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Articles

Synthesis of Hydrido−Vinylidene and Hydrido−Carbyne Osmium Complexes Containing Pyrazole: New Examples of N−H···Y (Y = N, F, Cl) Hydrogen Bonds

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The hydrido−carbyne complex $OsHCl_2(\equiv CCH_2Ph)(P^iPr_3)_2$ (**1**) reacts with pyrazole in the presence of KOH to afford the six-coordinate hydrido−vinylidene $OsH(pz)(=C=CHPh)(Hpz)(P^iPr_3)_2$ (**2**). The structure of **2** in the solid state has been determined by an X-ray diffraction study. The geometry around the metal center could be described as a distorted octahedron with the two phosphorus atoms of the phosphines occupying apical positions. The equatorial plane is defined by the hydride, the vinylidene, the pyrazole, and the pyrazolato ligands. The N−H hydrogen atom of the pyrazole lies between this azole group and the pyrazolate, forming an intramolecular N···H···N hydrogen bond. Reaction of **2** with HBF_4 leads to the fluoro−carbyne derivative $[OsHF(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (**3**), whose structure has been determined by an X-ray diffraction study. The geometry around the metal center could be also described as a distorted octahedron with the two phosphorus atoms of the phosphines occupying apical positions. The equatorial plane is defined by the hydride, the carbyne, the pyrazole group, and the fluoride ligand. The X-ray structure analysis of **3** shows that the N−H hydrogen atom of the pyrazole and the fluoride ligand are involved in intra- and intermolecular F···H−pz hydrogen bonding. Reaction of $[OsHCl(\equiv CCH_2Ph)(H_2O)(P^iPr_3)_2]BF_4$ (**4**) with pyrazole and acetonitrile leads to $[OsHCl(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (**5**) and $[OsHCl(\equiv CCH_2Ph)(CH_3CN)(P^iPr_3)_2]BF_4$ (**6**), respectively. Similarly to the fluoro−carbyne complex, the N−H hydrogen atom of the pyrazole group and the chloro ligand of complex **5** are involved in hydrogen bonding.

Introduction

Hydrido−vinylidene complexes are considered important intermediates in several homogeneous and heterogeneous catalytic reactions, including alkene oligomerization, polymerization, metathesis of olefins,[1] and Fischer−Tropsch synthesis.[2]

As a part of our studies on the reactivity of group 8 element hydrido compounds with alkynes,[3] in 1993 we reported that the six-coordinate dihydrido−osmium(IV) complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with terminal alkynes, $HC\equiv CR$, to give hydrido−carbyne derivatives of the type $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$,[4] which can be also prepared starting from α-olefins, $CH_2=CHR$.[5] Osmium(II) dihydrogen−vinylidene species were proposed as the key intermediates for the formation of the hydrido−carbyne derivatives from terminal alkynes. The reactions are rationalized as the electrophilic attack of the acidic hydrogen proton of the dihydrogen ligand on the C_β atom of the vinylidene.[4]

In agreement with this, it has been observed that the reaction of the hydrido−carbyne $OsHCl_2(\equiv CCH_2Ph)(P^iPr_3)_2$ with sodium methoxide leads to the five-coordinate hydrido−vinylidene $OsHCl(=C=CHPh)(P^iPr_3)_2$, which reacts with $HBF_4{\cdot}H_2O$ to give $[OsHCl(\equiv CCH_2Ph)(H_2O)(P^iPr_3)_2]BF_4$ and with HCl to regenerate $OsHCl_2(\equiv CCH_2Ph)(P^iPr_3)_2$.[6] Caulton and co-workers have recently reported that the reaction of the trihydrido complexes $MH_3Cl(PR_3)_2$ (M = Ru, Os; $PR_3 = P^tBu_2$-

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Me, P^iPr_3) with terminal alkynes is also a useful synthetic strategy to prepare hydrido−vinylidene complexes of the type $MHCl({=}C{=}CHR)(P^iPr_3)_2$ (M = Ru, Os).[7]

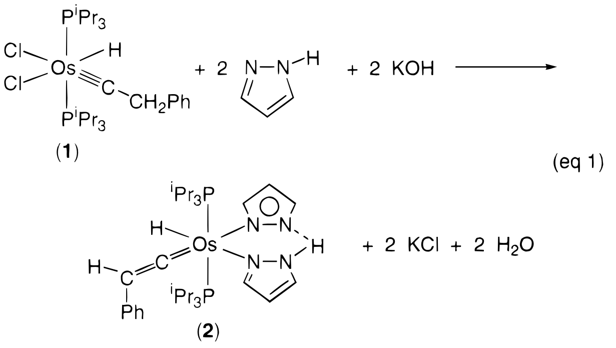
In addition to these five-coordinate derivatives, there are also known a few six-coordinate hydrido−vinylidene complexes of ruthenium and osmium, including $RuH(L{-}X)({=}C{=}CHSiEt_3)(PCy_3)_2$ (L−X = py−O, py−NH, quin−O),[8] $OsH(\kappa^2\text{-}OCOCH_3)({=}C{=}CHR)(P^iPr_3)_2$ [R = Ph,[9] $C(CH_3){=}CH_2$,[10] $C(OH)Ph_2$, $\overline{C{=}CH{-}(CH_2)_3CH_2}$[6]], $OsH(acac)({=}C{=}CHPh)(P^iPr_3)_2$, $OsHCl({=}C{=}CHPh)\{P(OMe)_3\}(P^iPr_3)_2$,[6] $OsHCl(CO)({=}C{=}CHCy)(P^iPr_3)_2$,[11] $(P^iPr_3)_2(CO)ClRu\{(E)\text{-}CH{=}CH{-}(CH_2)_4{-}CH{=}C{=}\}OsCl(CO)(P^iPr_3)_2$,[12] and $[OsH\{{=}C{=}CH(SiMe_3)\}(PP_3)]^+$ [$PP_3 = P(CH_2CH_2PPh_2)_3$].[13] With the exception of those containing bidentate ligands, the six-coordinate hydrido−vinylidene complexes are unstable, and in solution evolve to the corresponding five-coordinate alkenyl derivatives as a result of the migratory insertion of the vinylidene group into the Os−H bond.[11−13]

