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Osmium−Allenylidene Complexes Containing an N-Heterocyclic Carbene Ligand

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Summary: Complex $[(\eta^6\text{-}p\text{-cymene})OsCl(IPr)]OTf$ *(**1**) reacts with 1,1-diphenyl-2-propyn-1-ol to afford the hydroxyvinylidene derivative* $[(\eta^6\text{-}p\text{-cymene})OsCl\{{=}C{=}CHC(OH)Ph_2\}(IPr)]OTf$ *(**2**), which dehydrates to form* $[(\eta^6\text{-}p\text{-cymene})OsCl({=}C{=}C{=}CPh_2)(IPr)]OTf$ *(**3**). Treatment in acetonitrile under reflux of the* BF_4*-salt of **3** with* $AgBF_4$ *leads to the tetrakis(solvento) derivative* $[Os({=}C{=}C{=}CPh_2)(CH_3CN)_4(IPr)][BF_4]_2$ *(**4**). At 95 °C, the addition of* P^iPr_3 *to an acetonitrile solution of **4** yields the dicationic mixed* P^iPr_3*-IPr osmium−allenylidene complex* $[Os({=}C{=}C{=}CPh_2)(CH_3CN)_3(IPr)(P^iPr_3)][BF_4]_2$ *(**5**), which in 2-propanol and in the presence of NaCl evolves into the five-coordinate hydride−alkenylcarbyne* $[OsHCl({\equiv}CCH{=}CPh_2)(IPr)(P^iPr_3)][BF_4]$ *(**6**). The X-ray structures of **2**, **5**, and **6** are also reported.*

Ruthenium−allenylidene complexes have attracted a great deal of attention in recent years,[1] as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric[2] and catalytic processes.[3] Osmium, in addition to providing catalysts for carbon−carbon and carbon−heteroatom bond formation,[4] affords stable models of reactive intermediates proposed in catalytic transformations with their ruthenium counterparts.[5] However, osmium allenylidene complexes are very scarce, in particular the non-half-sandwich compounds that are limited to bis-phosphine derivatives.[6]

N-Heterocyclic carbenes (NHC) are an emergent class of versatile ancillary ligands. The interest in this type of groups is a consequence of their ability to stabilize a variety of transition metal complexes, some of which are active in catalytic reactions.[7] In agreement with this, we have recently reported the half-sandwich osmium−NHC complexes $[(\eta^6\text{-}p\text{-cymene})OsCl({=}CHPh)(NHC)]OTf$ (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), OTf = CF_3SO_3), which are efficient catalyst precursors for olefin metathesis.[8]

Octahedral half-sandwich osmium(II) complexes show ligand substitution activation energies higher than their ruthenium analogues, due to the dependence of the crystal field activation energy on Δ_0. Thus, while the arene substitution by solvent molecules or monodentate ligands easily occurs for half-

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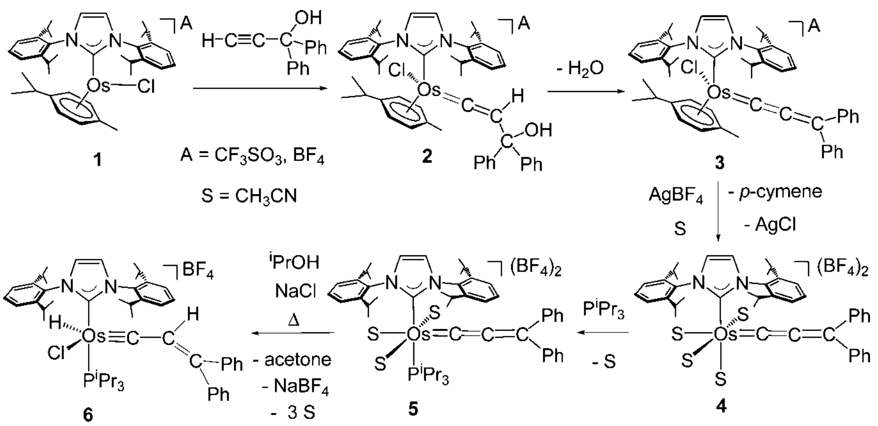
Scheme 1



sandwich ruthenium(II) complexes, it requires photochemical conditions in the osmium chemistry.[9]

The phenylmethylene ligand favors the arene dissociation. As a consequence of this, despite the kinetic inertness of the octahedral half-sandwich osmium(II) compounds, complex $[(\eta^6\text{-}p\text{-cymene})OsCl({=}CHPh)(IPr)]OTf$ is a useful starting material to prepare, under mild conditions, tris- and tetrakis(solvento) phenylmethylene–osmium derivatives,[10] which are the precursors of other interesting organometallic species.[11] Here, we show that the diphenylallenylidene ligand also favors the arene dissociation and that this property allows the preparation of unprecedented non-half-sandwich osmium–allenylidene complexes stabilized by an N-heterocyclic carbene coligand (Scheme 1).

