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Osmium(III) Complexes with POP Pincer Ligands: Preparation from Commercially Available $\mathrm{OsCl_3 \cdot 3H_2O}$ and Their X-ray Structures

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Complexes $\mathrm{OsCl_3\{dbf(P^iPr_2)_2\}}$ [**1**; $\mathrm{dbf(P^iPr_2)_2}$ = 4,6-bis(diisopropylphosphino)dibenzofuran], $\mathrm{OsCl_3\{xant(P^iPr_2)_2\}}$ [**2**; $\mathrm{xant(P^iPr_2)_2}$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene], and $\mathrm{OsCl_3\{xant(PPh_2)_2\}}$ [**3**; $\mathrm{xant(PPh_2)_2}$ = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene] have been obtained in high yield by the reaction of the corresponding diphosphine with $\mathrm{OsCl_3 \cdot 3H_2O}$. The ruthenium(III) counterparts $\mathrm{RuCl_3\{dbf(P^iPr_2)_2\}}$ (**4**), $\mathrm{RuCl_3\{xant(P^iPr_2)_2\}}$ (**5**), and $\mathrm{RuCl_3\{xant(PPh_2)_2\}}$ (**6**) are similarly obtained from $\mathrm{RuCl_3 \cdot 3H_2O}$ in moderate yields. The X-ray structures of $\mathrm{dbf(P^iPr_2)_2}$ and complexes **1**−**3** are also reported.

The number of complexes obtained in high yield directly from commercially available inorganic salts determines the development of the chemistry of a transition metal, in particular for those of the platinum group. Success in ruthenium chemistry during the past decade has been, in part, due to the ready accessibility of a wide range of these types of starting materials. In contrast to ruthenium, osmium is considered of no practical use in catalysis because it is more reducing than ruthenium and prefers to be saturated by coordination and redox isomers with more metal−carbon bonds.[1] As a consequence of this extended skepticism, very scarce effort to find starting materials from $\mathrm{OsCl_3 \cdot 3H_2O}$ or related salts has been done.[2] However, we have proven that osmium can be a promising alternative to the classical metal catalysts.[3]

Pincer ligands are having a tremendous impact in organometallics and homogeneous catalysts.[4] As a consequence of the disposition of their donor atoms, they develop marked abilities to stabilize less common metal oxidation states[5] and afford metal complexes capable of activating inert bonds.[6] The most commonly encountered linker groups consist of either a metalated aryl ring in anionic PCP ligands or uncharged PNP pyridines or neutral POP ethers. Among the latter, the xanthene-based systems occupy a prominent place.[7] The influence of coordinating parameters, such as the separation between the phosphorus atoms, the flexibility

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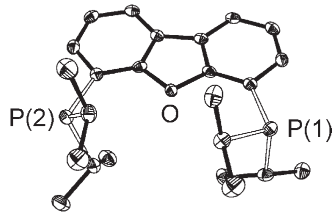
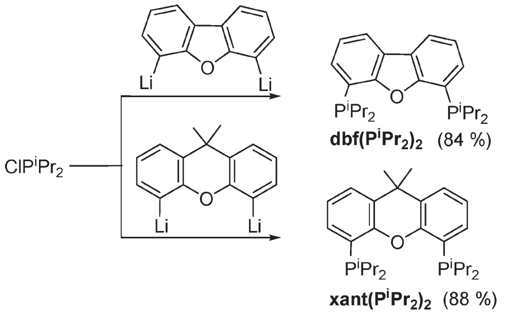


Figure 1. Molecular structure of dbf(P^{i}Pr$_2$)$_2$.