In this paper, we report the synthesis and characterization of the stable six-coordinate hydrido−vinylidene complex $OsH(pz)({=}C{=}CHPh)(Hpz)(P^iPr_3)_2$ (Hpz = pyrazole) and the hydrido−carbyne derivatives $[OsHX({\equiv}CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (X = F, Cl), which are of interest not only because they are novel examples of organometallic derivatives containing η^1-carbon ligands but also because the N−H hydrogen atom of the pyrazole is involved in hydrogen bonding. Of great importance in biological and organic chemistry,[14] the hydrogen bonding is presently attracting considerable interest in the chemistry of transition metals.[15]

Results and Discussion

1. Synthesis and Characterization of $OsH(pz)({=}C{=}CHPh)(Hpz)(P^iPr_3)_2$. Caulton and co-workers[16] have recently reported that the carbyne complexes $OsHCl_2({\equiv}CCH_2R)(P^iPr_3)_2$ (R = Ph, CH_3) react with carbon monoxide to give, after a 1,2-hydride migration from osmium to the C_α carbon atom of the carbyne ligand, the osmium carbene complexes $OsCl_2(CO)({=}CHCH_2R)(P^iPr_3)_2$, which can be also prepared by reaction of the dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ with the corresponding alkyne.[3d] In addition, it should be mentioned that the approach toward generating metal−carbene complexes involves electrophilic addition to nucleophilic carbyne ligands. Thus, a large number of carbene derivatives have been obtained by protonation of carbyne starting materials.[17]

Pyrazole is a molecule containing two nucleophilic nitrogen atoms and one electrophilic hydrogen atom,[18] which at first glance could act as the carbon monoxide, promoting the 1,2-hydride migration from the metal to the C_α carbon atom of the carbyne or, alternatively, protonating the η^1-carbon ligand. This characteristic prompted us to carry out the reaction of $OsHCl_2({\equiv}CCH_2Ph)(P^iPr_3)_2$ (**1**) with pyrazole. Treatment of **1** with pyrazole does not give rise to any change in the ^1H NMR spectrum of **1** in acetone-d_6, even when 3 equiv of pyrazole is used. However, the addition of 3 equiv of KOH in methanol to an acetone solution of **1** and pyrazole produces the deprotonation of both the carbyne ligand and one pyrazole molecule and the formation of the six-coordinate hydrido−vinylidene $OsH(pz)({=}C{=}CHPh)(Hpz)(P^iPr_3)_2$ (**2**), which was isolated as a dark orange solid in 70% yield, according to eq 1.



(eq 1)

Figure 1 shows a view of the molecular geometry of **2**. Selected bond distances and angles are listed in Table 1. At 200 K, the hydride ligand H(1A) and the hydrogen atom H(1B) were located in the difference Fourier maps and refined as isotropic atoms together with the rest of the non-hydrogen atoms of the structure, giving Os(1)−H(1A), N(2)−H(1B), and N(4)−H(1B) distances of 1.56(4), 1.53(6), and 1.10(6) Å, respectively.

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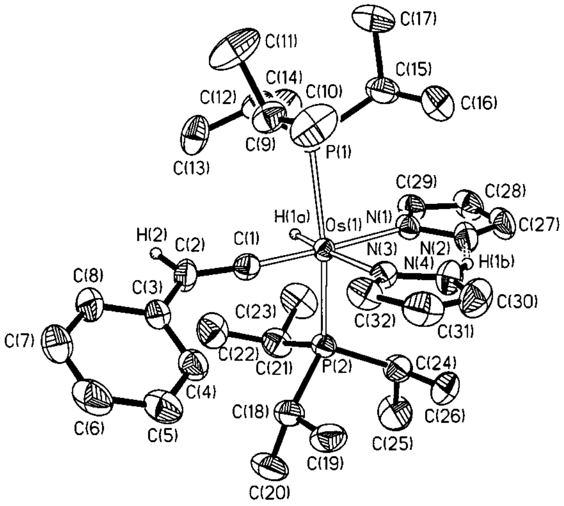

Figure 1. Molecular diagram of the complex $OsH(pz)(=C=CHPh)(Hpz)(P^{i}Pr_3)_2$ (**2**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH(pz)(=C=CHPh)(Hpz)(P^{i}Pr_3)_2$ (2)

Os(1)−C(1)	1.818(4)	N(3)−C(32)	1.339(5)
Os(1)−P(1)	2.4069(9)	N(4)−C(30)	1.344(5)
Os(1)−P(2)	2.3914(9)	N(2)−H(1B)	1.53(6)
Os(1)−N(1)	2.212(3)	N(4)−H(1B)	1.10(6)
Os(1)−N(3)	2.215(3)	C(1)−C(2)	1.345(5)
Os(1)−H(1A)	1.56(4)	C(2)−C(3)	1.456(5)
N(1)−N(2)	1.363(4)	C(27)−C(28)	1.378(6)
N(4)−N(3)	1.348(4)	C(28)−C(29)	1.377(5)
N(1)−C(29)	1.343(5)	C(30)−C(31)	1.364(6)
N(2)−C(27)	1.352(5)	C(31)−C(32)	1.391(6)

C(1)−Os(1)−N(3)	97.58(13)	C(1)−Os(1)−N(1)	173.20(13)
N(3)−Os(1)−N(1)	89.21(11)	C(1)−Os(1)−P(2)	90.13(11)
N(3)−Os(1)−P(2)	99.33(8)	N(1)−Os(1)−P(2)	88.68(8)
C(1)−Os(1)−P(1)	89.74(11)	N(3)−Os(1)−P(1)	96.12(8)
N(1)−Os(1)−P(1)	89.61(8)	P(2)−Os(1)−P(1)	164.43(3)
C(1)−Os(1)−H(1A)	91.1(14)	N(3)−Os(1)−H(1A)	170.9(14)
N(1)−Os(1)−H(1A)	82.1(14)	P(2)−Os(1)−H(1A)	77.9(14)
P(1)−Os(1)−H(1A)	86.6(14)	N(2)−N(1)−Os(1)	123.3(2)
N(1)−N(2)−H(1B)	110(2)	N(3)−N(4)−H(1B)	113(3)
N(4)−N(3)−Os(1)	124.6(2)	C(2)−C(1)−Os(1)	174.5(3)
C(1)−C(2)−C(3)	129.0(4)	N(2)−H(1B)−N(4)	159(5)

The osmium atom is coordinated in a somewhat octahedral fashion with the two triisopropylphosphine ligands in pseudo-*trans* positions [P(1)−Os(1)−P(2) = 164.43(3)°]. The perpendicular plane is formed by the hydride and vinylidene ligands, the N(3)−C(32)−C(31)−C(30)−N(4) azole group *trans* disposed to the hydride ligand [N(3)−Os(1)−H(1A) = 170.9(14)°], and the N(1)−C(29)−C(28)−C(27)−N(2) azole group *trans* disposed to the vinylidene [N(1)−Os−C(1) = 173.20(13)°].

