(Ph)B(NHC$_6$H$_4$R)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (R = H (**12**), CH_3 (**13**)), as a result of the migration of the aminoboryl ligands from the metal centers to the C$_\beta$ atoms of the alkynyl ligands. The weakening of the Os−B bonds, a consequence of the CO coordination, facilitates the 1,3-boryl shifts. The transformations are quantitative after 15 min. Complex **12** was isolated as a light yellow solid in 68% yield, whereas complex **13** was obtained as a light orange dry foam in 78% yield.

Complex **12** has been characterized by X-ray diffraction analysis. The structure (Figure 4) proves the formation of the unprecedented borylvinylidene ligand. The geometry around the osmium atom can be described as a distorted trigonal bipyramid with apical phosphines (P(1)−Os−P(2) = 171.08(4)°) and inequivalent angles within the Y-shaped equatorial plane (C(1)−Os−C(21) = 124.60(18)°, C(1)−Os−C(22) = 135.25(19)°, and C(21)−Os−C(22) = 100.0(2)°). The vinylidene ligand is bound to the metal in a nearly linear fashion with an Os−C(1)−C(2) angle of 176.6(3)°. The Os−C(1) and C(1)−C(2) bond lengths of 1.897(4) and 1.341(5) Å, respectively, compare well with those found in other osmium−vinylidene complexes and support the vinylidene formulation.[14f,23,44]

The ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra of **12** and **13** in benzene-d_6 at room temperature are consistent with the structure shown in Figure 4. The ^{1}H NMR spectra show the NH resonances at 5.86 (**12**) and 5.80 (**13**) ppm. In the ^{13}C{^{1}H} NMR spectra, the OsC$_\alpha$ resonances appear at 297.7 (**12**) and 298.2 (**13**) ppm as triplets with C−P coupling constants of 17.2 and 16.9 Hz, respectively. The C$_\beta$ signals are observed at 137.0 (**12**) and 137.1 (**13**) ppm, also as triplets but with a C−P coupling constant of 4.3 Hz. In the ^{31}P{^{1}H} NMR spectra, the

Scheme 3



equivalent phosphines display a singlet at 23.0 ppm for both compounds. The boron resonances in the ^{11}B NMR spectra are observed at 27 ppm (**12** and **13**).

Complexes **12** and **13** react with methanol to give the previously reported hydride−alkynyl derivative OsH(C≡CPh)-$(CO)_2(P^iPr_3)_2$ (**14**)[36a,45] and $CH_3OB(NHC_6H_4R)_2$ ($\delta_{^{11}B}$, 18.6). Its formation most probably takes place via the vinylidene intermediate Os(=C=CHPh)$(CO)_2(P^iPr_3)_2$ (**A**), which undergoes tautomerization. The difference in behavior between **A** and the aminoboryl counterparts **12** and **13** is noteworthy. Since the C−B bond energy is lower than C−H bond energy, the stability of the aminoboryl−vinylidenes with regard to the corresponding alkynyl−aminoboryl intermediates appears to be a consequence of the very weak Os−B bonds in the latter.

The alkynyl−amino(fluoro)boryl complexes **6** and **7** can be transformed into the corresponding amino(fluoro)borylvinylidenes by the same procedure as for **4** and **5** (Scheme 3). In toluene under a carbon monoxide atmosphere, complexes **6** and **7** coordinate a carbonyl group to afford the *cis*-dicarbonyl−alkynyl−boryl intermediates Os{$BF(NHC_6H_4R)$}(C≡CPh)$(CO)_2(P^iPr_3)_2$ (R = H (**15**), CH_3 (**16**)), which rapidly evolve into the vinylidenes Os-{=C=C(Ph)$BF(NHC_6H_4R)$}$(CO)_2(P^iPr_3)_2$ (R = H (**17**), CH_3 (**18**)) at room temperature. Complexes **17** and **18** are, however, much less stable than **12** and **13** toward the deborylation. Traces of water or of the acid used for the preparation of **6** and **7** prevent their isolation as pure substances. Thus, amounts of **14** higher than 10% always contaminate the samples. The alkynyl−boryl species **15** and **16** as well as their borylvinylidene tautomers **17** and **18** were fully characterized by ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{11}B, and ^{19}F NMR spectroscopy.

The NMR spectra of **15** and **16** in benzene-d_6 at 12 °C agree well with those of **10** and **11**. The ^{1}H NMR spectra show

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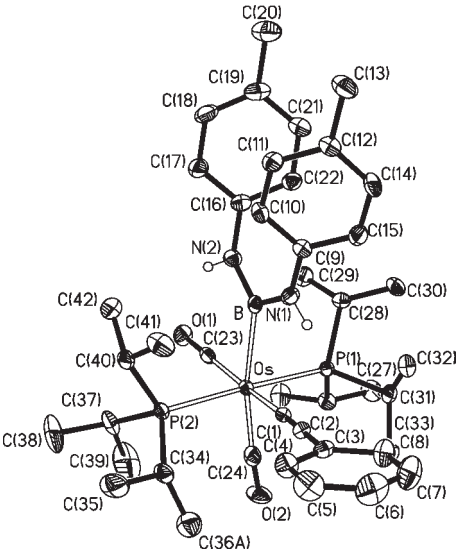

Figure 3. Molecular diagram of **11**. Selected bond lengths (Å) and angles (deg): Os−B 2.256(4), Os−C(1) 2.087(3), C(1)−C(2) 1.211(4), Os−C(24) 1.922(3), Os−C(23) 1.873(3), B−N(1) 1.433(4), B−N(2) 1.446(4); P(1)−Os−P(2) 177.59(3), C(23)−Os−C(24) 99.30(13), B−Os−C(24) 169.65(12), C(1)−Os−C(23) 167.88(12), Os−C(1)−C(2) 174.1(3), C(1)−C(2)−C(3) 178.8(3), N(1)−B−N(2) 118.4(3), N(1)−B−Os 117.9(2), N(2)−B−Os 123.4(2).

the NH-resonance at 7.94 (**15**) and 7.83 (**16**) ppm as doublets with H−F coupling constants of 26.0 and 26.1 Hz, respectively. The presence of two carbonyl ligands mutually *cis* disposed in these compounds is strongly supported by the $^{13}C\{^1H\}$ NMR spectra, which contain two triplets at 187.8 and 184.6 ppm (**15**) and 187.9 and 184.7 ppm (**16**) with C−P coupling constants between 8.1 and 7.7 Hz. The OsC_α resonances of the alkynyl ligands are observed at 104.3 (**15**) and 104.5 (**16**) ppm as triplets with C−P coupling constants of 14.6 and 14.5 Hz, respectively, whereas the C_β resonances appear at 113.0 (**15**) and 112.9 (**16**) ppm. The $^{31}P\{^1H\}$ NMR spectra show singlets at 6.8 (**15**) and 6.7 (**16**) ppm. Broad resonances at 49 (**15**) and 48 (**16**) ppm and at −37.3 (**15**) and −38.5 (**16**) ppm in the ^{11}B and ^{19}F spectra, respectively, are also characteristic of **15** and **16**.

The ^1H NMR spectra of **17** and **18** show the NH-resonances at 6.57 (**17**) and 6.51 (**18**) ppm as doublets with a H−F coupling constant of 20.1 Hz. In the $^{13}C\{^1H\}$ NMR spectra the OsC_α resonances of the vinylidene ligands appear at 302.3 (**17**) and 302.1 (**18**) ppm as triplets with C−P coupling constants of 12.3 and 11.9 Hz, respectively. Singlets at 22.7 (**17**) and 22.9 (**18**) ppm in the $^{31}P\{^1H\}$ NMR spectra and broad resonances at 29 ppm (**17** and **18**) and at −107.4 (**17**) and −108.1 (**18**) ppm in the ^{11}B and ^{19}F NMR spectra are also noticeable spectroscopic features of these vinylidene derivatives.

