

Silica as a Ligand: Reactivity of the Iridium–Oxygen Bond of Cp*Ir[silica](Ph)(PMe₃)

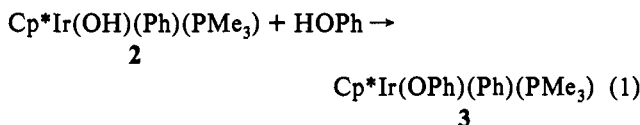
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Silica-supported metals and metallic complexes catalyze many significant reactions, such as olefin polymerization¹ and styrene/propylene oxide synthesis.² Although in most cases the catalyst supports do not participate in substrate transformations, they are postulated to contribute to the steric and electronic properties of the active metal center.³ The structures of these bound-metal species have been investigated, but the focus of these studies has been mainly spectroscopic.^{4–6} The use of chemical reactivity as a structural tool has not been developed extensively.⁷ In this communication we discuss the preparation and chemistry of Cp*Ir[silica](Ph)(PMe₃) (**1**). We have found methods not only to attach the iridium complex to silica but to also remove it cleanly by treatment with specific reagents, so that changes in its structural integrity can be monitored using homogeneous solution analytical methods. Moreover, equilibrium studies and reactivity comparisons with homogeneous analogues have provided information about the nature of the iridium–silica interaction.

Our recent observation that Cp*Ir(OH)(Ph)(PMe₃) (**2**)⁸ reacted with phenol to produce phenoxide **3** suggested to us a method for attaching the [Cp*(PMe₃)(Ph)Ir]⁺ fragment to the silanol-containing silica surface.



Silica⁹ treated with iridium hydroxide **2** in THF immediately became yellow as the supernatant changed from tan to nearly colorless. Although the ¹³C CPMAS NMR spectrum¹⁰ of the

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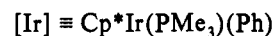
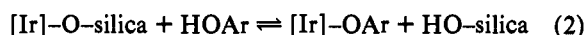
(8) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888.

(9) Degussa 300 m²/g; dried under vacuum for 48 h at 200 °C to remove surface H₂O.

supported complex is consistent with the formation of Cp*Ir[silica](Ph)(PMe₃) (**1**) (Scheme 1), the typical broadness of the NMR signals and lack of connectivity information prevent an unambiguous assignment. By exploiting the reactivity of the complex with phenols, however, we were able to obtain further structural evidence. Treatment of the iridium–silica species **1** with *p*-nitrophenol liberated the aryloxido complex Cp*Ir(*p*-OC₆H₄NO₂)(Ph)(PMe₃) (**4**) in >95% yield by ¹H NMR spectroscopy (78% isolated yield). Since these exchange reactions presumably involve only the Ir–O bound ligand, and hydroxide **2** and aryloxide **4** are otherwise analogous, the structure of bound-iridium species **1** illustrated in Scheme 1 can be inferred.¹¹ Evidence that the iridium complex is in fact chemisorbed by an iridium–oxygen bond, and not simply hydrogen-bonded to the silica surface, was obtained by monitoring the reactions of Cp*Ir(*p*-NHC₆H₄Me)(Ph)(PMe₃) (**5**) or Cp*Ir(OSiMe₂tBu)(Ph)(PMe₃) (**6**)¹² with silica. These reactions led to **1** and liberated 1 equiv of free *p*-toluidine or HOSiMe₂tBu, respectively, both of which were detected and quantified in the supernatant solution.

In contrast to the quantitative reaction of **1** with *p*-nitrophenol, the silica-bound iridium species reacted with phenol, *p*-methoxyphenol, *p*-chlorophenol, and 4-chloro-3,5-dimethylphenol to produce detectable equilibrium ratios of **1** and the corresponding aryloxido complexes **3**, **7**, **8**, and **9**. Silica-bound **1**, when generated from toluamide **5** or siloxide **6**, behaved analogously. In order to verify that the reaction of **1** with substituted phenols is an equilibrium process, a solution of Cp*Ir(*p*-OC₆H₄OMe)(Ph)(PMe₃) (**7**) of known concentration in THF-*d*₈ was treated with silica and monitored by ¹H NMR spectroscopy. The disappearance of **7** and the concurrent appearance of *p*-HOC₆H₄OMe confirmed the reversible nature of the reaction.