Both azole rings are almost planar, and the dihedral angle formed by the least-squares planes through the atoms of both cycles is 3.9(3)°. Between the heterocycles the related structural parameters are statistically identical, as well as the Os(1)−N(1) [2.212(3) Å] and the Os−N(3) [2.215(3) Å] bond lengths. The hydrogen atom H(1B) is situated between the nitrogen atom N(2) and N(4) of the heterocycles (Figure 2), and according to the previously mentioned values of the hydrogen−nitrogen separations, it appears to give rise to an intramolecular hydrogen bond,[15c,d] being the angle N(2)···H(1B)···N(4) 159(5)°. Similar values have been previously found for intramolecular hydrogen bonding between 2-cyanoguanidine and 3-chloro-6-(pyrazol-1-yl)pyridazines in copper(II) complexes.[19]

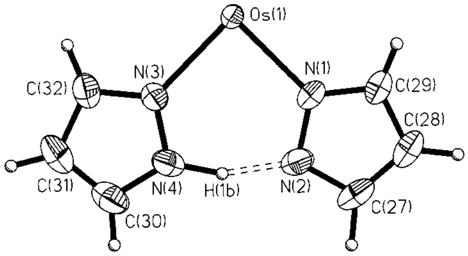

Figure 2. Partial view of the molecular diagram of complex **2** showing the intramolecular N···H···N bond.

The vinylidene ligand is bound to the metal in a nearly linear fashion with an Os(1)−C(1)−C(2) angle of 174.5(3)°. The Os(1)−C(1) [1.818(4) Å] and C(1)−C(2) [1.345(5) Å] bond lengths compare well with the ones found in other osmium−vinylidene complexes[20] and support the vinylidene formulation.

In agreement with the presence of the hydride and vinylidene ligands in **2**, the IR spectrum of this compound in KBr shows the ν(Os−H) and ν(C=C) bands at 2130 and 1606 cm^{-1}, respectively. In addition, it should be mentioned that the spectrum does not contain the characteristic ν(N−H) absorption of the pyrazole complexes between 3300 and 3200 cm^{-1}.[21] The same phenomenon has been previously observed in the complexes $OsH_3(pz)(Hpz)(P^{i}Pr_3)_2$[22] and $MH(pz)(CO)(Hpz)(PR_3)_2$ (M = Ru, Os; PR_3 = PPh_3,[23] $P^{i}Pr_3$[24]), where an intramolecular hydrogen bond between the nitrogen atoms of the azole groups has been also proposed. Like the ^1H NMR spectra of these complexes, the ^1H NMR spectrum of **2** in benzene-d_6 shows the N−H resonance at unusually low field, 20.78 ppm, which is a typical chemical shift for the N−H protons of the so-called *proton-sponge* compounds.[25]

Chaudret and co-workers have previously reported the reaction of $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ with 2 equiv of pyrazole to afford the dihydrogen derivative $RuH(pz)(\eta^2\text{-}H_2)(Hpz)(PCy_3)_2$, which in solution contains symmetrical azole groups. To rationalize this, they have suggested a rapid jump of the nitrogen-bonded pyrazole proton from one azole group to the other.[26]

The ^1H NMR spectrum of **2** also supports the presence of the vinylidene and hydride ligands; the resonance due to the =CHPh proton of the vinylidene appears at 1.88 ppm as a triplet with a H−P coupling constant of 3 Hz, and the hydride ligand gives rise at −9.48 ppm to a triplet with a H−P coupling constant of 17.4 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the vinylidene carbon atoms appear at 293.70 (C_α)

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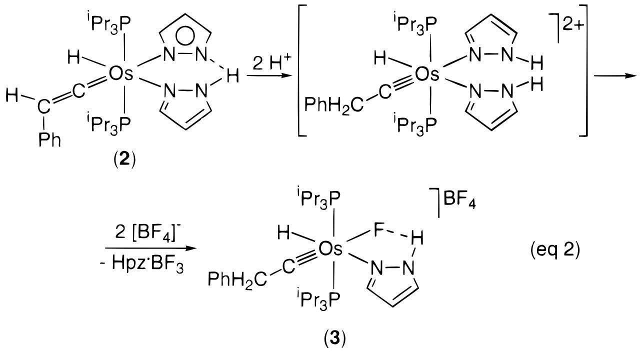
and 111.20 (C_β) ppm, as triplets with C−P coupling constants of 11.5 and 2.7 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains at 8.4 a singlet, that under off-resonance conditions is split into a doublet, as the result of the coupling with the hydride ligand. These spectra are temperature invariant and do not show significant changes upon changing the solvent.

2. Synthesis and Characterization of [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$. We have previously observed that the hydrogen bonding between the azole groups of the complex $OsH_3(pz)(Hpz)(P^iPr_3)_2$ can be broken by addition of HBF_4. This reaction leads to the cationic derivative $[OsH_3(Hpz)_2(P^iPr_3)_2]BF_4$.[22] In contrast to $OsH_3(pz)(Hpz)(P^iPr_3)_2$, the treatment of a diethyl ether solution of **2** with 1 equiv of $HBF_4{\cdot}Et_2O$ affords the fluoro complex $[OsHF(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (**3**), in 40% yield. When the reaction is carried out in a 1:2 molar ratio, the same compound in 83% yield is obtained.

