Preparation of [C,N,O]-Pincer Osmium Complexes by Alkylidene Metathesis with a Methyl Group of 2,6-Diacetylpyridine

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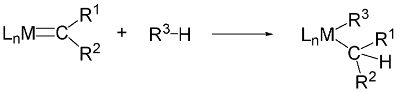
Received April 3, 2007

*Summary: The complex [(η^6-p-cymene)OsCl(=CHPh)(IPr)]OTf (**1**) reacts with 2,6-diacetylpyridine in acetonitrile at 40 °C to give the [C,N,O]-pincer derivative [OsCl{κ^3C,N,O-[=CHC(O)-pyC(CH_3)O]}($NCCH_3$)(IPr)]OTf (**2**), containing an alkylidene function at the terdentate ligand. Under the same conditions in dichloromethane, the neutral species OsCl(OTf){κ^3C,N,O-[=CHC(O)pyC(CH_3)O]}(IPr) (**3**) is formed.*

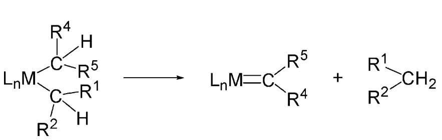
Transition-metal complexes with pincer ligands,[1] including N-heterocyclic carbene structures,[2] have attracted a substantial amount of interest, due to their important applications in synthesis, bond activation, and catalysis. However, the complexes with terdentate [C,N,O] ligands are rare.[3] Thus, as far as we know, those containing a carbene arm not stabilized by a heteroatom are unknown. The reported terdentate ligands with an alkylidene function are mainly diphosphine groups.[4] In general, they have been prepared by double C(sp^3)−H bond activation on a transition metal.[4b−f]

One strategy to activate inert C−H bonds is to utilize transition-metal complexes containing metal−ligand multiple bonds.[5] Girolami,[6] Gibson,[7] Hessen,[8] and Legzdins[9] have established that unsaturated complexes having an alkylidene ligand can promote intermolecular C−H bond activation reactions (eq 1).



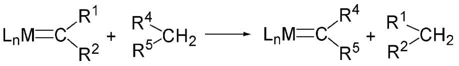
$$L_nM{=}CR^1R^2 + R^3{-}H \longrightarrow L_nM(R^3){-}CR^1R^2H \quad (1)$$

It has been known since 1974 that synthetically useful transition-metal alkylidene derivatives are generated by intramolecular α-elimination from a bis(alkyl) precursor (eq 2).[10]



(2)

The combination of the reactions shown in eqs 1 and 2 (R^3 = CHR^4R^5) suggests that alkylidene complexes should promote the formation of more stable alkylidene derivatives, by intermolecular double C(sp^3)−H bond activation: i.e., alkylidene metathesis with an alkyl substrate (eq 3).



$$L_nM{=}CR^1R^2 + R^4R^5CH_2 \longrightarrow L_nM{=}CR^4R^5 + R^1R^2CH_2 \quad (3)$$

The stability of a complex in which several donor atoms are part of the same ligand often appears to be much greater than if the same atoms were in separated ligands.[11] Thus, complexes containing terdentate ligands are usually more stable than similar compounds without rings. In accordance with this, among the various strategies to stabilize a transition-metal alkylidene bond, the terdentate-assistance strategy is without doubt a very promising way.

As a part of our work on the chemistry of the Os−C double bond,[12] we have recently reported the preparation of the half-

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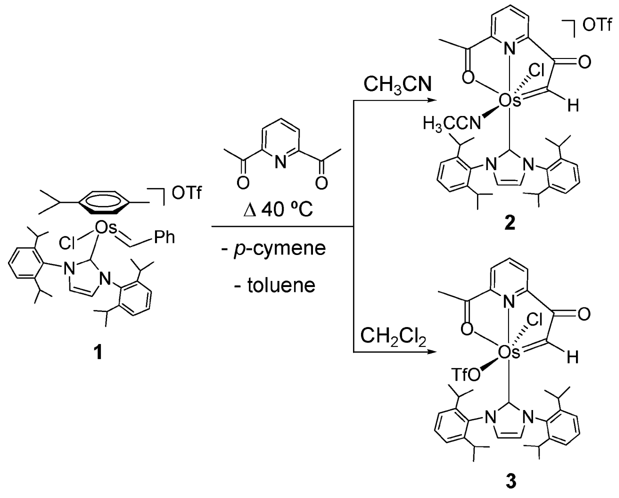
Scheme 1