For the overall reaction written in eq 2, an apparent equilibrium quotient, *K*_{app}, may be defined (eq 3). The “concentrations” of the insoluble species, designated by {}, are approximated by the ratio of molar quantity present to the volume of solvent.¹³ *K*_{app}'s, determined for a selection of phenols, were found to be independent of temperature (25–80 °C) and the initial concentrations of **1** or HOAr over the ranges of concentrations studied.¹⁴



$$K_{\text{app}} = \frac{[\text{Ir}]-\text{OAr}\{\text{HO}-\text{silica}\}}{\{[\text{Ir}]-\text{O}-\text{silica}\}\{\text{HOAr}\}} \quad (3)$$

By analysis of the reaction in terms of heterolytic O–X ionization free energies, these *K*_{app} data can be used to examine the relative affinity of the iridium fragment for the aryloxides vs silica. The proton-transfer equilibrium in eq 4 is expected to lie toward the left with *K*_{eq} = 2.5 × 10^{−4} to 6.3 × 10^{−7} based on the differences in the p*K*_a values of the phenols studied (9.6–10.2)^{15,16} and silica hydroxyls (4–7).¹⁷ Because the *K*_{app} values for the overall reaction in eq 2 are larger (0.026–0.25), it must be true that the [Ir]–O–silica/[Ir]–OAr equilibrium (eq 5) lies

(10) ¹³C{¹H} CPMAS NMR (75.74 MHz): δ 140.7, 124.2, 121.5 (m, C₆H₅); 86.5 (s, C₃Me₃); 10.6 (s, PMe₃) (peak broadness prevented observation of ³¹P coupling); 5.5 (s, C₃Me₃).

(11) Samples of silica which were inert to further reaction with **2** were calculated to occupy ca. 30% of the available silanol sites (based on the Degussa reported value of 2.5 silanols/nm²).

(12) Prepared by analogy to **1**. Iridium triflate **10** was treated with KOSi-t-BuMe₂ in THF/Et₂O to produce siloxide **6** in 33% yield.

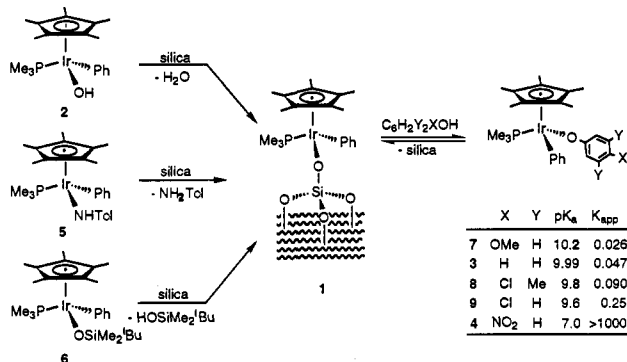
(13) Frommer, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5227.

(14) Note that this expression is accurate only if [HOAr] is sufficiently large to remain constant during the course of the reaction. We believe that a secondary reaction with silica complicates the equilibrium at lower [HOAr].

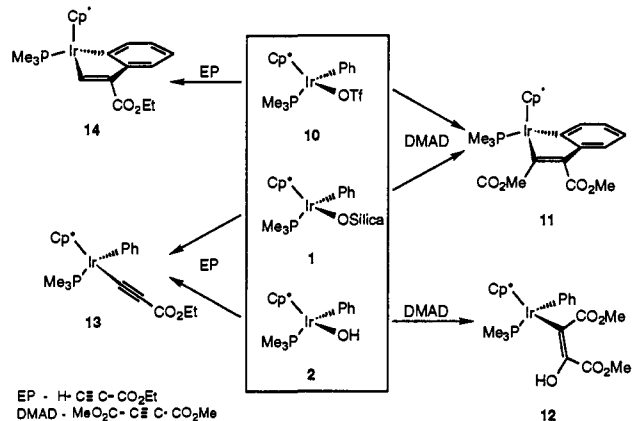
(15) Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Phys. Chem.* **1976**, *80*, 1306.

(16) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49*, 1424.

