Iridium−Silanol Complexes from Direct Oxidative Addition of Silanols to Ir(I). Synthesis and X-ray Structure of the Metallosilanolate $[(Et_3P)_2Ir(H)(Cl)(Si^iPr_2OLi)]_2$

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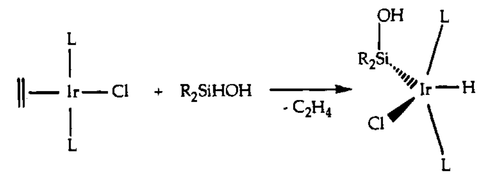
Organic silanols have been studied extensively[1] mainly due to the fact that they are intermediates in formation of important silicone polymers.[2] In contrast, metallosilanols,[3−6] i.e., compounds that contain a M−Si−OH moiety, form a relatively new class of compounds which has attracted attention only recently. However, these complexes, being interesting as such, can potentially be also synthetically useful. For example, they may find application in the synthesis of polymer-supported transition metal catalysts, metallofunctionalized silica, and organometallic polymers. Metallosilanols, which are still very limited in number, were reported to be formed either by hydrolysis of the corresponding silyl complexes,[3,4,6] or by oxyfunctionalization with dimethyldioxirane of a Si−H fragment bound to a metal center.[5,6] Their chemistry is relatively unexplored, the main reaction reported being formation of metallosiloxanes (i.e., compounds having a M−Si−O−Si moiety). The metallosilanols are expected to be less acidic than the organosilanols due to the electron-donating nature of the metal center. This is, perhaps, one of the reasons why, to the best of our knowledge, no synthesis and characterization of a metallosilanolate has been reported.[7] In the present communication we report on (i) the first examples of *direct* synthesis of metallosilanols, namely, $L_2Ir(H)(Cl)(SiR_2OH)$ (**2**, R = ^iPr; **3**, R = ^tBu; L = PEt_3), from a low-valent iridium(I) complex and corresponding dialkylsilanols; and (ii) the synthesis and X-ray structural characterization of the first fully characterized metallosilanolate, $[L_2Ir(H)(Cl)(Si^iPr_2OLi)]_2$ (**4**). This complex was obtained by selective deprotonation of **2**, which we have also characterized crystallographically.

Treatment of an orange benzene solution of *trans*-$L_2Ir(C_2H_4)Cl$[8] (**1**) with 1 equiv of $^iPr_2SiHOH$[9,10] (**5**) at room temperature rapidly leads to formation of a yellow solution from which the metallosilanol **2** can be isolated in 94% yield. The bulkier silanol $^tBu_2SiHOH$[10,11] (**6**) reacts similarly, but more slowly and without obvious color change, the isolated yield of **3** being 62% (eq 1). The trans arrangement of the phosphine ligands and the presence of a hydride and of a dialkylsilanol moiety unequivocally follow from ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopic data of complexes **2** and **3**.[10] The greater



(1)

1, L = PEt_3 **2**, R = ^iPr **3**, R = ^tBu

steric bulk of ^tBu substituents results in slightly inequivalent magnetic environments of phosphorus atoms in **3**, giving rise to an AB quartet with a typical large $^2J_{P-P,trans} = 335$ Hz in $^{31}P\{^1H\}$ NMR, instead of the singlet observed in the case of **2**.

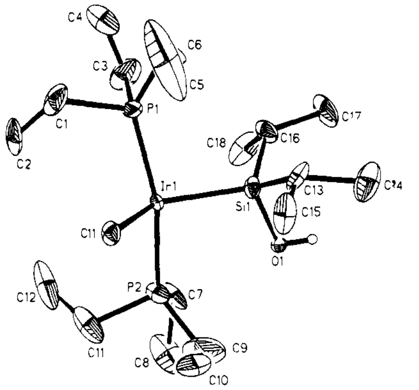


Figure 1. ORTEP view of **2** with H atoms omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−Cl(1), 2.421(6); Ir(1)−P(1), 2.278(13); Ir(1)−P(2), 2.291(9); Ir(1)−Si(1), 2.313(6); Si(1)−O(1), 1.660(21); P(1)−Ir(1)−P(2), 163.6(4); P(1)−Ir(1)−Cl(1), 90.1(3); P(1)−Ir(1)−Si(1), 97.3(3); P(2)−Ir(1)−Cl(1), 92.2(3); P(2)−Ir(1)−Si(1), 94.2(3); Ir(1)−Si(1)−O(1), 109.8(9); Cl(1)−Ir(1)−Si(1), 127.3(3).

