

C–H Bond Activation and Subsequent C–C Bond Formation Promoted by Osmium: 2-Vinylpyridine–Acetylene Couplings

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Systems that promote C–H bond activation and subsequent C–C bond formation are of great interest, in connection with the design of metal-mediated processes for the synthesis of functionalized organic molecules from basic hydrocarbon units.¹

An ideal process of this type would involve the entry in a consecutive and controlled way of organic fragments into a coordination transition-metal complex.² To assemble the organic fragments, developing multiple selective coupling reactions of unsaturated substrates is essential.

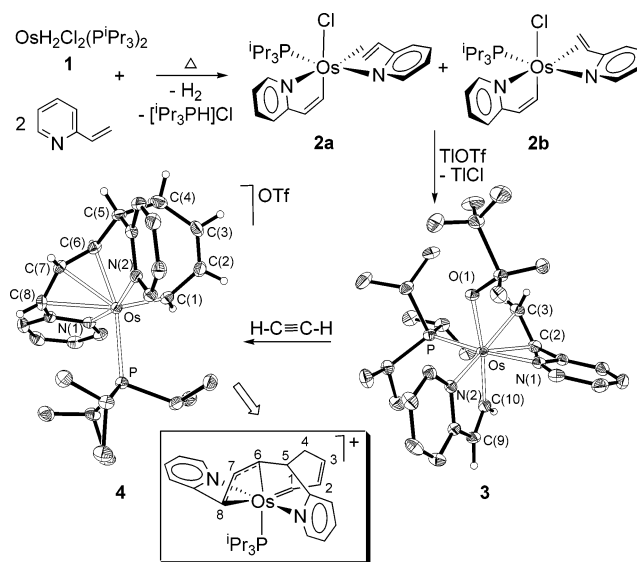
Complex $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ (**1**) has been one of the cornerstones in the development of the modern osmium organometallic chemistry.³ In this communication, we prove that it also promotes C–H bond activation and subsequent multiple C–C bond formation (Scheme 1).

Treatment for 10 h of **1** with 2 equiv of 2-vinylpyridine in toluene under reflux gives rise to the release of H_2 and $[\text{P}^i\text{Pr}_3\text{H}]\text{Cl}$ and the formation of the red complex **2**, which is isolated in 70% yield as a 6:4 mixture of the isomers **a** and **b** shown in Scheme 1. Complex **2** contains two substrate molecules. One of them is metalated, as a consequence of the $\text{C}(\text{sp}^2)\text{--H}$ bond activation of the CH_2 group of the vinyl substituent, whereas the other one is coordinated to the osmium atom by the nitrogen atom and the $\text{C}=\text{C}$ double bond of the olefin. In agreement with both types of pyridine ligands in **2**, its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows two groups of vinylic resonances, those due to the η^2 -coordinated substituent are observed at about 50 ppm, whereas those corresponding to the metalated substituent appear at ~ 130 (Cpy) and at ~ 185 (OsC) ppm.

The addition at room temperature of 1.0 equiv of $\text{TIClF}_3\text{SO}_3$ to a dichloromethane solution of the isomeric mixture of **2** produces the replacement of chloride by trifluoromethanesulfonate (OTf) to afford selectively **3**, the OTf counterpart of **2b**, which is isolated as red crystals in 90% yield, and it has been characterized by X-ray diffraction analysis. In agreement with an $\text{Os}\text{--C}(\text{sp}^2)$ single bond, the $\text{Os}\text{--C}(10)$ distance of 1.995(2) Å is similar to those found in osmium–alkenyl compounds.⁴ The osmium– η^2 -vinyl coordination exhibits $\text{Os}\text{--C}$ bond lengths of 2.162(2) Å ($\text{Os}\text{--C}(2)$) and 2.170(3) Å ($\text{Os}\text{--C}(3)$), which compare well with those found in other osmium–olefin complexes.⁵ The $\text{C}(2)\text{--C}(3)$ distance of 1.401(4) Å is also within the range reported for this type of compounds.^{5c} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is consistent with the spectra of **2** and those of other transition-metal compounds containing a metalated 2-vinylpyridine ligand.⁶ In this context, it should be mentioned that the chemical shift of the OsC signal (δ , 174.5) indicates a very low contribution of the carbene resonance form at the osmium–alkenyl bond.⁷

Under atmospheric pressure of acetylene, in dichloromethane at room temperature, complex **3** is converted into the spectacular compound **4**, which is obtained as a brown solid in high yield (85%), and that has been also characterized by X-ray diffraction analysis.