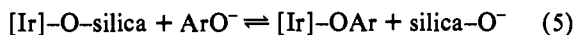
Scheme 1



Scheme 2



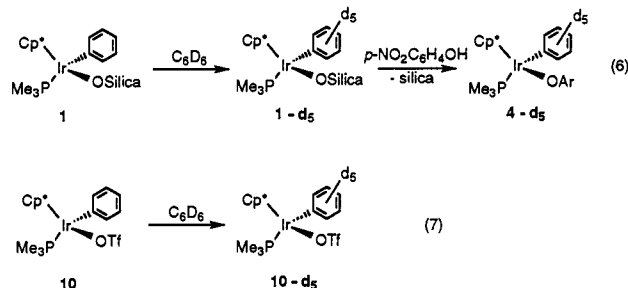
toward the right. That is, the relative affinity of the two alkoxide groups for [Cp*(PMe₃)(Ph)Ir]⁺ correlates with their affinity for protons.



The silica-iridium interaction was further investigated by comparison of the reactions of the supported complex with those of the analogous monomeric iridium hydroxide **2**⁸ and iridium triflate **10** (Scheme 2). Interestingly, with the three classes of substrates examined, the reactivity of silica-bound **1** was found to be intermediate between that of the hydroxide and that of the triflate. With phenols, for example, the iridium-silica complex **1** forms equilibrium mixtures with $K_{\text{app}} = 0.026\text{--}0.25$ (vide supra). Analogous reactions of phenols with hydroxide complex **2** proceed to completion ($K_{\text{eq}} > 1000$), whereas with the triflate species **10** no exchange is observed. In a second reaction, the internal alkyne dimethyl acetylenedicarboxylate (DMAD) reacted with both silica-bound **1** and triflate **10** (with 1 equiv of base) to produce iridacycle **11** in 82% (NMR) and 97% (isolated) yields, respectively (Scheme 2). Presumably, the reaction proceeds by π -coordination followed by an intramolecular electrophilic substitution reaction. Hydroxide **2**, however, is known to undergo

(17) The value reported by Degussa Corporation for Aerosil 300 was ~ 4 . pK_a values of 4–7 are typically reported for silica: Benesi, H. A.; Winquist, B. H. *Adv. Catal.* **1978**, *27*, 120.

insertion of DMAD into the Ir–OH bond to form vinyl hydroxide complex **12**.⁸ The terminal alkyne ethyl propiolate (EP) reacted with both the silica-bound species **1** and hydroxide **2** to form acetylide complex **13** in 85% (NMR) and 44% (isolated) yields, respectively. In contrast, triflate **10** led to iridacycle **14** in analogy to its reaction with DMAD. Finally, **10** and **1** activated the C–D bond of benzene-*d*₆ to produce **10-d**₅ (105 °C) and **1-d**₅ (135 °C) by aryl exchange (eqs 6 and 7), a class of reaction that was previously observed for Cp*Ir(OTf)(Me)(PMe₃).¹⁸ In the reaction of **1** with C₆D₆, formation of **1-d**₅ was established by complete removal of deuterated benzene, followed by treatment of the silica-bound product with *p*-nitrophenol. Free silica and a 15% yield of **4-d**₅ were obtained. Competing thermal decomposition reactions were responsible for the relatively low yields of **4-d**₅; hydroxide **2** completely decomposed at 80 °C before any C–D activation was observed. One explanation for the apparent



intermediate Ir–OH vs Ir–OTf reactivity of the iridium-silica complex **1**, which is consistent with the equilibrium studies described above, is that the reactivity correlates with the polarity of the Ir–O bond: Ir–OTf > Ir–OAr > Ir–O-silica > Ir–OH.

In summary, we have successfully prepared a silica-bound iridium complex and exploited the exchange reactivity of the complex to provide strong evidence for its structural identity and to probe the nature of the iridium-silica interaction. We have also shown that silica can be treated as a simple ligand¹⁹ in this system, and that a complex made with this ligand exhibits reactivity, including C–H activation, similar to that of its monomeric analogues. Further investigations of the reactivity of the iridium species **1** and extensions of this chemistry to metal complexes with additional reactive sites are ongoing.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **4**, **6–9**, **11–14** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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