4. Mechanism of the Alkynyl−Aminoboryl to Aminoborylvinylidene Transformation. The transformation of **10** to **12** was followed by $^{31}P\{^1H\}$ NMR spectroscopy. The decrease of **10** (with the corresponding increase of **12**) in benzene-d_6 is an exponential function of time, in agreement with a first-order process. The values obtained for the first-order rate constant k_{obs} in the temperature range studied are reported in Table 1. The activation parameters for the tautomerization process were obtained from the Eyring analysis shown in Figure 5, giving values of $\Delta H^{\ddagger} = 23 \pm 1$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -5 \pm 2$ cal·mol^{-1}·K^{-1}.

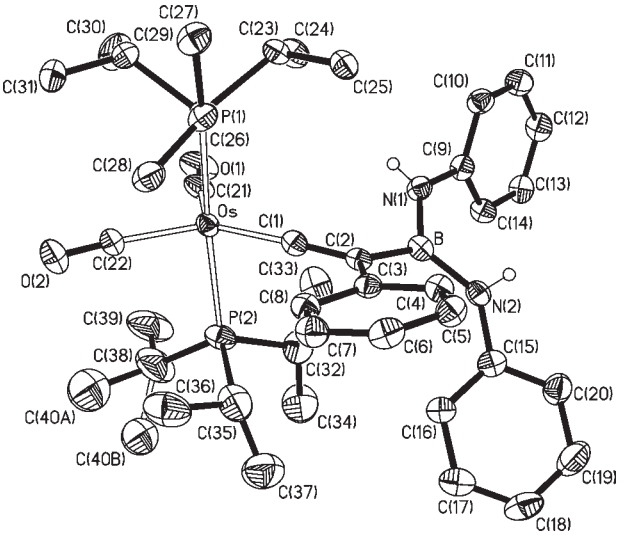

Figure 4. Molecular diagram of **12**. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.897(4), C(1)−C(2) 1.341(5); P(1)−Os−P(2) 171.08(4), C(1)−Os−C(21) 124.60(18), C(1)−Os−C(22) 135.25(19), C(21)−Os−C(22) 100.0(2), Os−C(1)−C(2) 176.6(3).

Table 1. Rate Constants for the Alkynyl−Aminoboryl (10) to Aminoborylvinylidene (12) Transformation

T (K)	k_{obs} ($\times 10^5$ s^{-1})
299	1.3
310	4.8
319	14.8
330	49.0
340	142.5

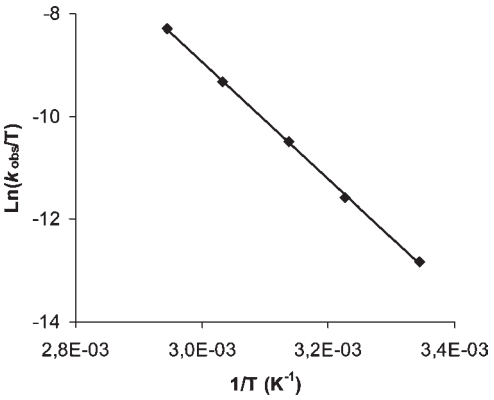

Figure 5. Eyring plot of k_{obs} for the formation of **12**.

The slightly negative value of the activation entropy suggests that the migration of the aminoboryl group from the metal center to the C_β atom of the alkynyl ligand is an intramolecular process that occurs by a mechanism with a geometrically highly oriented transition state. To obtain information about its nature, we have also performed DFT calculations (B3PW91) on the tautomerization using PMe_3 as model of P^iPr_3. The changes in free energy ΔG have been computed at 298.15 K and P = 1 atm. Figure 6 shows the energy profile.

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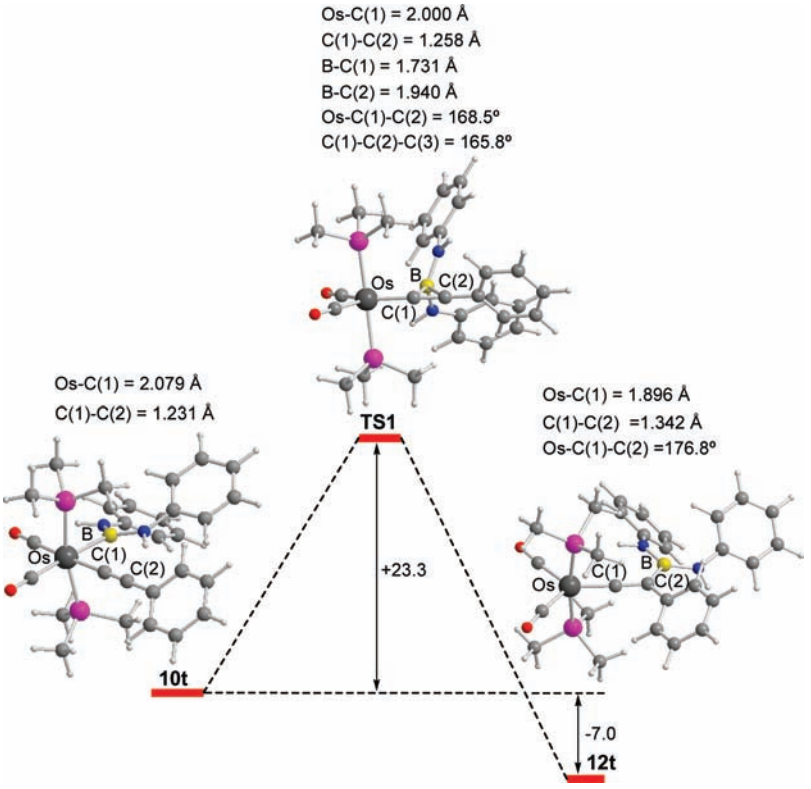

Figure 6. Energy profile (ΔG (kcal·mol^{-1})) for the tautomerization process.

The aminoborylvinylidene complex Os{=C=C(Ph)B(NHPh)$_2$}(CO)$_2$(PMe$_3$)$_2$ (**12t**) is 7.0 kcal·mol^{-1} more stable than the alkynyl−aminoboryl tautomer Os{B(NHPh)$_2$}(C≡CPh)(CO)$_2$(PMe$_3$)$_2$ (**10t**). The tautomerization takes place via the transition state **TS1**, which lies 23.3 kcal·mol^{-1} above **10t**. The activation enthalpy and entropy of 22.0 kcal·mol^{-1} and −4.4 cal·mol^{-1}·K^{-1}, respectively, agree well with the obtained experimental values. This activation barrier compares well with those calculated by De Angelis and co-workers[13d] and Grotjahn and co-workers[13c] for the unimolecular hydride−alkynyl to vinylidene transformations promoted by RhCl(P^{i}Pr$_3$)$_2$[46] and related rhodium systems.[13b,13e]

The transition state **TS1** can be described as a μ_2-η^2-alkynyl species[37] where the bent alkynyl ligand (Os−C(1)−C(2) = 168.5° and C(1)−C(2)−C(3) = 165.8°) is σ-bonded to the osmium atom of the metal fragment Os(CO)$_2$(PMe$_3$)$_2$ (Os−C(1) = 2.000 Å) and π-coordinated via the carbon−carbon triple bond C(1)−C(2) (1.258 Å) to the boron atom of the aminoboryl group. The coordination of the boron is unsymmetrical, the distance to the α-carbon atom of the alkynyl bridge C(1) (1.731 Å) being about 0.2 Å shorter than that to the β-carbon atom C(2) (1.940 Å).

CONCLUDING REMARKS

This paper shows the discovery of the first transition metal−borylvinylidene complexes and reveals that they can be formed through alkynyl−boryl intermediates via unimolecular 1,3-boryl migration from the metal center to the C$_\beta$ atom of the alkynyl ligand. Although a similar 1,3-hydrogen shift has been proposed as the rate-determining step for the alkyne−vinylidene tautomerization promoted by RhCl(P^{i}Pr$_3$)$_2$ and related rhodium systems, this 1,3-boryl shift is the first process of this type involving an atom other than hydrogen.