The formation of **3** can be rationalized according to eq 2. One equivalent of acid protonates the C_β carbon atom of the vinylidene to give a carbyne ligand, whereas the protonation of the pz−H···pz unit by the other equivalent leads to two pyrazole ligands. Subsequently, the decomposition of a $[BF_4]^-$ anion affords a fluorine ligand, which displaces one of the two pyrazole ligands.



(eq 2)

The formation of fluoride-containing compounds by controlled fluoride release through $[BF_4]^-$ decomposition in the presence of azole ligands has been previously reported by Reedijk and co-workers.[27] Recently, Pombeiro and co-workers[28] have succeeded in preparing a series of fluoro−carbyne complexes of rhenium, *trans*-[ReF(≡CCH$_2$R)(dppe)$_2$]BF$_4$, in which the $[BF_4]^-$ anion behaved as the metal fluorinating agent.

Although there is experimental evidence suggesting that the fluoro complexes are stable when π-back-bonding ligands are also present in the coordination sphere of the metal, the chemistry of these compounds is relatively unexplored.[29] To date, only a few osmium fluoride organometallic compounds have been previously reported, between them the derivatives $OsF(CO)_2(N{=}NPh)(PPh_3)_2$,[30] $[OsF_2(CO)_3]_4$,[31] $OsF(COF)(CO)_2(PPh_3)_2$,[32] and $OsF_2(CO)_2(PR_3)_2$ ($PR_3 = PPh_3$, PCy_3).[33] Fluoro−osmium−carbyne complexes are unknown, and in general, fluoro−carbyne complexes are very rare.[28,34]

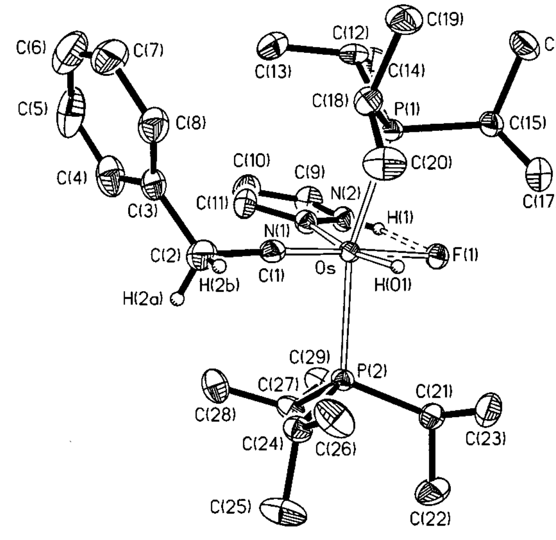


Figure 3. Molecular diagram of the cation of **3**, [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]$^+$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ (3)

Os−C(1)	1.721(4)	N(1)−C(11)	1.337(6)
Os−P(1)	2.4392(11)	N(2)−C(9)	1.337(6)
Os−P(2)	2.4315(12)	N(2)−H(1)	0.75(5)
Os−F(1)	2.087(2)	C(1)−C(2)	1.488(6)
Os−N(1)	2.209(4)	C(2)−C(3)	1.518(7)
Os−H(01)	1.45(6)	C(9)−C(10)	1.371(7)
N(1)−N(2)	1.349(5)	C(10)−C(11)	1.394(7)
C(1)−Os−F(1)	177.8(2)	C(1)−Os−N(1)	101.2(2)
F(1)−Os−N(1)	79.00(12)	C(1)−Os−P(2)	91.59(14)
F(1)−Os−P(2)	86.25(7)	N(1)−Os−P(2)	98.59(10)
C(1)−Os−P(1)	94.86(14)	F(1)−Os−P(1)	87.24(7)
N(1)−Os−P(1)	96.65(10)	P(2)−Os−P(1)	161.96(4)
C(1)−Os−H(01)	91(2)	F(1)−Os−H(01)	89(2)
N(1)−Os−H(01)	166(2)	P(2)−Os−H(01)	86(2)
P(1)−Os−H(01)	77(2)	C(2)−C(1)−Os	176.7(4)

Complex **3** was isolated as a white solid and characterized by elemental analysis, IR and ^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction. Figure 3 shows the molecular diagram of the structure of **3**. Selected bond distances and angles are listed in Table 2. The geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands in a pseudo-*trans* position [P(1)−Os−P(2) = 161.96(4)°]. The perpendicular plane is formed by the hydride and carbyne ligands, the azole group *trans* disposed to the hydride [N(1)−Os−H(01) = 166(2)°], and the fluoride atom *trans* disposed to the carbyne [C(1)−Os−F(1) = 177.8(2)°]. The carbyne formulation is supported by the Os−C(1) bond length [1.721(4) Å] and by the Os−C(1)−C(2) angle [176.7(4)°]. The very short Os−C(1) distance

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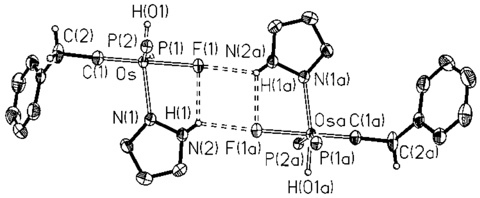

Figure 4. Intra- and intermolecular Os−F···H−N interactions in [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ (**3**). Substituents on the phosphines have been omitted for clarity.

is fully consistent with an osmium−carbon triple bond,[35] whereas the Os−C(1)−C(2) angle clearly indicates sp hybridization of C(1).

The Os−N(1) [2.209(4) Å] bond length and the C−C and C−N bond distances within the azole ring are statistically identical with the related parameters of **2**, while the N(2)−H(1) [0.75(5) Å] distance is slightly shorter. The Os−F(1) bond length [2.087(2) Å] is about 0.05 Å longer than the Os−F distances found in the dicarbonyl compounds OsF$_2$(CO)$_2$(PCy$_3$)$_2$ [2.023(4) and 2.022(4) Å] and OsF$_2$(CO)$_2$(PPh$_3$)$_2$ [2.023(5) Å].[33] Interestingly, the separation between the fluorine and the N−H hydrogen atom H(1) [2.20(5) Å] is shorter than the sum of the van der Waals radii of hydrogen and fluorine [$r_{\mathrm{vdW}}(\mathrm{H}) = 1.20$, $r_{\mathrm{vdW}}(\mathrm{F}) = 1.47$ Å],[36] suggesting that there is an intramolecular F···H hydrogen bond between these atoms, as a result of the interaction of the electronegative fluorine atom with the acidic N−H hydrogen. The H···F hydrogen bond gives rise to a five-membered Os−F···H−N−N ring. An extended view of the strucutre (Figure 4) indicates also short intermolecular interactions [2.23(5) Å] between the fluorine and the N−H hydrogen atoms of two adjacent molecules in the crystal.