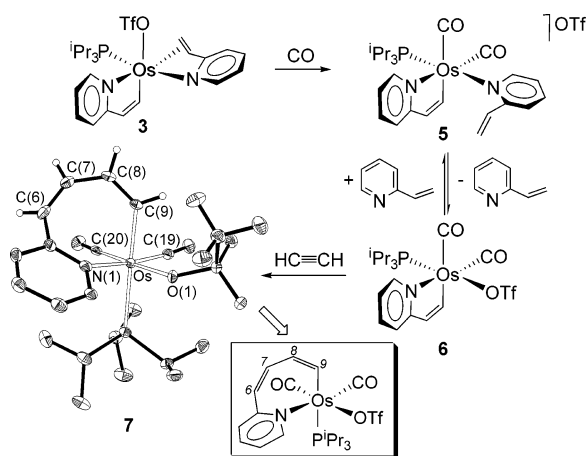
Scheme 1



The structure of the cation (Scheme 1) proves the formation of the $\text{py}\text{--C}(8)\text{H}\text{--C}(7)\text{H}\text{--C}(6)\text{H}\text{--C}(5)\text{H}\text{--}\{\text{C}(4)\text{H}_2\text{--C}(3)\text{H}=\text{C}(2)\text{H}\text{--C}(1)\text{H}\}\text{--py}$ ligand, which coordinates to the metal center by the nitrogen atoms of both pyridine rings ($\text{N}(1)\text{--Os--N}(2) = 164.57(10)^\circ$), by $\text{C}(8)\text{--C}(7)\text{--C}(6)$ in a η^3 -allyl manner and by $\text{C}(1)$ to form a carbene. The allyl moiety is bonded to the osmium atom in an asymmetrical fashion, with the separation between $\text{C}(6)$ and the metal (2.110(3) Å) being shorter than the separation between the metal and $\text{C}(7)$ (2.249(3) Å) or $\text{C}(8)$ (2.431(4) Å). The $\text{C}(6)\text{--C}(7)$ and $\text{C}(7)\text{--C}(8)$ distances are 1.440(5) and 1.378(5) Å, respectively. The $\text{Os}\text{--C}(1)$ bond length of 1.874(4) Å agrees well with those found in osmium–carbene complexes and supports the $\text{Os}\text{--C}$ double bond formulation.⁸ In accordance with osmium–allyl derivatives,⁹ the $\text{C}(6)$, $\text{C}(7)$, and $\text{C}(8)$ resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum appear at 42.1, 108.7, and 82.8 ppm, respectively. The $\text{C}(1)$ resonance is observed at 260.6 ppm, in agreement with the chemical shifts in osmium–carbene complexes. The chemical shift of the $\text{C}(1)\text{H}$ resonance in the ^1H NMR spectrum (δ , 19.27) is also consistent with an $\text{Os}=\text{C}(1)$ double bond.¹⁰