The procedure used to prepare the key alkynyl−boryl intermediates is simple and unprecedented and should be applicable to a wide range of transition metals. It starts from a tetrahydroborate complex, anilines, and a terminal alkyne. In contrast to Lewis bases such as phosphines, phosphites, and carbon monoxide, which abstract BH$_3$ from the metal center, we have discovered that the reactions of the tetrahydroborate complex with anilines generate aminoboryl derivatives with one of the amido substituents metalated by the phenyl. This metalated group undergoes a σ-bond metathesis reaction with the terminal alkyne to afford the alkynyl−boryl species.

Since fragments containing a C−B bond are established members of the tools utilized in modern organic synthetic chemistry[47] and vinylidene complexes are intermediates in a number of synthetically important transformations, one should expect that borylvinylidene complexes will open routes to prepare new tools for organic synthesis.

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 or obtained oxygen- and water-free from MBraun solvent purification apparatus. The starting material OsH(η^2-H$_2$BH$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**1**) was prepared by the published method.[28] Aniline, *p*-toluidine, and phenylacetylene were obtained from commercial sources. Aniline and phenylacetylene were purified by distillation, and *p*-toluidine was purified by sublimation in a Kugelrohr distillation oven. ^{1}H, ^{19}F, ^{11}B, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on either a Bruker ARX 300, Bruker Avance 300, Bruker Avance 400, or Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external H$_3$PO$_4$ (^{31}P{^{1}H}), BF$_3$(OEt)$_2$ (^{11}B), or CFCl$_3$

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(^{19}F). Coupling constants, *J* and *N*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer as CH_2Cl_2 solutions. C, H, N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). The intensity of the mass relative to that of the base peak is given in parentheses after the found mass.

Preparation of Os{B(NHC$_6$H$_5$)NHCCHCHCHCHC}(CO)(P^{i}Pr$_3$)$_2$ (2). A solution of OsH(η^2-H$_2$BH$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (230 mg, 0.41 mmol) in 8 mL of toluene was treated with 2.1 equiv of aniline (79 μL, 0.87 mmol) and heated for 15 h under reflux. After being cooled to room temperature, the resulting solution was filtered through Celite, and the solvent was removed in vacuo. The residue was treated with methanol (1.5 mL) at −78 °C to form an orange solid which was washed with cold methanol (2 × 1.5 mL) and dried in vacuo. Yield: 276 mg (91%). Anal. Calcd for $C_{31}H_{53}BN_2OOsP_2$: C, 50.81; H, 7.29; N, 3.82. Found: C, 50.70; H, 7.19; N, 3.75. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1865 (s). MS (HR-electrospray): *m*/*z* [M] − [2H] calcd for $C_{31}H_{51}BN_2OOsP_2$ 732.3186, found 732.3167 (5). ^{1}H NMR (500.13 MHz, THF-d_8, 298 K): δ 7.28 (d, J_{H-H} = 7.0, 1H, C$_6$H$_4$), 7.12 (dd, J_{H-H} = J_{H-H} = 7.5, 2H, *m*-H$_{aniline}$), 6.86 (d, J_{H-H} = 7.5, 2H, *o*-H$_{aniline}$), 6.74 (t, J_{H-H} = 7.5, 1H, *p*-H$_{aniline}$), 6.68 (dd, J_{H-H} = J_{H-H} = 7.0, 1H, C$_6$H$_4$), 6.56 (dd, J_{H-H} = J_{H-H} = 7.0, 1H, C$_6$H$_4$), 6.47 (d, J_{H-H} = 7.0, 1H, C$_6$H$_4$), 5.79 and 5.14 (both s, 2H, NH), 2.54 (m, 6H, PC*H*CH$_3$), 1.17 (dvt, *N* = 12.8, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.15 (dvt, *N* = 12.8, J_{H-H} = 6.8, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, THF-d_8, 298 K): δ 29.4 (s). ^{11}B NMR (160.5 MHz, THF-d_8, 298 K): δ 29 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (125.8 MHz, THF-d_8, 298 K): δ 200.9 (t, J_{C-P} = 8.6, CO), 168.5 (t, J_{C-P} = 11.2, OsC), 157.6 and 145.7 (both s, C$_{ipso}$-NH), 139.7 (s, C$_6$H$_4$), 130.0 (s, *m*-C$_{aniline}$), 123.6 (s, C$_6$H$_4$), 120.4 (s, *p*-C$_{aniline}$), 120.3 (s, *o*-C$_{aniline}$), 119.4 and 111.5 (both s, C$_6$H$_4$), 27.5 (vt, *N* = 24.7, PCHCH$_3$), 20.4 (s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_4$CH$_3$)NHCCHCHC(CH$_3$)CHC}(CO)(P^{i}Pr$_3$)$_2$ (3). A solution of OsH(η^2-H$_2$BH$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (197 mg, 0.35 mmol) in 8 mL of toluene was treated with 2.1 equiv of *p*-toluidine (80 mg, 0.75 mmol) and heated for 15 h under reflux. During this time the solution changed from light yellow to orange. After being cooled to room temperature, the resulting solution was filtered through Celite, and the solvent was removed in vacuo. The residue was treated with methanol (1.5 mL) at −78 °C to form an orange solid which was washed with cold methanol (2 × 1.5 mL) and dried in vacuo. Yield: 252 mg (93%). Anal. Calcd for $C_{33}H_{57}BN_2OOsP_2$: C, 52.10; H, 7.55; N, 3.68. Found: C, 52.31; H, 7.48; N, 3.52. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1863 (s). MS (HR-electrospray): *m*/*z* [M] - [2H] calcd for $C_{33}H_{55}BN_2OOsP_2$ 760.3499, found 760.3445 (4). ^{1}H NMR (500.13 MHz, THF-d_8, 298 K): δ 7.12 (s, 1H, C$_6$H$_3$), 6.93 (d, J_{H-H} = 7.6, 2H, *m*-H$_{toluidine}$), 6.75 (d, J_{H-H} = 7.6, 2H, *o*-H$_{toluidine}$), 6.48 (d, J_{H-H} = 7.2, 1H, C$_6$H$_3$), 6.33 (d, J_{H-H} = 7.2, 1H, C$_6$H$_3$), 5.60 and 5.00 (both s, 2H, NH), 2.53 (m, 6H, PC*H*CH$_3$), 2.20 (s, 3H, C$_6$H$_4$-C*H*$_3$), 2.15 (s, 3H, C$_6$H$_3$-C*H*$_3$), 1.17 (dvt, *N* = 14.0, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), 1.15 (dvt, *N* = 15.2, J_{H-H} = 6.8, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (162.0 MHz, THF-d_8, 298 K): δ 29.5 (s). ^{11}B NMR (96.3 MHz, THF-d_8, 298 K): δ 29 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.6 MHz, THF-d_8, 298 K): δ 200.8 (t, J_{C-P} = 8.6, CO), 168.6 (t, J_{C-P} = 11.5, OsC), 155.0 and 143.2 (both s, C$_{ipso}$-NH), 140.8 (s, C$_6$H$_3$), 130.5 (s, *m*-C$_{toluidine}$), 129.3 (s, C$_5$H$_4$C-CH$_3$), 126.9 (s, C$_5$H$_3$C-CH$_3$), 124.1 (s, C$_6$H$_3$), 120.4 (s, *o*-C$_{toluidine}$), 111.0 (s, C$_6$H$_3$), 27.6 (vt, *N* = 24.7, PCHCH$_3$), 21.9 (s, C$_6$H$_3$-*C*H$_3$), 20.9 (s, C$_6$H$_4$-*C*H$_3$), 20.4 (s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_5$)$_2$}(C≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (4). An orange solution of **2** (289 mg, 0.39 mmol) in 8 mL of toluene was treated with 1.5 equiv of phenylacetylene (65.6 μL, 0.59 mmol) and stirred for 4 h at room temperature. After this time, the mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The addition of methanol (2.5 mL) at 0 °C afforded an orange solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 223 mg (68%). Anal. Calcd for $C_{39}H_{59}BN_2OOsP_2$: C, 56.11; H, 7.12; N, 3.36. Found: C, 56.19; H, 7.26; N, 3.26. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2073 (w); ν(CO) 1875 (s). MS (HR-electrospray): *m*/*z* [M] calcd for $C_{39}H_{59}BN_2OOsP_2$ 836.3814, found 836.3821 (4); [M] − [NHC$_6$H$_5$] calcd for $C_{33}H_{53}BNOOsP_2$ 744.3312, found 744.3309 (100). ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 298 K): δ 7.58 (d, J_{H-H} = 7.5, 2H, *o*-H$_{Ph}$), 7.15 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H$_{Ph}$), 6.98 (t, J_{H-H} = 7.5, 1H, *p*-H$_{Ph}$), 6.95 (dd, J_{H-H} = $J_{H-H'}$ = 7.3, 4H, *m*-H$_{aniline}$), 6.86 (d, J_{H-H} = 7.3, 4H, *o*-H$_{aniline}$), 6.64 (t, J_{H-H} = 7.3, 2H, *p*-H$_{aniline}$), 5.5 (br, 2H, NH), 2.80 (m, 6H, PC*H*CH$_3$), 1.28 (dvt, *N* = 13.3, J_{H-H} = 6.8, 18H, PCHC*H*$_3$), 1.20 (dvt, *N* = 13.0, J_{H-H} = 6.5, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$, 298 K): δ 32.8 (s). ^{11}B NMR (160.5 MHz, C$_6$D$_6$, 298 K): δ 31 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (125.8 MHz, C$_6$D$_6$, 298 K): δ 196.3 (t, J_{C-P} = 8.7, CO), 144.0 (br, C$_{ipso}$-aniline), 141.8 (t, J_{C-P} = 15.4, OsC≡C), 130.6 (s, *o*-C$_{Ph}$), 129.3 (s, *m*-C$_{aniline}$), 129.2 (s, *m*-C$_{Ph}$), 129.0 (s, C$_{ipso}$-Ph), 128.5 (s, OsC≡*C*), 126.4 (s, *p*-C$_{Ph}$), 119.6 (s, *p*-C$_{aniline}$), 119.3 (s, *o*-C$_{aniline}$), 26.6 (vt, *N* = 24.9, PCHCH$_3$), 20.5 and 20.4 (both s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_4$CH$_3$)$_2$}(C≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (5). An orange solution of **3** (230 mg, 0.30 mmol) in 7 mL of toluene was treated with 1.5 equiv of phenylacetylene (50.3 μL, 0.45 mmol) and stirred for 3 h at room temperature. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The addition of methanol (2.5 mL) at 0 °C caused the precipitation of a dark red solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 188 mg (72%). Anal. Calcd for $C_{41}H_{63}BN_2OOsP_2$: C, 57.07; H, 7.36; N, 3.25. Found: C, 57.20; H, 7.19; N, 3.38. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2072 (w); ν(CO) 1874 (s). MS (HR-electrospray): *m*/*z* [M] calcd for $C_{41}H_{63}BN_2OOsP_2$ 864.4127, found 864.4103 (1.5); [M] − [NHC$_6$H$_4$CH$_3$] calcd for $C_{34}H_{55}BNOOsP_2$ 758.3469, found 758.3446 (100). ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 298 K): δ 7.59 (d, J_{H-H} = 7.5, 2H, *o*-H$_{Ph}$), 7.16 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H$_{Ph}$), 6.99 (t, J_{H-H} = 7.5, 1H, *p*-H$_{Ph}$), 6.83 (d, J_{H-H} = 7.3, 4H, *o*-H$_{toluidine}$), 6.79 (d, J_{H-H} = 7.3, 4H, *m*-H$_{toluidine}$), 5.5 (br, 2H, NH), 2.82 (m, 6H, PC*H*CH$_3$), 1.98 (s, 6H, CH$_3$), 1.30 (dvt, *N* = 13.5, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.21 (dvt, *N* = 13.0, J_{H-H} = 7.0, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$, 298 K): δ 33.9 (s). ^{11}B NMR (128.4 MHz, C$_6$D$_6$, 298 K): δ 31 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (125.8 MHz, C$_6$D$_6$, 298 K): δ 196.3 (t, J_{C-P} = 7.0, CO), 142.0 (t, J_{C-P} = 15.4, OsC≡C), 141.8 (s, C$_{ipso}$-toluidine), 130.6 (s, *o*-C$_{Ph}$), 129.9 (s, *m*-C$_{toluidine}$), 129.1 (s, *m*-C$_{Ph}$), 129.0 (s, C$_{ipso}$-Ph), 128.4 (s, OsC≡*C*), 128.0 (s, *C*CH$_3$), 126.3 (s, *p*-C$_{Ph}$), 119.2 (s, *o*-C$_{toluidine}$), 26.6 (vt, *N* = 24.8, PCHCH$_3$), 21.0 (s, CH$_3$), 20.5 and 20.4 (both s, PCH*C*H$_3$).