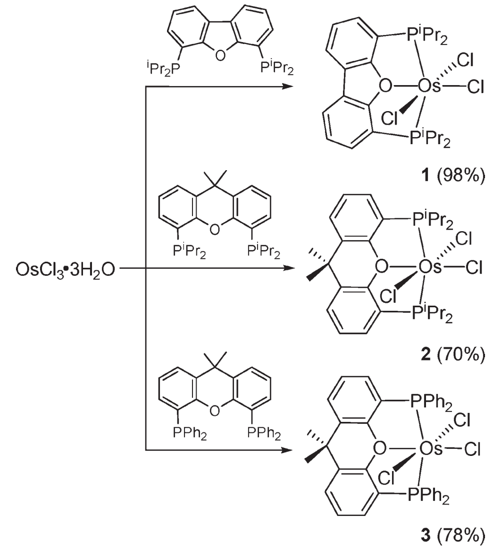
Scheme 1



range, or the natural bite angle, on the selectivity and activity of precursors containing these types of ligands in some catalytic processes has been discussed.[7a−c] In contrast to the remaining platinum group metals, osmium-pincer chemistry is a little studied field,[8] in particular that of POP ligands. In the search for osmium-pincer starting materials, we have investigated the reactions of $OsCl_3 \cdot 3H_2O$ with xanthene-type ligands. In this Communication, we report the synthesis of 4,6-bis(diisopropylphosphino)dibenzofuran [dbf(P^{i}Pr$_2$)$_2$] and 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene [xant(P^{i}Pr$_2$)$_2$] and the preparation and X-ray structures of novel[9] Os^{III}POP compounds.

The new ligands have been synthesized under an argon atmosphere according to Scheme 1. Because of the presence of the ether oxygen, the addition of 3.0 equiv of *sec*-butyllithium to diethyl ether solutions of dibenzofuran and 9,9-dimethylxanthane in the presence of tetramethylethylenediamine produces dilithiation of the heterocycles at the positions ortho to the ether bridge.[10] The reactions of the corresponding dilithiated species with chlorodiisopropylphosphine afford dbf(P^{i}Pr$_2$)$_2$ and xant(P^{i}Pr$_2$)$_2$, which are isolated as a white solid in 84% yield and a yellow oil in 88% yield, respectively.

Scheme 2



The diphosphine dbf(P^{i}Pr$_2$)$_2$ has been characterized by X-ray diffraction analysis. The structure (Figure 1) reveals that the separation between the phosphorus atoms of 6.192(2) Å is significantly longer, about 2.2 Å, than that in 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene [xant(PPh$_2$)$_2$; 4.080[11] and 4.155(1) Å[12]] and between 0.4 and 0.2 Å longer than those calculated for 4,6-bis(diphenylphosphino)dibenzofuran [dbf(PPh$_2$)$_2$; 5.760 Å by MM calculations and 5.956 Å by PM3 calculations].[11] The most noticeable spectroscopic feature of dbf(P^{i}Pr$_2$)$_2$ is a singlet at 9.2 ppm in the ^{31}P{^{1}H} NMR spectrum in dichloromethane at room temperature. In contrast to dbf(P^{i}Pr$_2$)$_2$, the spectrum of xant(P^{i}Pr$_2$)$_2$ at room temperature shows a broad signal, which is converted into a singlet at 248 K, δ −12.2.

Ligands dbf(P^{i}Pr$_2$)$_2$, xant(P^{i}Pr$_2$)$_2$, and xant(PPh$_2$)$_2$ react with $OsCl_3 \cdot 3H_2O$ in 2-propanol under reflux to provide after 60 h the osmium(III) derivatives OsCl$_3${dbf(P^{i}Pr$_2$)$_2$} (**1**), OsCl$_3${xant(P^{i}Pr$_2$)$_2$} (**2**), and OsCl$_3${xant(PPh$_2$)$_2$} (**3**), which are isolated as yellow solids in 98%, 70%, and 78% yield, respectively, according to Scheme 2. Under the same conditions, the reactions of these diphosphines with $RuCl_3 \cdot 3H_2O$ led to the ruthenium counterparts RuCl$_3${dbf(P^{i}Pr$_2$)$_2$} (**4**), RuCl$_3${xant(P^{i}Pr$_2$)$_2$} (**5**), and RuCl$_3${xant(PPh$_2$)$_2$} (**6**). However, they are obtained in moderate yields (30−60%), as red (**4**) or orange (**5** and **6**) solids.

Complexes **1**−**3** have been characterized by X-ray diffraction analysis. Figure 2 shows views of their molecular geometries and summarizes some structural parameters. The coordination polyhedron around the osmium atom in the three compounds can be rationalized as being derived from a distorted octahedron with the chloride ligands in a *mer* disposition [Cl(1)−Os−Cl(3) = 171.60(3)° (**1**), 170.06(5)° and 169.47(5)° (**2**), and 165.81(5)° (**3**)]. The structures reveal

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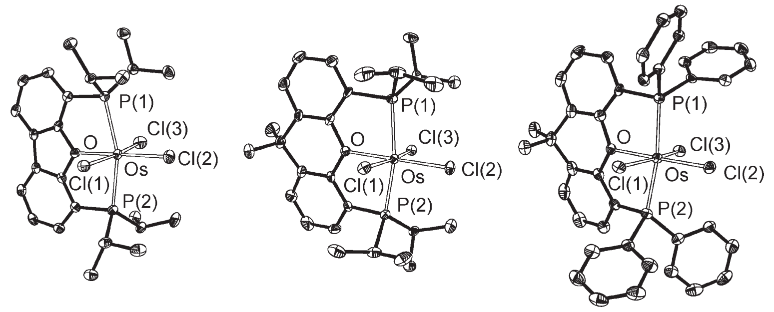