These F···H hydrogen bonds are also supported by the IR spectrum of **3** in KBr, which shows the N−H stretching frequency at 3287 cm^{-1}, shifted 63 cm^{-1} to lower wavenumbers in comparison with that observed in the complex [OsH$_3$(Hpz)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (3350 cm^{-1}).[22] In addition, it should be mentioned the ν(Os−H) band, which appears at 2156 cm^{-1}, and the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry between 1000 and 1100 cm^{-1}.

In polar solvents such as acetone-d_6, dichloromethane-d_2, and chloroform-d, the intermolecular N−H···F hydrogen bond is broken, while the intramolecular NH···F interaction seems to be retained. Thus, in the three solvents, the ^{1}H NMR spectrum of **3** shows the N−H resonance at about 12 ppm, as a doublet instead of the triplet that should be expected for an association as that shown in Figure 4. The H−F coupling constant depends on the solvent, decreasing in the sequence chloroform-d (24 Hz) > dichloromethane-d_2 (21.6 Hz) > acetone-d_6 (18.3 Hz). This suggests that the strength of the intramolecular N−H···F hydrogen bond decreases by increasing the polarity of the solvent, in agreement with the electrostatic character of the interaction.

The ^{1}H NMR spectrum of **3** in chloroform-d shows in the low-field region, in addition to the above-mentioned doublet, a singlet N−H resonance displaced 0.7 ppm toward low field with regard to the doublet. This resonance could correspond to a [OsH(F···DCl)(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$[37] species, where the N−H···F hydrogen bond is broken as a consequence of the solvation of the fluoride ligand by the adventitious presence of trace amounts of DCl in the solvent. The interaction between the fluoride ligands of Cp$_2$TiF$_2$ and HCl has been proven by matrix isolation techniques combined with infrared spectroscopy.[38]

We note that that synthesis of IrH$_2$F{py-N(Ph)-H}(PPh$_3$)$_2$ has been previously reported.[39] In contrast to **3**, the Ir−F···H−Npy unit forms a six-membered ring, which probably gives rise to a shorter F···H separation. As a result, in dichloromethane-d_2, the value of the coupling constant between the NH hydrogen and the fluoride nucleus (65.1 Hz) is higher than that observed in **3**.

The ^{1}H NMR spectra also support the presence of the carbyne and hydride ligands. In acetone-d_6, the −CH$_2$− hydrogen atoms of the carbyne ligand display at 3.24 a singlet, whereas the hydride ligand gives rise at −5.75 ppm to a double triplet with H−P and H−F coupling constants of 17.1 and 8.4 ppm, respectively. The ^{19}F, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra agree well with the ^{1}H NMR spectrum and with the molecular diagram shown in Figure 3. The ^{19}F NMR spectrum shows at −281.6 ppm a multiplet due to the fluoride ligand, whereas the ^{31}P{^{1}H} NMR spectrum contains at 40.3 a doublet with a P−F coupling constant of 40 Hz. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonance is that due to the C$_\alpha$ carbon atom of the carbyne ligand, which appears at 279.33 ppm, as a double triplet, with C−F and C−P coupling constants of 121.0 and 9.9 Hz, respectively.

3. Synthesis and Characterization of [OsHCl(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$. The water molecule of the complex [OsHCl(≡CCH$_2$Ph)(H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**) can be displaced by N-donor ligands such as pyrazole and acetonitrile. The addition of 1 equiv of pyrazole to dichloromethane solutions of **4** affords [OsHCl(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**), whereas the treatment of a dichloromethane solution of **4** with 1 equiv of acetonitrile leads to [OsHCl(≡CCH$_2$Ph)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (**6**). These compounds were isolated as white solids in 59% (**5**) and 75% (**6**) yield, according to Scheme 1.

The IR spectrum of **5** in KBr suggests that, similarly

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(37) Selected ^{1}H and ^{31}P{^{1}H} NMR data of [OsH(F···D-Cl)(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ at 223 K. ^{1}H NMR (300 MHz, CDCl$_3$): δ 12.43 (s, 1H, NH), 2.89 (s, 2H, ≡CCH_2Ph), −6.45 (dt, 1H, $J_{\mathrm{P-H}} = 15.0$ Hz, $J_{\mathrm{F-H}} = 9.0$ Hz, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$): δ 32.7 (d, $J_{\mathrm{P-F}} = 32.5$ Hz).

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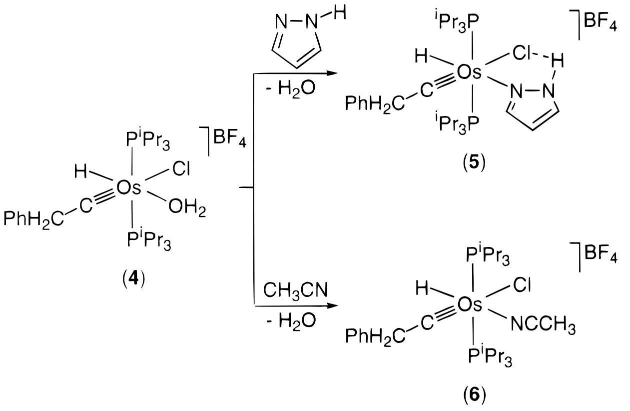
Scheme 1



to **3**, the N−H hydrogen and chloride atoms are involved in hydrogen bonding. Thus, in the IR spectrum the N−H stretching frequency appears at 3291 cm^{-1}, shifted 59 cm^{-1} to lower wavenumbers in comparison with that observed in the complex [OsH$_3$(Hpz)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$. Furthermore, the spectrum shows at 2163 cm^{-1} the ν(Os−H) band, and between 1000 and 1100 cm^{-1}, the absorption due to the [BF$_4$]$^-$ anion, with T_d symmetry.