Preparation of Os{BF(NHC$_6$H$_5$)}(C≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (6). An orange solution of **4** (127 mg, 0.15 mmol) in 6 mL of toluene was treated with 1.05 equiv of HBF$_4$·OEt$_2$ (21.9 μL, 0.16 mmol) and stirred for 3.30 h at room temperature. The resulting mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The addition of an 8:1 pentane/diethyl ether mixture (2 and 0.3 mL) at 0 °C afforded an orange solid, which was washed with further portions of cold pentane/diethyl ether mixture (8:1) and dried in vacuo. Yield: 72 mg (62%). Anal. Calcd for $C_{33}H_{53}BFNOOsP_2$: C, 52.03; H, 7.01; N, 1.84. Found: C, 51.94; H, 6.85; N, 1.63. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2072 (w); ν(CO) 1904 (s). MS (HR-electrospray): *m*/*z* [M] calcd for $C_{33}H_{53}BFNOOsP_2$ 763.3296, found 763.3180 (6); [M − H] − [BFNHC$_6$H$_5$] − [C$_8$H$_5$] calcd for $C_{19}H_{41}OOsP_2$ 539.2242, found 539.2241 (100). ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K): δ 7.57 (d, J_{H-H} = 7.5, 2H, *o*-H$_{Ph}$), 7.31 (d, J_{H-H} = 7.2, 1H, *o*-H$_{aniline}$), 7.30 (d, J_{H-H} = 7.2, 1H, *o*-H$_{aniline}$), 7.15 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 4H, *m*-H$_{Ph}$ (2H) + *m*-H$_{aniline}$ (2H)), 6.99 (t, J_{H-H} = 7.5, 1H, *p*-H$_{Ph}$), 6.77 (t, J_{H-H} = 7.2, 1H, *p*-H$_{aniline}$), 6.62 (d, J_{H-F} = 21.9, 1H, NH), 2.83 (m, 6H, PC*H*CH$_3$), 1.22 (dvt, *N* = 13.5, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), 1.21 (dvt, *N* = 12.9, J_{H-H} = 6.9, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 298 K): δ 35.6 (s). ^{11}B NMR (160.5 MHz, C$_6$D$_6$, 298 K): δ 28 (br). ^{19}F NMR

(282.4 MHz, C_6D_6, 298 K): δ −35.7 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 298 K): δ 194.0 (t, J_{C-P} = 7.8, CO), 144.0 (t, J_{C-P} = 14.7, OsC≡C), 144.0 (s, C_{ipso}-aniline, overlapped with OsC≡C), 130.6 (s, *o*-C_{Ph}), 130.0 (s, *m*-$C_{aniline}$), 129.2 (s, *m*-C_{Ph}), 128.4 (s, OsC≡*C*), 128.2 (s, C_{ipso}-Ph), 126.3 (s, *p*-C_{Ph}), 120.2 (s, *p*-$C_{aniline}$), 118.8 and 118.7 (both s, *o*-$C_{aniline}$), 27.0 (vt, *N* = 25.4, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$).