P(1)-Os-P(P2)	159.95(3)	165.95(5)	166.20(5)	165.38(5)
Os-P(1)	2.4065(9))	2.3524(15)	2.3459(15)	2.3318(15)
Os-P(2)	2.4156(9)	2.3541(15)	2.3497(16)	2.3259(15)
Os-Cl(1)	2.3748(8)	2.3432(14)	2.3392(14)	2.3595(14)
Os-Cl(2)	2.3203(9)	2.3113(14)	2.3170(14)	2.3018(15)
Os-Cl(3)	2.3502(9)	2.3648(14)	2.3686(14)	2.3575(14)
Os-O	2.0296(19)	2.129(3)	2.142(4)	2.140(3)

Figure 2. Molecular structures of complexes **1**−**3** and selected angles (deg) and distances (Å).

that the rigid polycyclic backbones do not have any significant influence in the coordination of the diphosphines because $\mathrm{OsCl_3}$ produces a leveling effect on the relevant coordinating parameters of the ligands, such as the separation between the phosphorus atoms or the P−M−P bite angle. Thus, although the separation between the phosphorus atoms in the free ligands is very sensitive to the rigidity imposed by the central ring of the polycycle, the sum of the Os−P bond lengths in the three compounds is similar [≈4.81 Å (**1**), ≈4.70 Å (**2**), and ≈4.65 Å (**3**)]; i.e., $\mathrm{OsCl_3}$ shortens, by about 1.4 Å, the separation between the phosphorus atoms of $\mathrm{dbf(P^iPr_2)_2}$, while it separates, by about 0.5 Å, the phosphorus atoms of $\mathrm{xant(P^iPr_2)_2}$ and $\mathrm{xant(PPh_2)_2}$.[13] The differences between the P−Os−P angles and between the Os−O distances are not significant. The P−Os−P angle in **1** is about 6° smaller than those of **2** and **3**, the same as the Cl(1)−Os−Cl(3) angle of **3** with regard to those of **1** and **2**, whereas the Os−O separation in **1** is about 0.1 Å shorter than those in **2** and **3**.

The electron paramagnetic resonance (EPR) spectra of the $\mathrm{dbf(P^iPr_2)_2}$ complexes **1** and **4** in the solid state were recorded in order to corroborate the paramagnetic character of these species. The room temperature spectra of both compounds consist of a broad featureless signal whose shape indicates an anisotropic environment. Upon measurement at lower temperature (namely, 15 K), three features are clearly resolved, indicating an orthorhombic symmetry, and the spectra can be described by taking into account only a Zeeman term described by a **g** tensor with principal values of $g_1 = 2.63(2)$, $g_2 = 2.54(3)$, and $g_3 = 2.03(3)$ for **1** and $g_1 = 2.51(2)$, $g_2 = 2.20(2)$, and $g_3 = 2.01(2)$ for **4**.

In conclusion, diphosphineosmium(III) complexes can be prepared in high yield, directly from $\mathrm{OsCl_3 \cdot 3H_2O}$, by the reaction of the commercially available inorganic salt with POP ligands such as $\mathrm{dbf(P^iPr_2)_2}$, $\mathrm{xant(P^iPr_2)_2}$, or $\mathrm{xant(PPh_2)_2}$. The comparison of the structures of the free ligands with those of the resulting complexes $\mathrm{OsCl_3\{dbf(P^iPr_2)_2\}}$, $\mathrm{OsCl_3\{xant(P^iPr_2)_2\}}$, and $\mathrm{OsCl_3\{xant(PPh_2)_2\}}$ reveals that the polycyclic backbones of the diphosphines do not have any significant influence on the structural parameters of the complexes because the metal produces a leveling effect on the relevant coordinating features of the ligands.

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Supporting Information Available: Experimental details regarding the synthesis and characterization and crystallographic data (CIF) for $\mathrm{dbf(P^iPr_2)_2}$ and **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The separations between the phosphorus atoms in these compounds are 4.748(1) Å for **1**, 4.671(2) and 4.666(2) Å for **2**, and 4.620(2) Å for **3**.