The ^{1}H NMR spectrum in acetone-d_6 contains only one N−H resonance at 12.4 ppm. The −CH$_2$− hydrogen atoms of the carbyne ligand display at 3.35 ppm a singlet, whereas the hydride ligand gives rise at −7.49 to a triplet with a H−P coupling constant of 16.8 Hz. In the ^{13}C{^{1}H} NMR spectrum, the C$_\alpha$ resonance of the carbyne ligand is observed at 274.10 ppm as a triplet with a C−P coupling constant of 9.8 Hz. The ^{31}P{^{1}H} NMR spectrum shows at 23.4 ppm a singlet.

In chloroform-*d*, complex **5** shows a behavior similar to the one described for **3**. In addition to the resonances of **5**, the ^{1}H NMR spectrum shows peaks that could be assigned to a [OsH(Cl···DCl)(≡CCH$_2$Ph)(HPz)(P^{i}Pr$_3$)$_2$]BF$_4$ species.[40] This suggests that, like in **3**, the intramolecular NH···Cl hydrogen bond is retained in solution.

The most noticeable features of the IR spectrum of **6** in Nujol are the ν(CN) and ν(Os−H) bands, which appear at 2322 and 2170 cm^{-1}, respectively. In the ^{1}H NMR spectrum, the CH$_3$ protons of the acetonitrile ligand and the −CH$_2$− hydrogen atoms of the carbyne group give rise to singlets at 2.68 and 2.72 ppm, respectively, whereas the hydride ligand displays a triplet at −6.35 ppm, with a H−P coupling constant of 16.5 Hz. In the ^{13}C{^{1}H} NMR spectrum the C$_\alpha$ resonance of the carbyne appears at 271.52 ppm as a triplet with a C−P coupling constant of 8.7 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 27.6 ppm.

Concluding Remarks

This study has revealed that the hydrido−carbyne complex OsHCl$_2$(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$ reacts with pyrazole in the presence of KOH to give OsH(pz)(=C=CHPh)(Hpz)(P^{i}Pr$_3$)$_2$. Although this complex is a six-coordinate hydrido−vinylidene derivative and the metal does not contain bidentate ligands on its coordination sphere, the complex is stable and does not evolve, by migratory insertion of the vinylidene into the Os−H bond, to the corresponding alkenyl species. Furthermore, from a structural point of view, it should be mentioned that the N−H hydrogen atom of the pyrazole ligand lies between this azole group and the pyrazolate, forming a N···H···N hydrogen bond, which gives rise to an $\overline{\text{Os−N−N···H−N−N}}$ six-membered ring.

In the presence of OsH(pz)(=C=CHPh)(Hpz)(P^{i}Pr$_3$)$_2$, the [BF$_4$]$^-$ anion of HBF$_4$ behaves as metal fluorinating reagent. Thus, addition of 1 or 2 equiv of this acid to the vinylidene complex affords the fluoro−carbyne compound [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$. The X-ray structure analysis of this complex shows that the N−H hydrogen atom of the pyrazole and the fluoride ligand are involved in intra- and intermolecular F···H−pz hydrogen bonding. In polar solvents the intermolecular hydrogen bond is broken. However, the intramolecular interaction is retained. The strength of this interaction appears to depend on the polarity of the solvent, decreasing in the sequence chloroform > dichloromethane > acetone.

The related chloro−carbyne complex [OsHCl(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ has been prepared by reaction of [OsHCl(≡CCH$_2$Ph)(H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ with pyrazole. Similarly to the fluoro−carbyne complex, the N−H hydrogen atom of the pyrazole and the chloro ligand are involved in hydrogen bonding. In solution, the intramolecular interaction is retained.

In conclusion, we report the synthesis, X-ray structure, and spectroscopic characterization of novel hydrido−vinylidene and hydrido−carbyne osmium(II) derivatives, which contain pyrazole, and where the N−H hydrogen atom of this ligand is involved in pz−H···Y (Y = N, F, Cl) hydrogen bonding.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. OsHCl$_2$(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$ (**1**)[4] and [OsHCl(≡CCH$_2$Ph)(H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**)[6] were prepared as reported. Infrared spectra were run on a Nicolet 550 spectrometer as solids (KBr pellet or Nujol mull). ^{1}H, ^{19}F, ^{31}P, and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian Gemini 2000 or a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external H$_3$PO$_4$ (^{31}P), or external CFCl$_3$ (^{19}F). Coupling constants, J and N ($N = J_{P-H} + J_{P'-H}$ for ^{1}H and $N = J_{P-C} + J_{P'-C}$ for ^{13}C{^{1}H}), are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of OsH(pz)(=C=CHPh)(Hpz)(P^{i}Pr$_3$)$_2$ (2). Pyrazole (23.8 mg, 0.35 mmol) was added to a yellow solution of **1** (80 mg, 0.117 mmol) in acetone (10 mL), and immediately after that, the resulting solution was treated with a solution of KOH in MeOH (0.35 mmol). After stirring for 5 min at room temperature the color of the solution had changed to orange-reddish. The acetone solution was taken to dryness, the orange residue was disolved in toluene (8 mL), and the resulting suspension was filtered through Celite. The toluene solution was dried in vacuo, and methanol was added to afford a deep orange solid, which was washed with methanol and dried in vacuo. Yield: 62 mg (70%). Anal. Calcd for C$_{32}$H$_{56}$N$_4$OsP$_2$: C, 51.32; H, 7.54; N, 7.48. Found: C, 51.01; H, 6.89; N, 7.41. IR (KBr, cm^{-1}): ν(Os−H) 2130 (s), ν(C=C) 1606. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 20.78 (s, 1H, N−H), 8.13 (d, $J_{H-H} = 1.8$ Hz, 1H, pz), 7.76 (d, $J_{H-H} = 1.8$ Hz, 1H, pz), 7.52 (d, $J_{H-H} =$

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[40] Selected ^{1}H and ^{31}P{^{1}H} NMR data of [OsH(Cl···DCl)(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ at 223 K. ^{1}H NMR (300 MHz, CDCl$_3$): δ 12.22 (s, 1H, NH), 2.97 (s, 2H, ≡CCH_2Ph), −8.04 (t, 1H, $J_{P-H} = 15.4$ Hz, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$): δ 23.2 (s).