Preparation of Os{BF(NHC$_6$H$_4$CH$_3$)}(C≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (7). A red solution of **5** (139 mg, 0.16 mmol) in 7 mL of toluene was treated with 1.05 equiv of $HBF_4\cdot OEt_2$ (23.2 μL, 0.16 mmol) and stirred for 3 h at room temperature. The red solution was filtered through Celite, and the solvent was removed in vacuo. The addition of an 8:1 pentane/diethyl ether mixture (2 and 0.3 mL) at 0 °C caused the precipitation of an orange solid, which was washed with further portions of cold pentane/diethyl ether mixture (8:1) and dried in vacuo. Yield: 70 mg (56%). Anal. Calcd for $C_{34}H_{55}BFNOOsP_2$: C, 52.64; H, 7.15; N, 1.81. Found: C, 52.53; H, 7.10; N, 1.74. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2072 (w); ν(CO) 1902 (s). MS (HR-electrospray): *m*/*z* [M + H] calcd for $C_{34}H_{56}BFNOOsP_2$ 778.3531, found 778.3490 (5); [M − H] − [BFNHC$_6$H$_4$CH$_3$] − [C_8H_5] calcd for $C_{19}H_{41}OOsP_2$ 539.2242, found 539.2270 (100). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.57 (d, J_{H-H} = 7.5, 2H, *o*-H_{Ph}), 7.24 (d, J_{H-H} = 8.2, 1H, *o*-$H_{toluidine}$), 7.23 (d, J_{H-H} = 8.2, 1H, *o*-$H_{toluidine}$), 7.15 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H_{Ph}), 6.98 (t, J_{H-H} = 7.5, 1H, *p*-H_{Ph}), 6.96 (d, J_{H-H} = 8.2, 2H, *m*-$H_{toluidine}$), 6.52 (d, J_{H-F} = 21.9, 1H, NH), 2.83 (m, 6H, PC*H*CH$_3$), 2.08 (s, 3H, CH$_3$), 1.23 (dvt, *N* = 13.5, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), 1.21 (dvt, *N* = 11.1, J_{H-H} = 6.9, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 35.5 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 298 K): δ 30 (br). ^{19}F NMR (282.4 MHz, C_6D_6, 298 K): δ −36.5 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 298 K): δ 194.0 (t, J_{C-P} = 7.7, CO), 144.1 (t, J_{C-P} = 14.7, OsC≡C), 141.6 (s, C_{ipso}-toluidine), 130.6 (s, *o*-C_{Ph}), 130.4 (s, *m*-$C_{toluidine}$), 129.1 (s, *m*-C_{Ph}), 128.9 (s, *C*-CH$_3$), 128.5 (s, C_{ipso}-Ph), 128.3 (s, OsC≡*C*), 126.3 (s, *p*-C_{Ph}), 118.8 and 118.7 (both s, *o*-$C_{toluidine}$), 27.0 (vt, *N* = 25.3, P*C*HCH$_3$), 21.0 (s, CH$_3$), 20.4 (s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_5$)$_2$}(κ^2-O$_2$CCH$_3$)(CO)(P^{i}Pr$_3$)$_2$ (8). An orange solution of **4** (129 mg, 0.15 mmol) in 7 mL of toluene was treated with 15 equiv of CH$_3$COOH (132 μL, 2.25 mmol) and stirred for 2 h at room temperature. The solution was filtered through Celite, and the solvent was removed in vacuo. Pentane (3 mL) was added, and the resulting solution was dried in vacuo, giving a light orange oil. Yield: 106 mg (86%). Anal. Calcd for $C_{33}H_{57}BN_2O_3OsP_2$: C, 50.00; H, 7.25; N, 3.53. Found: C, 50.18; H, 7.19; N, 3.45. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1868 (s); ν_{asym}(OCO) 1601 (s); ν_{sym}(OCO) 1497 (s). MS (HR-electrospray): *m*/*z* [M] − [CH$_3$COO] calcd for $C_{31}H_{54}BN_2OOsP_2$ 735.3420, found 735.3488 (100). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 6.98 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 4H, *m*-$H_{aniline}$), 6.88 and 6.84 (both d, J_{H-H} = 7.5, 2H + 2H, *o*-$H_{aniline}$), 6.69 and 6.67 (both t, J_{H-H} = 7.5, 1H + 1H, *p*-$H_{aniline}$), 6.44 and 5.75 (both s, 2H, NH), 2.46 (m, 6H, PC*H*CH$_3$), 1.72 (s, 3H, CH$_3$), 1.29 (dvt, *N* = 13.4, J_{H-H} = 7.1, 18H, PCHC*H*$_3$), 1.17 (dvt, *N* = 12.6, J_{H-H} = 6.9, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 25.2 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 298 K): δ 37 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 298 K): δ 189.6 (t, J_{C-P} = 9.7, CO), 181.7 (s, CH$_3$COO), 145.7 and 144.5 (both s, C_{ipso}-aniline), 129.2 and 129.1 (both s, *m*-$C_{aniline}$), 119.7 (s, *o*-$C_{aniline}$ and *p*-$C_{aniline}$), 119.6 (s, *o*-$C_{aniline}$), 119.0 (s, *p*-$C_{aniline}$), 26.9 (vt, *N* = 23.8, P*C*HCH$_3$), 26.2 (s, *C*H$_3$COO), 20.3 and 20.1 (both s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_4$CH$_3$)$_2$}(κ^2-O$_2$CCH$_3$)(CO)(P^{i}Pr$_3$)$_2$ (9). A red solution of **5** (160 mg, 0.18 mmol) in 7 mL of toluene was treated with 15 equiv of CH$_3$COOH (159 μL, 2.70 mmol) and stirred for 2 h at room temperature. The solution was filtered through Celite, and the solvent was removed in vacuo. Pentane (3 mL) was added, and the resulting solution was dried in vacuo, giving a yellow oil. Yield: 137 mg (90%). Anal. Calcd for $C_{35}H_{61}BN_2O_3OsP_2$: C, 51.21; H, 7.49; N, 3.41. Found: C, 51.32; H, 7.41; N, 3.29. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1868 (s); ν_{asym}(OCO) 1613 (s); ν_{sym}(OCO) 1514 (s). MS (HR-electrospray): *m*/*z* [M] − [CH$_3$COO] calcd for $C_{33}H_{58}BN_2OOsP_2$ 763.3734, found 763.3784 (100). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 6.88−6.77 (m, 8H, *o*-$H_{toluidine}$ + *m*-$H_{toluidine}$), 6.38 and 5.70 (both s, 2H, NH), 2.48 (m, 6H, PC*H*CH$_3$), 2.03 and 2.01 (both s, 6H, CH$_3$ of *p*-toluidine), 1.73 (s, 3H, CH$_3$), 1.32 (dvt, *N* = 13.2, J_{H-H} = 6.9, 18H, PCHC*H*$_3$), 1.20 (dvt, *N* = 12.9, J_{H-H} = 6.9, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 25.2 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 298 K): δ 37 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 298 K): δ 189.7 (t, J_{C-P} = 9.7, CO), 181.6 (s, CH$_3$COO), 143.5 and 142.3 (both s, C_{ipso}-toluidine), 129.8 and 129.7 (both s, *m*-$C_{toluidine}$), 128.2 and 127.5 (both s, *C*-CH$_3$), 119.6 and 119.5 (both s, *o*-$C_{toluidine}$), 26.9 (vt, *N* = 23.8, P*C*HCH$_3$), 26.3 (s, *C*H$_3$COO), 21.0 (s, CH$_3$), 20.4 and 20.2 (both s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_5$)$_2$}(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (10). An orange solution of **4** (125 mg, 0.15 mmol) in 6 mL of toluene was stirred under carbon monoxide atmosphere for 5 min at room temperature. Immediately, the solution changed from red to light yellow. After this time, the solution was concentrated to dryness. The addition of methanol (2 mL) at −78 °C afforded a white solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 111 mg (86%). Anal. Calcd for $C_{40}H_{59}BN_2O_2OsP_2$: C, 55.68; H, 6.89; N, 3.25. Found: C, 55.98; H, 6.92; N, 3.39. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2099 (w); ν(CO) 1979 (s), 1913 (s). MS (HR-electrospray): *m*/*z* [M + H] calcd for $C_{40}H_{60}BN_2O_2OsP_2$ 865.3841, found 865.3810 (13); [MH] − [P^{i}Pr$_3$] calcd for $C_{31}H_{39}BN_2O_2OsP$ 705.2458, found 705.2447 (100). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.09 (s, 1H, NH), 7.60 (d, J_{H-H} = 7.5, 2H, *o*-H_{Ph}), 7.18 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H_{Ph}), 6.99 (t, J_{H-H} = 7.5, 1H, *p*-H_{Ph}), 6.97−6.88 (m, 6H, *o*-$H_{aniline}$ (2H) + *m*-$H_{aniline}$ (4H)), 6.78 (d, J_{H-H} = 7.4, 2H, *o*-$H_{aniline}$), 6.67 (t, J_{H-H} = 7.4, 2H, *p*-$H_{aniline}$), 5.94 (s, 1H, NH), 2.60 (m, 6H, PC*H*CH$_3$), 1.33 (dvt, *N* = 13.7, J_{H-H} = 7.1, 18H, PCHC*H*$_3$), 1.20 (dvt, *N* = 13.2, J_{H-H} = 6.9, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 4.6 (s). ^{11}B NMR (160.5 MHz, C_6D_6, 298 K): δ 44 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 298 K): δ 192.1 (t, J_{C-P} = 7.7, CO), 183.4 (t, J_{C-P} = 8.2, CO), 146.5 and 146.3 (both s, C_{ipso}-aniline), 131.1 (s, *o*-C_{Ph}), 129.8 (s, C_{ipso}-Ph), 129.3 (s, *m*-C_{Ph}), 129.1 (s, *m*-$C_{aniline}$), 126.0 (s, *p*-C_{Ph}), 120.3 and 120.1 (both s, *o*-$C_{aniline}$), 120.0 (s, *p*-$C_{aniline}$), 114.5 (s, OsC≡*C*), 104.9 (t, J_{C-P} = 16.0, OsC≡C), 28.2 (vt, *N* = 26.9, P*C*HCH$_3$), 20.6 and 20.0 (both s, PCH*C*H$_3$).