sandwich osmium−alkylidene complex $[(\eta^6\text{-}p\text{-cymene})\text{OsCl}(=\text{CHPh})(\text{IPr})]\text{OTf}$ (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene, OTf = CF_3SO_3), which is an efficient catalyst precursor for olefin metathesis.[13] The alkylidene ligand of this compound labilizes the osmium−arene bond. Thus, despite the kinetic inertia of the octahedral half-sandwich osmium(II) species,[12a,14] complex **1** affords the solvento derivative $[\text{OsCl}(=\text{CHPh})(\text{IPr})(\text{NCCH}_3)_3]\text{OTf}$, in acetonitrile at 40 °C, and the five-coordinate hydride alkylidyne compounds $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{PR}_3)]\text{OTf}$ ($PR_3 = P^iPr_3$, PPh_3), in dichloromethane solutions containing triisopropylphosphine or triphenylphosphine.[15] We now show that the alkylidene ligand of **1**, in addition to facilitating the dissociation of the arene, promotes the formation of [C,N,O]-pincer complexes according to our hypothesis shown in eq 3.

Treatment at 40 °C of acetonitrile solutions of **1** with 1.5 equiv of 2,6-diacetylpyridine for 2 h leads to the [C,N,O]-pincer derivative $[\text{OsCl}\{\kappa^3C,N,O\text{-}[=\text{CHC(O)pyC(CH}_3)\text{O}]\}(\text{NCCH}_3)(\text{IPr})]\text{OTf}$ (**2**). Under the same conditions in dichloromethane, the neutral species $\text{OsCl(OTf)}\{\kappa^3C,N,O\text{-}[=\text{CHC(O)pyC(CH}_3)\text{O}]\}(\text{IPr})$ (**3**) is formed (Scheme 1). Complexes **2** and **3** are isolated as violet solids in 91% and 85% yields, respectively. They are the result of the release of the arene and the hydrogenation of the alkylidene ligand. The hydrogen source is the methyl group of one of the acetyl substituents of the pyridinic substrate which undergoes dehydrogenation, to be transformed into an alkylidene according to eq 3. The release of free *p*-cymene and the formation of toluene were confirmed by GC-MS.

These reactions can be rationalized as follows: the release of the arene from the starting compound affords a highly unsaturated species, which coordinates the pyridinic substrate. The coordination facilitates the migration of a hydrogen atom from the methyl group of one of the acetyl substituents to the alkylidene ligand to give one of the key intermediates of the process, a bis(alkyl) species as shown in eq 1. This intermediate should decompose into the formed products according to eq 2, by α-elimination on the terdentate alkyl group and subsequent reductive elimination of the monodentate alkyl ligand.