The unprecedented formation of **4** is a one-pot synthesis of multiple complex reactions. In addition to a 1,3-hydrogen shift, three selective C–C coupling processes are assembled to afford this species: (i) coupling of the vinyl substituents of the pyridines to afford an $\text{Os}\{\kappa, \text{N}, \text{N}, \text{C}(5)[\text{py}\text{--C}(8)\text{H}=\text{C}(7)\text{H}\text{--C}(6)\text{H}_2\text{--C}(5)\text{H}\text{--py}]\}$ unit, by insertion of the $\text{py}\text{--CH}=\text{CH}_2$ olefin into the $\text{Os}\text{--alkenyl}$ bond of **3**; (ii) coupling on the osmium atom of two acetylene molecules to give an $\text{Os}\{\text{C}(4)\text{H}\text{--C}(3)\text{H}=\text{C}(2)\text{H}\text{--C}(1)\text{H}=\}$ –osmacyclopentatriene moiety,¹¹ resulting in the $\text{Os}\text{--C}(1)$ and $\text{C}(2)\text{--C}(3)$ double bonds of **4**; and (iii) $\text{C}(4)\text{--C}(5)$ bond

Scheme 2



formation by migratory insertion of the Os=C(4) double bond of the osmacyclopentatriene unit into the Os–C(5) single bond of the Os{ κ ,N,N,C(5)[py–C(8)H=C(7)H–C(6)H₂–C(5)H–py]} moiety. The 1,3-hydrogen shift takes places between C(6) and C(4).

The 3 \rightarrow 4 transformation indicates that the insertion of the η^2 -coordinated –CH=CH₂ group into the bond between the osmium atom and the metalated substituent is favored with regard to the insertion of acetylene. The latter occurs in absence of olefin (Scheme 2).

Under an atmosphere of carbon monoxide, in dichloromethane at room temperature, the OTf[–] anion and the η^2 -coordinated vinyl substituent of 3 are displaced by CO molecules to afford the dicarbonyl derivative 5. This complex is isolated as a gray solid in 90% yield. Its IR spectrum strongly supports the mutually *cis* disposition of the carbonyl ligands, showing two ν (CO) bands at 2027 and 1960 cm^{–1}. In the ¹³C{¹H} NMR spectrum, the resonances due to the free olefin group appear at 124.6 (CH₂) and 137.4 (CH) ppm, shifted about 80 ppm toward lower field with regard to 3 and 2. The OsC and Cpy resonances of the metalated substituent are observed at 180.6 and 140.0 ppm, respectively.

In dichloromethane at room temperature, the cation of 5 slowly dissociates 2-vinylpyridine and coordinates the OTf[–] anion to give the yellow complex 6, which is isolated in 65% yield. The reaction is reversible, and the addition of 2-vinylpyridine to a dichloromethane solution of 6 regenerates 5. In the IR spectrum of 6, the ν (CO) bands are observed at 2025 and 1954 cm^{–1}, whereas in the ¹³C{¹H} NMR spectrum, the resonances corresponding to the metalated substituent of the pyridine appear at 174.0 (OsC) and 143.6 (Cpy) ppm.

Under atmospheric pressure of acetylene, the dichloromethane solutions of 6 react with acetylene to give 7, which is obtained as a white solid in 74% yield. This compound contains a metalated 2-butadienylpyridine ligand. The butadienyl group is a result of the insertion of the C–C triple bond of acetylene into the bond between the metal and the substituent of the pyridine of 6. Insertions of terminal alkynes into the M–C bond of an iridium complex containing a metalated 2-Me₂Npy ligand have been recently reported.¹² Like 3 and 4, complex 7 has been characterized by X-ray diffraction analysis. The bond lengths in the sequence¹³ Os–C(9)–C(8)–C(7)–C(6)–C(1) are 2.085(5), 1.334(7), 1.453(7), 1.331(7), and 1.459(7) Å. These values strongly support the butadienyl

formulation for the pyridine substituent. In the ¹³C{¹H} NMR spectrum, the resonances due to C(9), C(8), C(7), and C(6) appear at 153.4, 133.2, 143.7, and 124.3 ppm, respectively. In agreement with the mutually *cis* disposition of the carbonyl ligands, the IR spectrum contains two ν (CO) bands at 2033 and 1956 cm^{–1}.

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Supporting Information Available: Experimental details for the synthesis of the new complexes as well as X-ray crystallographic data (bond distances, bond angles, and anisotropic parameters) for 3, 4, and 7 in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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