The coordination geometry of **2** was determined by an X-ray structural study of its single crystal grown from a pentane solution at −20 °C (Figure 1).[10] As seen from Figure 1, complex **2** adopts a distorted trigonal bipyramidal configuration with axial phosphine ligands and with the silanol group, the chloride, and the hydride, which was not located, in the equatorial plane. Surprisingly, no intramolecular hydrogen bond between the chloride and the silanol hydrogen is observed, the O···Cl distance (more than 5 Å) falling outside the range of typical O···Cl contacts found in compounds that contain such bonds.[4,12] However, the *intermolecular* O···Cl distance is relatively short (3.28(2) Å), suggesting the presence of a weak *intermolecular* hydrogen bond. Interestingly, the structure of complex **2** exhibits a planar arrangement of the O−Si−M−P fragment, as was already observed in the structure of the first metallosilanol, namely, $(dcpe)Pt(Ph)[Si(SiMe_3)_2(OH)]$.[3] The Ir−Si bond in **2** is short[13] (2.313(6) Å) despite the presence of bulky alkyl substituents on the silicon and the phosphorus atoms. This may be due to the coordinative unsaturation of **2**. Another, probably main, reason for this is an increased metal-to-silicon back-bonding when Si bears electronegative substituents. Similarly, short M−Si bond distances were reported for Pt[3] and Os[4] silanol complexes. The Si−O bond length (1.660(21) Å) is quite normal as compared to organo-[14] and metallosilanols.[3,4]

The fact that the coordinatively unsaturated 16-electron d^6 complex **2** has a trigonal bipyramidal, rather than a square

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[7] A lithium derivative of the ferriosilanol $Cp(CO)_2FeSiMe_2OH$ was mentioned in a review (see ref 6), but no preparative and analytical data were given.

[8] Orange crystals of pure complex **1** can be isolated from extraction of its saturated precursor $L_2Ir(C_2H_4)_2Cl$ with pentane: Aizenberg, M.; Milstein, D. Manuscript in preparation.

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[10] See supplementary material.

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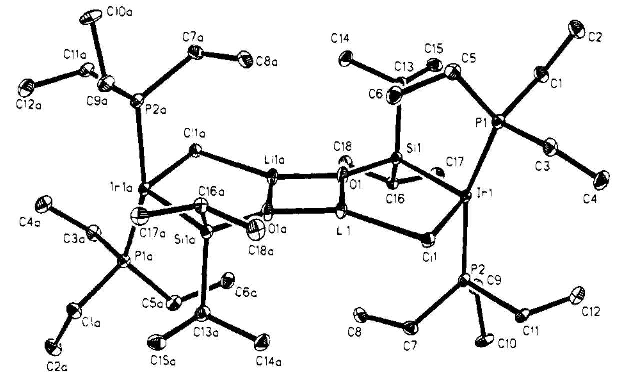
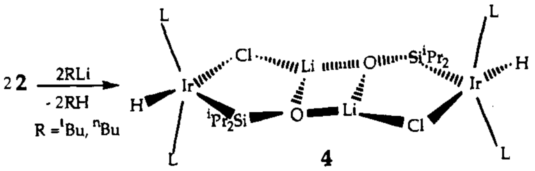


Figure 2. ORTEP view of **4** with hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−Cl(1), 2.482(2); Ir(1)−P(1), 2.306(2); Ir(1)−P(2), 2.310(2); Ir(1)−Si(1), 2.344(2); Si(1)−O(1), 1.601(5); Cl(1)−Li(1), 2.354(12); O(1)−Li(1), 1.874(14); O(1)−Li(1A), 1.789(13); Li(1)···Li(1A), 2.378(25); P(1)−Ir(1)−P(2), 158.6(1); P(1)−Ir(1)−Cl(1), 90.4(1); P(1)−Ir(1)−Si(1), 100.5(1); P(2)−Ir(1)−Cl(1), 87.7(1); P(2)−Ir(1)−Si(1), 100.3(1); Ir(1)−Si(1)−O(1), 103.8(2); Cl(1)−Ir(1)−Si(1), 109.8(1).

pyramidal, configuration may be due to the presence of a π-donor, namely, Cl, in it. Stabilization of one configuration over another due to a partial multiple bond between the metal center and the π-donor was predicted by theoretical studies.[15]

Treatment of a pentane solution of complex **2** with a stoichiometric amount of a strong base, such as ^{t}BuLi or ^{n}BuLi in pentane at 0 °C, results in clean, selective deprotonation[16] (eq 2). On cooling of the resulting solution to −20 °C, small yellow crystals of the metallosilanolate **4** can be isolated in 90% yield. Spectroscopic characterization of complex **4**[10] revealed



4 (2)

that the base had selectively deprotonated the OH proton, leaving the hydride untouched. Overall, there were only minor changes in ^{1}H and ^{31}P{^{1}H} NMR of **4** as compared to those of **2**. However, a significant high-field shift from δ 19.57 to 3.74 ppm was observed in ^{29}Si{^{1}H} NMR, indicating significant shielding of the silicon center in the silanolate as compared to the silanol.[17] A concomitant decrease in the coupling constant $^2J_{\mathrm{Si-P,cis}}$ (compare: 26 Hz in **2** *vs* 15 Hz in **4**) was also observed.