Preparation of Os{B(NHC$_6$H$_4$CH$_3$)$_2$}(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (11). A dark red solution of **5** (155 mg, 0.18 mmol) in 6 mL of toluene was stirred under carbon monoxide atmosphere for 5 min at room temperature. Immediately, the color of the solution changed from dark red to light yellow. The resulting solution was then concentrated to dryness. The addition of methanol (2 mL) at 0 °C afforded a white solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 149 mg (93%). Anal. Calcd for $C_{42}H_{63}BN_2O_2OsP_2$: C, 56.62; H, 7.13; N, 3.14. Found: C, 56.79; H, 7.02; N, 3.06. IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2099 (w); ν(CO) 1978 (s), 1910 (s). MS (HR-electrospray): *m*/*z* [M + H] calcd for $C_{42}H_{64}BN_2O_2OsP_2$ 893.4155, found 893.4123 (15); [MH] − [P^{i}Pr$_3$] calcd for $C_{33}H_{42}BN_2O_2OsP_2$ 733.2772, found 733.2789 (100). ^{1}H NMR (400.16 MHz, C_6D_6, 298 K): δ 8.02 (s, 1H, NH), 7.60 (d, J_{H-H} = 7.6, 2H, *o*-H_{Ph}), 7.20 (dd, J_{H-H} = $J_{H-H'}$ = 7.6, 2H, *m*-H_{Ph}), 7.01 (t, J_{H-H} = 7.6, 1H, *p*-H_{Ph}), 6.89−6.75 (m, 8H, C$_6$*H*$_4$NH), 5.89 (s, 1H, NH), 2.61 (m, 6H, PC*H*CH$_3$), 2.01 (s, 6H, CH$_3$), 1.34 (dvt, *N* = 13.2, J_{H-H} = 6.8, 18H, PCHC*H*$_3$), 1.22 (dvt, *N* = 12.8, J_{H-H} = 6.8, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 4.4 (s). ^{11}B NMR (128.4 MHz, C_6D_6, 298 K): δ 43 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (100.6 MHz, C_6D_6, 298 K): δ 192.2 (t, J_{C-P} = 7.8, CO), 183.5 (t, J_{C-P} = 8.2, CO), 144.3 and 144.0 (both s, C_{ipso}-toluidine), 131.2 (s, *o*-C_{Ph}), 130.0 (s, C_{ipso}-Ph),

129.7 (s, *m*-$C_{toluidine}$), 129.0 (s, *m*-C_{Ph}), 128.8 and 128.5 (both s, *C*-CH_3), 125.9 (s, *p*-C_{Ph}), 120.2 and 119.9 (both s, *o*-$C_{toluidine}$), 114.5 (t, J_{C-P} = 2.3, OsC≡*C*), 105.1 (t, J_{C-P} = 16.1, OsC≡C), 28.3 (vt, *N* = 26.8, PCHCH$_3$), 21.0 and 20.8 (both s, CH_3), 20.6 and 20.0 (both s, PCHCH_3).

Preparation of Os{=C=C(Ph)B(NHC$_6$H$_5$)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (12). A solution of **10** (110 mg, 0.13 mmol) in 6 mL of toluene was heated at 353 K for 10 min. During this time, the color of the solution changed from colorless to light yellow. The resulting mixture was filtered through Celite, and the filtrate was evaporated. The residue was treated with pentane at −78 °C to give a light yellow solid, which was washed with further portions of cold pentane and dried in vacuo. Yield: 75 mg (68%). Anal. Calcd for $C_{40}H_{59}BN_2O_2OsP_2$: C, 55.68; H, 6.89; N, 3.25. Found: C, 55.75; H, 6.76; N, 3.13. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1949 (s), 1885 (s). MS (HR-electrospray): *m*/*z* [M + H] calcd for $C_{40}H_{60}BN_2O_2OsP_2$ 865.3841, found 865.3807 (0.3); [M] − [$BN_2C_{12}H_{12}$] calcd for $C_{28}H_{47}O_2OsP_2$ 669.2667, found 669.2662 (100). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.55 (d, J_{H-H} = 7.5, 2H, *o*-H_{Ph}), 7.19 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H_{Ph}), 7.01−6.95 (m, 5H, *p*-H_{Ph} (1H) + *m*-$H_{aniline}$ (4H)), 6.88 (d, J_{H-H} = 7.4, 4H, *o*-$H_{aniline}$), 6.72 (d, J_{H-H} = 7.4, 2H, *p*-$H_{aniline}$), 5.86 (s, 2H, NH), 2.40 (m, 6H, PC*H*CH$_3$), 1.20 (dvt, *N* = 13.3, J_{H-H} = 6.9, 18H, PCHCH_3), 1.17 (dvt, *N* = 14.1, J_{H-H} = 7.2, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 23.0 (s). ^{11}B NMR (160.5 MHz, C_6D_6, 298 K): δ 27 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.6 MHz, C_6D_6, 298 K): δ 297.7 (t, J_{C-P} = 17.2, Os=C), 194.6 (t, J_{C-P} = 7.9, CO), 194.3 (t, J_{C-P} = 8.3, CO), 144.9 (s, C_{ipso}-aniline), 137.0 (t, J_{C-P} = 4.3, Os=C=*C*), 130.8 (s, C_{ipso}-Ph), 129.3 (s, *m*-$C_{aniline}$), 128.9 (s, *o*-C_{Ph}), 128.6 (s, *m*-C_{Ph}), 124.7 (s, *p*-C_{Ph}), 121.3 (s, *o*-$C_{aniline}$), 121.2 (s, *p*-$C_{aniline}$), 27.8 (vt, *N* = 27.8, P*C*HCH$_3$), 21.0 and 20.7 (both s, PCH*C*H$_3$).