2.1 Hz, 1H, pz), 7.41 (d, $J_{H-H} = 2.1$ Hz, 1H, pz), 7.32−6.83 (m, 5H, Ph), 6.29 (br, 1H, pz), 6.21 (t, $J_{H-H} = 1.8$ Hz, 1H, pz), 2.16 (m, 6H, PC*H*(CH_3)$_2$), 1.88 (t, $J_{P-H} = 3.0$ Hz, 1H, Os=C=C*H*Ph), 1.04 (dvt, $J_{H-H} = 7.2$ Hz, $N = 14.1$ Hz, 18H, PCH(CH_3)$_2$), 0.95 (dvt, $J_{H-H} = 7.2$ Hz, $N = 14.1$ Hz, 18H, PCH(CH_3)$_2$), −9.48 (t, $J_{P-H} = 17.4$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 8.4 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 293 K): δ 293.70 (t, $J_{P-C} = 11.5$ Hz, Os=*C*=CHPh), 145.24 (br s, pz), 144.69 (br s, pz), 132.84 (br s, pz), 131.84 (t, $J_{P-C} = 1.8$ Hz, Ph C_{ipso}), 130.60 (br s, pz), 124.00 (s, Ph), 122.40 (s, Ph), 111.20 (t, $J_{P-C} = 2.7$ Hz, Os=C=*C*HPh), 105.95 (s, pz), 105.20 (s, pz), 25.03 (vt, $N = 23.4$ Hz, P*C*H(CH_3)$_2$), 19.52 (s, PCH(*C*H_3)$_2$), 19.27 (s, PCH(*C*H_3)$_2$).

Preparation of [OsHF(≡CCH_2Ph)(Hpz)(P^iPr_3)$_2$]BF_4 (3). A solution of **2** (100 mg, 0.134 mmol) in diethyl ether (10 mL) was treated with HBF_4·OEt_2 (36 μL, 0.267 mmol). Immediately a white suspension was obtained, and it was stirred for 5 min at room temperature. The white solid obtained was washed with diethyl ether, and it was dried in vacuo. Yield: 87 mg (83%). Anal. Calcd for $C_{29}H_{54}BF_5N_2OsP_2$: C, 44.16; H, 6.85; N, 3.55. Found: C, 44.12; H, 6.24; N, 3.57. IR (KBr, cm^{-1}): ν(N−H) 3287 (m, br), ν(Os−H) 2156 (m), ν(BF_4) 1100−1000 (vs). ^1H NMR (300 MHz, acetone-d_6, 293 K): δ 12.36 (d, $J_{F-H} = 18.3$ Hz, 1H, N−H), 8.37 (s, 1H, pz), 8.04 (s, 1H, pz), 7.45−7.36 (m, 5H, Ph), 6.79 (s, 1H, pz), 3.24 (s, 2H, −CH_2Ph), 2.39 (m, 6H, PC*H*(CH_3)$_2$), 1.32 (dvt, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, 18H, PCH(CH_3)$_2$), 1.04 (dvt, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, 18H, PCH(CH_3)$_2$), −5.75 (dt, $J_{P-H} = 17.1$ Hz, $J_{F-H} = 8.4$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, 293 K): δ 40.3 (d, $J_{P-F} = 40$ Hz). ^{19}F NMR (282.33 MHz, acetone-d_6, 293 K): δ −147.7 (s, BF_4), −281.6 (m, Os−F). $^{13}C\{^1H\}$ NMR (75.47 MHz, acetone-d_6, 293 K): δ 279.33 (dt, $J_{C-F} = 121.0$ Hz, $J_{P-C} = 9.9$ Hz, Os≡*C*), 144.00 (br s, pz), 131.97 (s, pz), 131.17, 130.45, 129.45 (all s, Ph), 110.39 (br s, pz), 58.23 (d, $J_{C-F} = 12.2$ Hz, Os≡C*C*H_2Ph), 25.44 (vt, $N = 26.0$ Hz, P*C*H(CH_3)$_2$), 19.44 (s, PCH(*C*H_3)$_2$), 18.68 (s, PCH(*C*H_3)$_2$).

Preparation of [OsHCl(≡CCH_2Ph)(Hpz)(P^iPr_3)$_2$]BF_4 (5). A solution of **4** (75 mg, 0.099 mmol) in dichloromethane (10 mL) was treated with pyrazole (8.75 mg, 0.129 mmol). After stirring for 45 min at room temperature, the solution was concentrated until ca. 1 mL. Addition of diethyl ether leads to a white solid that was washed several times with diethyl ether and dried in vacuo. Yield: 50.8 mg (59%). Anal. Calcd for $C_{29}H_{54}BClF_4N_2OsP_2$: C, 43.16; H, 6.75; N, 3.47. Found: C, 43.44; H, 6.45; N, 3.90. IR (KBr, cm^{-1}): ν(N−H) 3291 (m), ν(Os−H) 2163 (w), ν(BF_4) 1000−1100 (m). ^1H NMR (300 MHz, acetone-d_6, 293 K): δ 12.4 (s, 1H, N−H), 8.43 (s, 1H, pz), 8.06 (s, 1H, pz), 7.45−7.39 (m, 5H, Ph), 6.75 (s, 1H, pz), 3.35 (s, 2H, Os≡CCH_2Ph), 2.66 (m, 6H, PC*H*(CH_3)$_2$), 1.34 (dvt, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, 18H, PCH(CH_3)$_2$), 1.01 (dvt, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, 18H, PCH(CH_3)$_2$), −7.49 (t, $J_{P-H} = 16.8$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, 293 K): δ 23.4 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, acetone-d_6, 293 K): δ 274.10 (t, $J_{P-C} = 9.8$ Hz, Os≡*C*CH_2Ph), 146.40 (br s, pz), 133.30 (s, pz), 131.34, 130.95, 129.79, 129.28 (each one s, Ph), 110.17 (br s, pz), 57.70 (s, Os≡C*C*H_2Ph), 26.77 (vt, $N = 27.5$ Hz, P*C* H(CH_3)$_2$), 20.12 (s, PCH(*C*H_3)$_2$), 18.62 (s, PCH(*C*H_3)$_2$).