Treatment at room temperature of dichloromethane solutions of the 16-valence-electron complex $[(\eta^6\text{-}p\text{-cymene})OsCl(IPr)]OTf$ (**1**) with 1.0 equiv of 1,1-diphenyl-2-propyn-1-ol for 15 min affords the hydroxyvinylidene derivative $[(\eta^6\text{-}p\text{-cymene})OsCl\{{=}C{=}CHC(OH)Ph_2\}(IPr)]OTf$ (**2**), which is isolated as a pink solid in 77% yield.

Figure 1 shows a view of the structure of the cation of **2**. The geometry around the osmium atom is close to octahedral with the arene occupying three sites of a face. The vinylidene is bound to the metal in a nearly linear fashion with an Os–C(1)–C(2) angle of 166.8(6)°. The Os–C(1) (1.864(7) Å) and C(1)–C(2) (1.283(9) Å) bond lengths compare well with those found in other osmium–vinylidene complexes.[12] The separation between the metal center and the NHC ligand of 2.099(8) Å agrees well with the reported distances for the few NHC–osmium compounds[13] characterized by X-ray diffraction analysis[8,10,11] and those found in the tautomerized-quinoline derivatives $OsCl_2\{\kappa\text{-}C\text{-}[HNC_{10}H_8]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (2.005(6) Å)[14] and $OsCl_2\{\kappa\text{-}C\text{-}[HNbq]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (bq = benzo[*h*]quinoline; 2.055(11) and 2.030(10) Å)[15] and in the tautomerized pyridine complexes $[OsH_2\{C_6H_4C(O)Ph\}\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$ (2.110(5) Å) and $[OsH\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(CH_3CN)_2(P^iPr_3)_2]BF_4$ (1.993(6) Å).[16]

In agreement with the presence of an OH group at the vinylidene ligand, the IR spectrum of **2** shows a ν(OH) band at 3374 cm^{-1}. The ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound in dichloromethane-d_2 at −30 °C reveal the presence in solution of two rotational isomers resulting from the steric requirement of the ligands that impose high barriers for the rotations around the M–L bonds. In the ^1H NMR spectrum, the most noticeable resonances are those corresponding to the OH and $C_\beta H$ protons of the vinylidene, which appear between 3.6 and 3.2 ppm and about 1.8 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum the C_α and C_β resonances of the vinylidene are observed at about 293 and at about 118 ppm, respectively.

Complex **2** dehydrates in dichloromethane at 40 °C to give $[(\eta^6\text{-}p\text{-cymene})OsCl({=}C{=}C{=}CPh_2)(IPr)]OTf$ (**3**), which is isolated as a brown solid in 88% yield. In accordance with the presence of an allenylidene ligand in the complex, the IR spectrum of **3** shows the characteristic ν(C=C=C) band for this ligand at 1942 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum contains resonances at 254.1, 196.5, and 153.9 ppm corresponding to the C_α, C_β, and C_γ atoms, respectively, of the C_3-chain.

Treatment of the BF_4-salt of **3**[17] with 1.0 equiv of $AgBF_4$ in acetonitrile under reflux for 15 h produces the abstraction of the chloride ligand and the release of the arene to form the tetrakis(solvento) allenylidene derivative $[Os({=}C{=}C{=}CPh_2)(CH_3CN)_4(IPr)][BF_4]_2$ (**4**), which is isolated as a red-brown solid in 83% yield. Its formation proves that the diphenylallenylidene ligand, like the alkylidene group, facilitates the dissociation of *p*-cymene from the osmium atom. Complex **4** is a rare example of a non-half-sandwich allenylidene derivative in osmium chemistry, which has no precedent. It is notable not only because it is an allenylidene species stabilized with four solvent molecules in the coordination sphere of the metal but also by its dicationic nature.