Preparation of Os{=C=C(Ph)B(NHC$_6$H$_4$CH$_3$)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (13). A solution of **11** (0.128 mg, 0.14 mmol) in 6 mL of toluene was heated at 353 K for 15 min. During this time, the solution changed from colorless to light orange. The resulting mixture was filtered through Celite, and the filtrate was evaporated. Pentane was added, and the solvent was removed in vacuo, leading to the formation of a dry light orange foam. Yield: 100 mg (78%). Anal. Calcd for $C_{42}H_{63}BN_2O_2OsP_2$: C, 56.62; H, 7.13; N, 3.14. Found: C, 56.75; H, 7.18; N, 3.21. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1948 (s), 1876 (s). MS (HR-electrospray): *m*/*z* [M + H] calcd for $C_{42}H_{64}BN_2O_2OsP_2$ 893.4160, found 893.4122 (0.8); [M] − [$BN_2C_{14}H_{16}$] calcd for $C_{28}H_{47}O_2OsP_2$ 669.2667, found 669.2659 (100). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.59 (d, J_{H-H} = 7.5, 2H, *o*-H_{Ph}), 7.20 (dd, J_{H-H} = $J_{H-H'}$ = 7.5, 2H, *m*-H_{Ph}), 6.96 (t, J_{H-H} = 7.5, 1H, *p*-H_{Ph}), 6.87 (d, J_{H-H} = 9.4, 4H, *o*-$H_{toluidine}$), 6.82 (d, J_{H-H} = 9.4, 4H, *m*-$H_{toluidine}$), 5.80 (s, 2H, NH), 2.41 (m, 6H, PC*H*CH$_3$), 2.04 (s, 6H, CH_3), 1.23 (dvt, *N* = 13.6, J_{H-H} = 7.2, 18H, PCHCH_3), 1.18 (dvt, *N* = 14.0, J_{H-H} = 7.2, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6, 298 K): δ 23.0 (s). ^{11}B NMR (128.4 MHz, C_6D_6, 298 K): δ 27 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.6 MHz, C_6D_6, 298 K): δ 298.2 (t, J_{C-P} = 16.9, Os=C), 194.8 (t, J_{C-P} = 8.0, CO), 194.5 (t, J_{C-P} = 8.3, CO), 142.5 (s, C_{ipso}-toluidine), 137.1 (t, J_{C-P} = 4.3, Os=C=*C*), 130.8 (s, C_{ipso}-Ph), 130.0 (s, *C*-CH_3), 129.9 (s, *m*-$C_{toluidine}$), 128.8 (s, *o*-C_{Ph}), 128.6 (s, *m*-C_{Ph}), 124.6 (s, *p*-C_{Ph}), 121.3 (s, *o*-$C_{toluidine}$), 27.8 (vt, *N* = 27.7, P*C*HCH$_3$), 21.1 (s, CH_3), 21.0 and 20.8 (both s, PCH*C*H$_3$).

Reaction of 12 and 13 with Methanol: Formation of OsH(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (14). A solution of **12** (110 mg, 0.13 mmol) or **13** (115 mg, 0.13 mmol) in 6 mL of toluene was treated with 0.5 mL of methanol. The mixture was stirred for 2 h at room temperature. After this time the solution was filtered through Celite, and the solvent was removed in vacuo. The addition of methanol (1.5 mL) at −78 °C caused the precipitation of a white solid, which was washed with cold methanol and dried in vacuo. Yield: 78 mg (92%). The spectroscopic data of the solid agree well with those previously reported for **14**.[36a]

Preparation of Os{BF(NHC$_6$H$_5$)}(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (15). A Young cap NMR tube containing **6** (55 mg, 0.07 mmol) in 0.5 mL of C_6D_6 was sealed under CO atmosphere. The instantaneous formation of complex **15** was observed in quantitative yield. ^{1}H NMR (400.13 MHz, C_6D_6, 285 K): δ 7.94 (d, J_{H-F} = 26.0, 1H, NH), 7.58 (d, J_{H-H} = 7.6, 2H, *o*-H_{Ph}), 7.50 (d, J_{H-H} = 7.6, 2H, *o*-$H_{aniline}$), 7.18 (dd, J_{H-H} = $J_{H-H'}$ = 7.6, 4H, *m*-H_{Ph} (2H) + *m*-$H_{aniline}$ (2H)), 6.99 (t, J_{H-H} = 7.6, 1H, *p*-H_{Ph}), 6.81 (t, J_{H-H} = 7.6, 1H, *p*-$H_{aniline}$), 2.55 (m, 6H, PC*H*CH$_3$), 1.27 (dvt, *N* = 14.0, J_{H-H} = 7.2, 18H, PCHCH_3), 1.17 (dvt, *N* = 13.4, J_{H-H} = 7.0, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6, 285 K): δ 6.8 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 285 K): δ 49 (br). ^{19}F NMR (282.4 MHz, C_6D_6, 285 K): δ −37.3 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 285 K): δ 187.8 (t, J_{C-P} = 7.7, CO), 184.6 (t, J_{C-P} = 8.1, CO), 144.7 (s, C_{ipso}-aniline), 131.1 (s, *o*-C_{Ph}), 130.0 (s, *m*-$C_{aniline}$), 129.1 (s, *m*-C_{Ph}), 128.6 (s, C_{ipso}-Ph), 125.9 (s, *p*-C_{Ph}), 121.1 (s, *p*-$C_{aniline}$), 119.3 and 119.2 (s, *o*-$C_{aniline}$), 113.0 (s, OsC≡*C*), 104.3 (t, J_{C-P} = 14.6, OsC≡C) 28.1 (vt, *N* = 27.3, P*C*HCH$_3$), 20.4 and 19.7 (both s, PCH*C*H$_3$).

Preparation of Os{BF(NHC$_6$H$_4$CH$_3$)}(C≡CPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (16). This complex was prepared as described for **15**, starting from **7** (0.057 mg, 0.07 mmol). ^{1}H NMR (300.13 MHz, C_6D_6, 285 K): δ 7.83 (d, J_{H-F} = 26.1, 1H, NH), 7.56 (d, J_{H-H} = 7.6, 2H, *o*-H_{Ph}), 7.40 (d, J_{H-H} = 8.1, 2H, *o*-$H_{toluidine}$), 7.18 (dd, J_{H-H} = $J_{H-H'}$ = 7.6, 2H, *m*-H_{Ph}), 7.00 (t, J_{H-H} = 7.6, 1H, *p*-H_{Ph}), 6.99 (d, J_{H-H} = 8.1, 2H, *p*-$H_{toluidine}$), 2.58 (m, 6H, PC*H*CH$_3$), 2.08 (s, 3H, CH_3), 1.29 (dvt, *N* = 13.8, J_{H-H} = 7.2, 18H, PCHCH_3), 1.20 (dvt, *N* = 13.4, J_{H-H} = 7.1, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 285 K): δ 6.7 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 285 K): δ 48 (br). ^{19}F NMR (282.4 MHz, C_6D_6, 285 K): δ −38.5 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 285 K): δ 187.9 (t, J_{C-P} = 7.7, CO), 184.7 (t, J_{C-P} = 8.1, CO), 142.4 (s, C_{ipso}-toluidine), 131.1 (s, *o*-C_{Ph}), 130.6 (s, *m*-$C_{toluidine}$), 130.2 (s, *C*-CH_3), 129.6 (s, C_{ipso}-Ph), 129.1 (s, *m*-C_{Ph}), 125.9 (s, *p*-C_{Ph}), 119.2 and 119.1 (s, *o*-$C_{toluidine}$), 112.9 (t, J_{C-P} = 2.0, OsC≡*C*), 104.5 (t, J_{C-P} = 14.5, OsC≡C), 28.1 (vt, *N* = 27.3, P*C*HCH$_3$), 21.1 (s, CH_3), 20.4 and 19.7 (both s, PCH*C*H$_3$).