Preparation of [OsHCl(≡CCH_2Ph)($NCCH_3$)(P^iPr_3)$_2$]BF_4 (6). CH_3CN (20.8 μL, 0.39 mmol) was added via syringe to a solution of **4** (227 mg, 0.30 mmol) in dichloromethane (10 mL). The resulting solution was stirred 30 min at room temperature, and during this time bleaching of the solution color was observed. The solvent was evaporated until ca. 0.5 mL, and diethyl ether was added, resulting in a white suspension. The white solid was washed twice with diethyl ether and dried in vacuo. Yield: 192 mg (75%). Anal. Calcd for $C_{28}H_{53}BClF_4NOsP_2$: C, 43.12; H, 6.85; N, 1.80. Found: C, 43.41; H, 6.85; N, 1.78. IR (Nujol, cm^{-1}): ν(C≡N) 2322 (m), ν(Os−H) 2170 (s), ν(BF_4) 1000−1100 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.40−7.20 (m, 5H, Ph), 2.72 (s, 2H, ≡CCH_2Ph), 2.68 (s, 3H, N≡CCH_3), 2.56 (m, 6H, PC*H*(CH_3)$_2$), 1.37 (dvt, $J_{P-H} = 7.5$ Hz, $N = 14.4$ Hz, 18H, PCH(CH_3)$_2$), 1.28 (dvt, $J_{P-H} = 5.4$ Hz, $N = 12.6$ Hz, 18H, PCH(CH_3)$_2$), −6.35 (t, $J_{P-H} = 16.5$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 27.6 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 271.52 (t, $J_{P-C} = 8.7$ Hz, Os≡*C*), 130.03 (s, Ph), 129.98 (s, Ph), 129.23 (s, Ph), 127.21 (s, Os−N≡*C*CH_3), 57.57 (s, Os≡C*C*H_2Ph), 26.84 (vt, $N = 27.1$ Hz, P*C*H(CH_3)$_2$), 19.16 (s, PCH(*C*H_3)$_2$), 19.10 (s, PCH(*C*H_3)$_2$), 3.72 (s, Os−N≡C*C*H_3).

Table 3. Crystal Data and Data Collection and Refinement for OsH(pz)(=C=CHPh)(Hpz)(P^iPr_3)$_2$ (2) and [OsHF(≡CCH_2Ph)(Hpz)(P^iPr_3)$_2$]BF_4 (3)

	2	**3**
formula	$C_{32}H_{56}N_4OsP_2$	$C_{29}H_{54}BF_5N_2OsP_2$
mol wt	748.95	788.69
color, habit	dark orange, prismatic block	pale yellow, prismatic block
cryst size, mm	0.51 × 0.18 × 0.16	0.26 × 0.25 × 0.17
space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	10.529(1)	11.752(2)
b, Å	10.905(1)	12.169(2)
c, Å	15.444(2)	13.116(2)
α, deg	80.473(9)	88.21(1)
β, deg	83.253(6)	77.847(8)
γ, deg	88.06(1)	67.092(7)
V, Å^3	1736.5(3)	1686.4(5)
Z	2	2
D(calcd), g cm^{-3}	1.432	1.553
μ, mm^{-1}	3.789	3.924
scan type	θ/2θ	θ/2θ
2θ range, deg	$6 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 50$
temp, K	200.0(2)	200.0(2)
no. of data collcd	7310	7125
no. of unique data	6233	5914
no. of params refined	374	462
$R_1{}^a$ ($F_o \geq 4.0\sigma(F_o)$)	0.0217	0.0210
$wR_2{}^b$ (all data)	0.0567	0.0511
S^c (all data)	0.978	1.011

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$ (**2**, $a = 0.0346$, $b = 1.7805$; **3**, $a = 0.0326$, $b = 1.4359$). [c] $S = [\sum[w(F_o{}^2 - F_c{}^2)2]/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

Crystal Data for 2 and 3. Crystals suitable for the X-ray diffraction study were obtained by cooling at 243 K a solution of **2** in pentane or by slow diffusion of diethyl ether into a concentrated solution of **3** in acetone at room temperature. A summary of crystal data and refinement parameters is reported in Table 3. The dark orange (**2**) and pale yellow (**3**) crystals (0.51 × 0.18 × 0.16 mm (**2**) and 0.26 × 0.25 × 0.17 mm (**3**)) were glued on a glass fiber and mounted on a Siemens P4 diffractometer, with graphite-monochromated Mo Kα radiation. A group of 59 reflections in the range 20° < 2θ < 45° (**2**) or 55 reflections in the range 35° < 2θ < 44° (**3**) were carefully centered at 200 K and used to obtain by least-squares methods the unit cell dimensions. Three standard reflections were monitored at periodic intervals throughout data collection. All data were corrected for absorption using a semiempirical method.[41] The structures were solved by Patterson (Os atom, SHELX97)[42] and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELX97).[42] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated in idealized positions and refined riding on carbon atoms using a common isotropic thermal parameter (**2**) or using thermal parameters related to bonded atoms (**3**). The hydrogen atoms H(1A) and H(1B) (**2**) and H(01) and H(1) (**3**) were refined as free isotropic atoms from observed positions.

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(41) North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(42) Sheldrick, G. *SHELX97. Programs for Crystal Structure Solution and Refinement*; Institut für Anorganische Chemie: Göttingen, Germany, 1997.

The $[BF_4]^-$ anion of **3** was found to be disordered and was refined using geometry restraints.[42] Atomic scattering factors, corrected for anomalous dispersion of Os and P, were implemented by the program. The refinement converged to $R_1 = 0.0217$ (**2**) or 0.0210 (**3**) $[F^2 > 2\sigma(F^2)]$ and wR^2 (all data) $= 0.0567$ (**2**) or 0.0511 (**3**), with weighting parameters $x = 0.0346$, $y = 1.7805$ (**2**) and $x = 0.0326$, $y = 1.4359$ (**3**).

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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