Final verification of the structure of **4**, the first fully characterized metallosilanolate, came from an X-ray crystallographic study (Figure 2).[10] There are several important features in the structures of **2** and **4**, which, despite the formal analogy in composition of the compounds, are very different. In contrast to **2**, complex **4** crystallizes as a centrosymmetrical dimer, rather than as a monomer. An almost planar core (Figure 2), consisting of two iridiums, two silicons, two chlorines, two oxygens, and two lithiums, is the most remarkable feature of the structure. The largest deviation from the Li(1)−O(1)−Li(1A)−O(1A) plane is observed for Si (0.1637 Å), and the Cl(1)−Ir(1)−Si(1) plane is tilted with respect to it only by 3.2°. The arrangement with three-coordinate lithium atoms, involved in the Li−O−Li−O square, is not without precedence in lithium silanolate chemistry.[18] However, the Li−O bond lengths (1.874(14), 1.789(13) Å) and Li···Li contacts (2.378(25) Å) in **4** are among the shortest known,[19] again, despite the fact that substituents at the silicons, namely, two isopropyls and (bisphosphine)iridium−(hydrido)(chloride), are bulky. The short Li···Li distance is probably a consequence of the four-membered Li_2O_2 ring. The Si−OLi bond in **4** (1.601(5) Å) is about 0.06 Å shorter than the Si−OH bond in **2** (1.660(21) Å). An analogous phenomenon was observed for organosilanols and -silanolates.[18] *Ab initio* calculations of optimized geometries of H_3SiOH and H_3SiO^- also predict 0.06 Å bond shortening for the silanolate anion.[20] It probably reflects an increase in Si−O bond order due to partial back-bonding from the negatively charged oxygen to the silicon. In particular case of **4** it may cause a concomitant decrease in competitive iridium-to-silicon back-bonding, which leads to an increase of the Ir−Si bond length in **4** (2.344(2) Å) as compared to that in **2** (2.313(6) Å). The observed elongation of the Ir−Cl bond (2.482(2) Å in **4** vs 2.421(6) Å in **2**) is undoubtedly due to participation of Cl in an additional coordination to Li. It probably also causes some contraction of the Cl−Ir−Si angle (compare: 127.3(3)° in **2** *vs* 109.8(1)° in **4**), making the coordination geometry around Ir closer to square pyramidal. The fact that **4** crystallizes as a very stable dimer with strongly bound chelates in the central core is in agreement with the general tendency of organolithium compounds to form oligomers. It is usually attributed to the high ionicity of lithium bonds and hence large energies of association.[19]

The dimeric nature of **4** is likely to be preserved in solution as well. It is reflected in the high stability of this metallosilanolate toward TMEDA and 12-crown-4, which possess exclusively high affinity for lithium ions. All our attempts to extract Li^+ from **4**, using these reagents in THF or benzene solutions, were unsuccessful. Remarkably, when [Li(12-crown-4)$_2$][CHPh$_2$][21] is used as a base, the silanolate **4** is again quantitatively formed as a result of Li^+ extraction from the 12-crown-4 complex. This fact demonstrates an outstanding thermodynamic stability of the metallosilanolate. However, **4** reacts instantaneously with water in benzene or THF, yielding quantitatively its parent compound **2**. We did not observe dimetallosiloxane formation.

In conclusion, we have directly synthesized and fully characterized the first iridium−silanol complexes **2** and **3**. For the first time, we have isolated and fully characterized a metallosilanolate complex **4**. This complex exhibits unusual structural features and a remarkable lithium binding ability. Importantly, although this complex is dimeric, it remains coordinatively unsaturated at iridium. Studies aimed at further exploration of the reactivity of iridium and silicon centers in these new complexes are in progress.

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Supplementary Material Available: Complete NMR data for compounds **2**−**6** and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and packing diagrams for **2** and **4** (27 pages); observed and calculated structure factors for **2** and **4** (25 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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