The IR spectrum of **4** shows the characteristic ν(C=C=C) band of the allenylidene ligand at 1939 cm^{-1}. In agreement with the structure proposed for this complex in Scheme 1, its ^1H NMR spectrum at room temperature in dichloromethane-d_2

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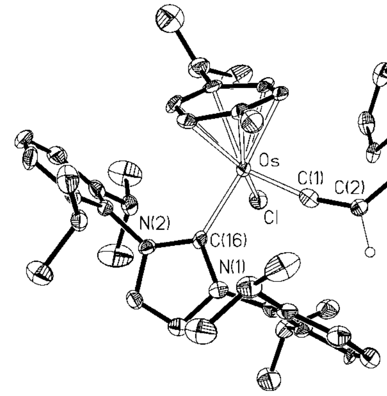

Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.864(7), Os−C(16) 2.099(8), C(1)−C(2) 1.283(9); Os−C(1)−C(2) 166.8(6).

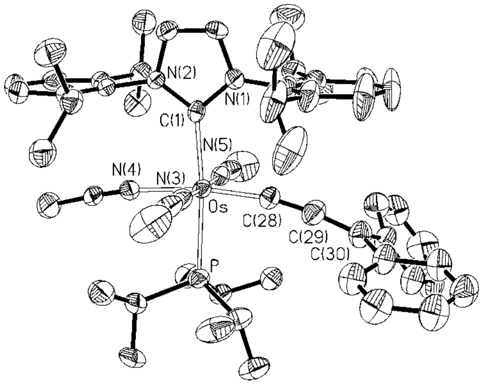

Figure 2. Molecular diagram of the cation of **5**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.118(6), Os−C(28) 1.882(6), C(28)−C(29) 1.246(8), C(29)−C(30) 1.362(9); C(1)−Os−P 173.93(14), C(28)−Os−N(4) 170.2(2), N(5)−Os−N(3) 177.29 (19), Os−C(28)−C(29) 168.2(5), C(28)−C(29)−C(30) 172.6(7).

contains three methyl resonances for the coordinated acetonitrile molecules, at 2.48, 2.43, and 2.39 ppm, in a 2:1:1 intensity ratio. In the $^{13}C\{^{1}H\}$ NMR spectrum, these ligands display six signals at 132.8, 121.7, and 120.1 ppm (CN) and at 4.4, 4.0, and 3.5 ppm (CH_3). The C_α, C_β, and C_γ resonances corresponding to the C_3-chain of the allenylidene appear at 264.9, 210.1, and 150.2 ppm, respectively.

Complex **4** is the entry point to the first mixed phosphine−NHC osmium−allenylidene derivative. Treatment at 95 °C for 15 h of an acetonitrile solution of **4** with 5.0 equiv of triisopropylphosphine produces the substitution of one of the solvent molecules of the tetrakis(solvento) starting compound by a phosphine ligand, to form $[Os(=C=C=CPh_2)(CH_3CN)_3(IPr)(P^iPr_3)][BF_4]_2$ (**5**), which is isolated as a brown solid in 92% yield.

Figure 2 shows a view of the geometry of the cation of **5**. The coordination around the osmium atom can be described as a distorted octahedron with the phosphine and the NHC ligands occupying *trans* positions (C(1)−Os−P = 173.93(14) Å). The perpendicular plane is formed by the allenylidene *trans* disposed to N(4) (C(28)−Os−N(4) = 170.2(2)°) and the two mutually *trans*-disposed acetonitrile molecules (N(5)−Os−N(3) = 177.29 (19)°). The diphenylallenylidene group is bonded to the metal in a nearly linear fashion with Os−C(28)−C(29) and C(28)−C(29)−C(30) angles of 168.2(5)° and 172.6(7)°, respectively. The Os−C(28), C(28)−C(29), and C(29)−C(30) bond lengths of 1.882(6), 1.246(8), and 1.362(9) Å, respectively, compare well with those reported for the previously structurally characterized osmium−allenylidene complexes.[6]

In agreement with the presence of the allenylidene ligand, the IR spectrum of **5** shows a $\nu(C=C=C)$ band at 1929 cm^{-1}. The ^{1}H NMR spectum is consistent with the *mer* disposition of the acetonitrile molecules. Thus, it contains two methyl-acetonitrile resonances at 2.96 and 2.41 ppm with a 2:1 intensity ratio. In solution, the *trans* disposition of the NHC and phosphine ligands is strongly supported by the $^{13}C\{^{1}H\}$ NMR spectrum, which shows the resonance due to C(1) at 157.5 ppm as a doublet with a C−P coupling constant of 82.4 Hz. The allenylidene C_α, C_β, and C_γ resonances are observed at 267.5, 212.2, and 149.7 ppm, respectively; the first of them appears as a doublet with a C−P coupling constant of 9.8 Hz. The $^{31}P\{^{1}H\}$ NMR spectrum contains a singlet at −6.1 ppm.