Preparation of Os{=C=C(Ph)BF(NHC$_6$H$_5$)}(CO)$_2$(P^{i}Pr$_3$)$_2$ (17). The same sample used above in the preparation of the complex **15** was left to evolve in solution at room temperature to give complex **17**. This complex always appears contaminated with the compound OsH(CO)(C≡CPh)(P^{i}Pr$_3$)$_2$ (**14**). ^{1}H NMR (300.13 MHz, C_6D_6, 285 K): δ 7.82 (d, J_{H-H} = 7.8, 2H, *o*-H_{Ph}), 7.43 (d, J_{H-H} = 7.8, 2H, *o*-$H_{aniline}$), 7.31 (dd, J_{H-H} = $J_{H-H'}$ = 7.8, 2H, *m*-H_{Ph}), 7.18 (dd, J_{H-H} = $J_{H-H'}$ = 7.8, 2H, *m*-$H_{aniline}$), 7.05 (t, J_{H-H} = 7.8, 1H, *p*-H_{Ph}), 6.85 (t, J_{H-H} = 7.8, 1H, *p*-$H_{aniline}$), 6.57 (d, J_{H-F} = 20.1, 1H, NH), 2.31 (m, 6H, PC*H*CH$_3$), 1.14 (dvt, *N* = 13.5, J_{H-H} = 7.2, 18H, PCHCH_3), 1.12 (dvt, *N* = 13.5, J_{H-H} = 7.9, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 285 K): δ 22.7 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 285 K): δ 29 (br). ^{19}F NMR (282.4 MHz, C_6D_6, 285 K): δ −107.4 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 285 K): δ 302.3 (t, J_{C-P} = 12.3, Os=C), 194.1 (t, J_{C-P} = 7.9, CO), 193.7 (t, J_{C-P} = 8.3, CO), 143.7 (s, C_{ipso}-aniline), 135.7 (t, J_{C-P} = 9.1, Os=C=*C*), 130.0 (s, *m*-$C_{aniline}$), 128.6 (s, *m*-C_{Ph}), 128.4 (s, *o*-C_{Ph}), 128.1 (s, C_{ipso}-Ph), 124.9 (s, *p*-C_{Ph}), 121.8 (s, *p*-$C_{aniline}$), 119.3 and 119.2 (both s, *o*-$C_{aniline}$), 27.8 (vt, *N* = 28.0, PCHCH$_3$), 20.9 and 20.6 (both s, PCH*C*H$_3$).

Preparation of Os{=C=C(Ph)BF(NHC$_6$H$_4$CH$_3$)}(CO)$_2$(P^{i}Pr$_3$)$_2$ (18). The same sample used above in the preparation of the complex **16** was left to evolve in solution at room temperature to give complex **18**. This complex always appears contaminated with the compound OsH(CO)(C≡CPh)(P^{i}Pr$_3$)$_2$ (**14**). ^{1}H NMR (300.13 MHz, C_6D_6, 285 K): δ 7.83 (d, J_{H-H} = 7.8, 2H, *o*-H_{Ph}), 7.39 (d, J_{H-H} = 8.0, 2H, *o*-$H_{toluidine}$), 7.31 (dd, J_{H-H} = $J_{H-H'}$ = 7.8, 2H, *m*-H_{Ph}), 7.00 (d, J_{H-H} = $J_{H-H'}$ = 8.0, 2H, *m*-$H_{toluidine}$), 6.99 (t, J_{H-H} = 7.8, 1H, *p*-H_{Ph}), 6.51 (d, J_{H-F} = 20.1, 1H, NH), 2.32 (m, 6H, PC*H*CH$_3$), 2.11 (s, 3H, CH_3), 1.15 (dvt, *N* = 13.8, J_{H-H} = 6.9, 18H, PCHCH_3), 1.12 (dvt,

N = 14.1, J_{H-H} = 7.2, 18H, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 285 K): δ 22.9 (s). ^{11}B NMR (96.3 MHz, C_6D_6, 285 K): δ 29 (br). ^{19}F NMR (282.4 MHz, C_6D_6, 285 K): δ −108.1 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.5 MHz, C_6D_6, 285 K): δ 302.1 (t, J_{C-P} = 11.9, Os=C), 194.2 (t, J_{C-P} = 7.8, CO), 193.8 (t, J_{C-P} = 8.3, CO), 141.2 (s, C_{ipso}-toluidine), 135.8 (t, J_{C-P} = 8.6, Os=C=*C*), 130.6 (s, *m*-$C_{toluidine}$), 128.7 (s, C_{ipso}-Ph), 128.6 (s, *m*-C_{Ph}), 128.3 (s, *o*-C_{Ph}), 125.2 (s, *p*-C_{Ph}), 119.4 and 119.3 (both s, *o*-$C_{toluidine}$), 27.8 (vt, N = 28.0, P*C*HCH$_3$), 21.0 (s, CH_3), 20.9 and 20.7 (both s, PCH*C*H$_3$).

Kinetic Analysis for the Alkynyl−Aminoboryl (10) to Aminoborylvinylidene (12) Transformation. The transformation of **10** to **12** was followed quantitatively by $^{31}P\{^1H\}$ NMR spectroscopy in C_6D_6. The decrease of the intensity of the phosphorus resonance was measured automatically at intervals in a Bruker ARX-300 spectrometer. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by least-squares fit of the Eyring plot. Errors were computed according to published methods.[48]

Computational Details. The theoretical calculations were carried out on the model complexes by optimizing the structure at the B3PW91-DFT levels with the Gaussian 03 program.[49] The basis sets used were LANL2DZ basis and pseudopotentials for Os, and 6-31G(d, p) for the rest of the atoms. The transition state has been found by carrying out potential energy surfaces of the process following the reaction coordinates, optimizing the maxima, and confirming by frequency calculations. The connections between the starting and final reactants have been checked by slightly perturbing the TS geometry toward the minimum geometries and reoptimizing.

Structural Analysis of Complexes 2, 3, 5, 11, and 12. X-ray data were collected on a Bruker Smart APEX CCD (**2**, **3**, **5**, **12**) and an Oxford Diffraction Xcalibur TS (**11**) instrument using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the complete sphere and were corrected for absorption by using a multiscan method applied with the CrisAlys RED package[50] for complex **11** and with SADABS for **2**, **3**, **5**, and **12**.[51] The structures were solved by direct methods. Refinement of complexes was performed by full-matrix least-squares on F^2 with SHELXL97,[52] including isotropic and subsequently anisotropic displacement parameters. The disordered groups observed along all the structures were refined with two moieties, complementary occupancy factors, and isotropic thermal parameters.

■ ASSOCIATED CONTENT

Supporting Information. Crystal details for **2**, **3**, **5**, **11**, and **12**; spectroscopic data for **14**; complete ref 49; optimized coordinates for complexes **10t**, **TS1**, and **12t**; and CIF files giving crystal data for **2**, **3**, **5**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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