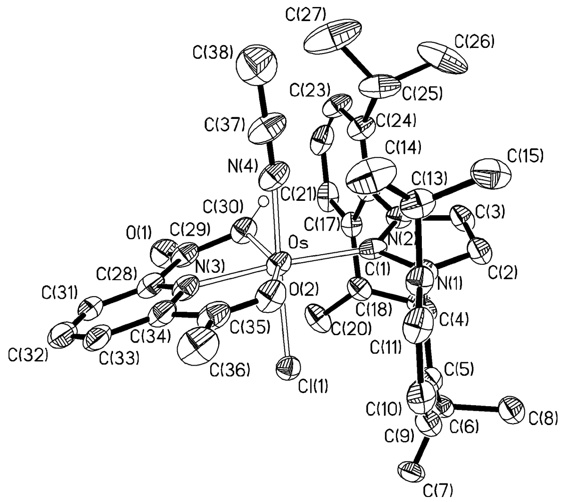


Figure 1. Molecular diagram of the cation of **1**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 2.074(5), Os−C(30) = 1.884(5), Os−N(3) = 2.047(4), Os−O(2) = 2.267(3); N(3)−Os−C(1) = 174.85(15), N(4)−Os−Cl = 168.51(11), O(2)−Os−C(30) = 150.56(17), Cl−Os−C(1) = 91.27(12), Cl−Os−N(3) = 83.86(11), N(4)−Os−C(1) = 88.61(17), N(4)−Os−N(3) = 95.83(16), C(30)−Os−C(1) = 101.81(19).

Caulton and co-workers have previously reported that two benzylic hydrogens of $[2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O}]^-$ coordinated to $\text{RuCl}(=\text{CHPh})(\text{PCy}_3)_2$ are transferred to the benzylidene ligand, liberating toluene to form a new carbene which is covalently linked to the aryloxide ligand.[16]

Complexes **2** and **3** are interesting not only because they are novel examples of unrepresented [C,N,O]-pincer compounds but also because an N-heterocyclic carbene ligand is present, since the NHC−osmium derivatives are extremely rare.[13,15,17] Both **2** and **3** were characterized by elemental analysis and IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **2** was further characterized by an X-ray crystallographic study. A view of the structure of the cation is shown in Figure 1.

The geometry around the osmium atom can be described as a distorted octahedron, with the terdentate group occupying three mer positions (C(30)−Os−O(2) = 150.56(17)°) and the NHC ligand disposed trans to the nitrogen atom of the pincer (N(3)−Os−C(1) = 174.85(15)°). The separation of 1.884(5) Å between the osmium atom and the alkylidene, which supports the Os−C(30) double-bond formulation,[13,15,18] is about 0.2 Å shorter than that between the metal and the N-heterocyclic carbene ligand (Os−C(1) = 2.074(5) Å). The latter agrees well with the reported distances for the few NHC−osmium compounds characterized by X-ray diffraction analysis[13,15] and that found in the tautomerized-quinoline derivative $\text{OsCl}_2(\eta^2\text{-H}_2)\{\kappa C\text{-}(\text{C}_{10}\text{H}_8\text{NH})\}(\text{P}^i\text{Pr}_3)_2$ (2.005(6) Å).[19] In agreement with the sp^2 hybridization at C(30), the Os−C(30)−C(29) angle is 115.0(3)°.

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The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** and **3** are consistent with the structure shown in Figure 1. The ^1H NMR spectra contain singlets at 20.88 (**2**) and 22.95 ppm (**3**), corresponding to the Os═CH alkylidene proton. In the $^{13}C\{^1H\}$ NMR spectra, the Os═C alkylidene resonances are observed at 242.0 (**2**) and 232.8 ppm (**3**). The coordination of the trifluoromethanesulfonate anion to the metal center in **3** is mainly supported by the IR spectrum of this compound, which in agreement with spectra for other compounds containing a monodentate $CF_3SO_3^-$ ligand,[20] shows the $\nu_a(SO_3)$ band at 1336 cm^{-1}: i.e., shifted 64 cm^{-1} to higher wavenumber with regard to **2** (1272 cm^{-1}).

In conclusion, the additional stabilization produced by the coordination of the nitrogen and the oxygen atom of one of the acetyl substituents of 2,6-diacetylpyridine allows a metathesis reaction between the methyl group of the other acetyl substituent of this substrate and the alkylidene ligand of the metal fragment $[OsCl({=}CHPh)(IPr)]^+$, to afford novel [C,N,O]-pincer osmium compounds with an alkylidene function at the terdentate group.

Acknowledgment. Financial support from the MEC of Spain (Project No. CTQ2005-00656) and the Diputación General de Aragón (E35) is acknowledged. R.C. thanks the CSIC and the Spanish MEC for funding through the "Ramon y Cajal" Program.

Supporting Information Available: Text giving experimental details, NMR data, and details of the crystal structure determination and a CIF file giving crystal data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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