There is a class of allenylidene derivatives that show the typical behavior of Lewis base transition metal complexes.[1] Extended Hückel theory−molecular orbitals calculations indicate that the HOMO orbital of these species is mainly located at the C_β atom of the unsaturated chain.[6,18a,e] In accordance with this, the reactions of these compounds with electrophiles lead to alkenylcarbyne derivatives, which are stable with electron-rich coligands.[2,6n,b,e,i,l,m] The tris(solvento) complex **5** appears to be a member of this family, despite that one should expect an electron-poor character for the metal center given the dicationic nature of the complex. Thus, in 2-propanol at 85 °C and in the presence of 15.0 equiv of NaCl, it evolves into the five-coordinate hydride−alkenylcarbyne derivative $[OsHCl(\equiv CCH=CPh_2)(IPr)(P^iPr_3)][BF_4]$ (**6**), which is isolated as a pale red solid in 85% yield. The formation of **6** involves, in addition to the coordination of chloride to the osmium atom, the electrophilic attack of the OH proton of the solvent to the C_β atom of the allenylidene ligand and the subsequent coordination of the resulting isopropoxide group to the metal center. The process affords an isopropoxy−carbyne intermediate, which gives the hydride−carbyne by a β-hydrogen elimination from the alcoholate.[6m]

Complex **6** has been also characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. The drawing of one of them is shown in Figure 3. The geometry around the osmium atom can be rationalized as a distorted trigonal bipyramid with the phosphine and NHC ligands in apical positions (P−Os−C(16) = 165.6(4)° in molecule **A** and 164.7(5)° in molecule **B**) and inequivalent angles within the Y-shaped equatorial plane. The angles C(1)−Os−Cl, Cl−Os−H(1), and C(1)−Os−H(1) are 135.8(5)°, 139(4)°, and 85(4)° in **A** and 133.5(5)°, 143(4)°, and 81(4)° in **B**. The Os−C(1) bond lengths of 1.680(7) Å in **A** and 1.671(7) Å in **B** are fully consistent with an Os−C triple-bond formulation.[19]

In agreement with the presence of a hydride ligand in the complex, its ^{1}H NMR spectrum shows a doublet at −11.62 ppm with an H−P coupling constant of 13.8 Hz. In the low-field region the most noticeable signal is a singlet at 3.38 ppm, corresponding to the $C(sp^2)$−H proton of the alkenyl substituent of the carbyne ligand. In the $^{13}C\{^{1}H\}$ NMR spectrum the Os−C_α resonance appears at 270.2 ppm as a doublet with a C−P coupling constant of 8.8 Hz, whereas the resonance due to the donor atom of the NHC ligand is observed at 183.8 ppm,

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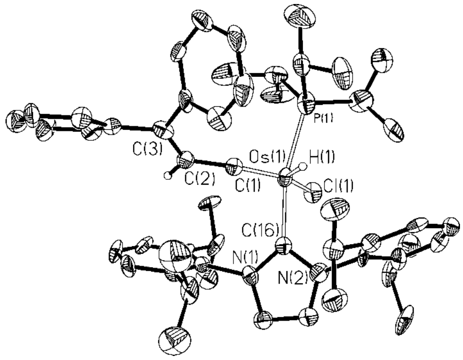

Figure 3. Molecular diagram of molecule **A** of the cation of **6**. Selected bond lengths (Å) and angles (deg): Os(1)−C(1) 1.680(7) **A**, Os(2)−C(52) 1.671(7) **B**; Os(1)−C(16) 2.086(14) **A**, Os(2)−C(67) 2.016(16) **B**; P(1)−Os(1)−C(16) 165.6(4) **A**, P(2)−Os(2)−C(67) 164.7(5) **B**; C(1)−Os(1)−Cl(1) 135.8(5) **A**, C(52)−Os(2)−Cl(2) 133.5(5) **B**; Cl(1)−Os(1)−H(1) 139(4) **A**, Cl(2)−Os(2)−H(2) 143(4) **B**; C(1)−Os−H(1) 85(4) **A**; C(52)−Os(2)−H(3) 81(4) **B**.

also as a doublet but with a C−P coupling constant of 78.4 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 51.2 ppm.

In conclusion, the diphenylallenylidene ligand $C{=}C{=}CPh_2$, like the phenylmethylene group, facilitates the dissociation of the arene from octahedral half-sandwich arene osmium derivatives. As a consequence of this, in coordinating solvents such as acetonitrile, tetrakis(solvento) cations of formula $[Os({=}C{=}C{=}CPh_2)(S)_4(NHC)]^{2+}$ can be stabilized and used as entry to dicationic mixed phosphine−NHC osmium−allenylidene complexes with Lewis base character.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques and dried solvents (see Supporting Information for full details).

Preparation of [(η^6-*p*-cymene)OsCl(IPr){=C=CH-C(OH)-Ph$_2$)}]OTf (2). A green solution of **1** (500 mg, 0.557 mmol) in dichloromethane (15 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (120 mg, 0.576 mmol). After 15 min at room temperature the solvent was removed in vacuo. Addition of diethyl ether gave rise to a pink solid, which was washed with diethyl ether (3 × 4 mL) and was dried in vacuo. Yield: 470 mg (77%). Anal. Calcd for $C_{53}H_{62}N_2SClF_3O_4Os$: C, 57.56; H, 5.61; N, 2.53; S, 2.90. Found: C, 57.41; H, 5.75; N, 2.68; S, 3.01.

Preparation of [(η^6-*p*-cymene)OsCl(IPr)(=C=C=CPh$_2$)]OTf (3). A pink solution of **2** (300 mg, 0.271 mmol) in dichloromethane (15 mL) was heated at 40 °C for 2 h. Subsequent evaporation and precipitation with pentane afforded a brown solid, which was washed with pentane (3 × 4 mL) and was dried in vacuo. Yield: 260 mg (88%). Anal. Calcd for $C_{53}H_{60}N_2SClF_3O_4Os$: C, 58.51; H, 5.55; N, 2.57; S, 2.94. Found: C, 58.43; H, 5.73; N, 2.71; S, 2.99.

Preparation of [Os(=C=C=CPh$_2$)(CH$_3$CN)$_4$(IPr)][BF$_4$]$_2$ (4). A light-protected mixture of the [BF$_4$]-salt of **3** (600 mg, 0.585 mmol) and AgBF$_4$ (114 mg, 0.585 mmol) in acetonitrile (20 mL) was refluxed for 15 h. Then, the solvent was evaporated to dryness and the crude product was redissolved in dichloromethane and filtered through Celite. Subsequent evaporation and precipitation with diethyl ether yielded a dark red-brown powder, which was washed with diethyl ether (3 × 5 mL) and pentane (2 × 5 mL) and was dried in vacuo. Yield: 540 mg (83%). MS (HR-electrospray): $[M - 4CH_3CN]^{2+} = C_{42}H_{46}N_2Os$ calcd 385.1634; found 385.1624.

Preparation of [Os(=C=C=CPh$_2$)(CH$_3$CN)$_3$(IPr)(P^{i}Pr$_3$)]-[BF$_4$]$_2$ (5). An acetonitrile solution (10 mL) of **4** (500 mg, 0.451 mmol) in a Schlenk flask provided with a Teflon closure was treated with P^iPr_3 (430 μL, 2.26 mmol) at 95 °C for 15 h. Then, the volatiles were evaporated and the crude product was washed with diethyl ether and pentane. After recrystallization from dichloromethane (1 mL) and pentane a brown solid is obtained, which was washed with diethyl ether (3 × 4 mL) and was dried in vacuo. Yield: 512 mg (92%). Anal. Calcd for $C_{57}H_{76}N_5B_2F_8OsP$: C, 55.84; H, 6.25; N, 5.71. Found: C, 55.55; H, 6.32; N, 5.55.

Preparation of [OsHCl(≡CCH=CPh$_2$)(IPr)(P^{i}Pr$_3$)][BF$_4$] (6). A 2-propanol (6 mL) solution of **5** (300 mg, 0.245 mmol) in a Schlenk flask provided with a Teflon closure was treated with NaCl (210 mg, 3.68 mmol) at 85 °C for 24 h. The resulting solution was filtered through Celite and then evaporated to dryness. Recrystallization in dichloromethane/diethyl ether afforded a pale red solid, which was washed with diethyl ether (3 × 4 mL) and was dried in vacuo. Yield: 220 mg (85%). Anal. Calcd for $C_{51}H_{69}N_2BClF_4OsP$: C, 58.14; H, 6.60; N, 2.66. Found: C, 58.28; H, 6.27; N, 3.05.

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Supporting Information Available: Full spectroscopic data and X-ray crystal structure determinations of compounds **2**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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