Synthesis of Bridging Iridium Bis(imido) and Imido–Oxo Complexes. Imide and Oxygen Transfer Reactions and Hydrogenation of an Imido Ligand

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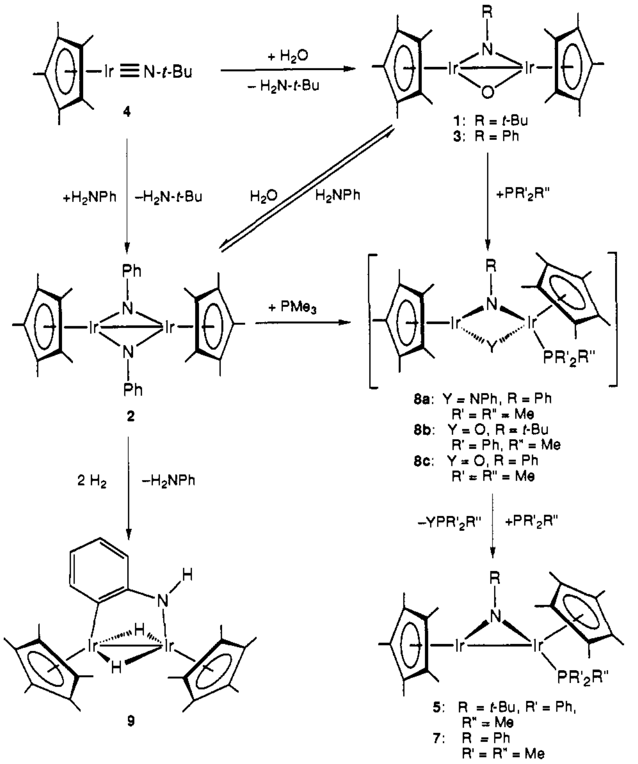
Oxygen atom transfer from transition-metal oxo complexes is well documented.[1] However, there exist very few examples of imido group transfer from metal complexes.[2–7] Furthermore imide transfer from bridging imide (nitrene) complexes[8–14] has rarely been observed.[15] We wish to report (a) the synthesis of a series of bridging bis(imido) and imido–oxo complexes of iridium, Cp*Ir(μ-X)(μ-NR)IrCp* (**1**, X = O, R = *t*-Bu; **2**, X = NR, R = Ph; **3**, X = O, R = Ph); (b) imide and oxygen transfer from these compounds to phosphines; and (c) the reduction of the bis(imido) complex **2** by H_2.

Treatment of Cp*Ir≡N-*t*-Bu (**4**)[16] with 0.5 equiv of H_2O resulted in the formation of Cp*Ir(μ-O)(μ-N-*t*-Bu)IrCp* (**1**) and H_2N-*t*-Bu (Scheme I). Complex **1** was isolated in 96% yield after extraction with pentane and has been characterized by standard spectroscopic and analytical methods.[17] Addition of excess H_2O (>20 equiv) to imido complex **4** resulted in formation of the known tris-bridging hydroxide [Cp*Ir(μ-OH)$_3$-IrCp*]$^+$OH$^-$ [18] and H_2N-*t*-Bu.

The imido–oxo complex **1** is an oxygen atom donor, as demonstrated by its reaction with phosphines. Treatment of **1** with PPh_2Me at room temperature resulted in the production of 1 equiv of O=PPh_2Me and Cp*Ir(μ-N-*t*-Bu)Ir(PPh_2Me)Cp* (**5**) in 51% yield. A similar reaction has been observed with the isoelectronic complex Cp*Ir(μ-O)$_2$IrCp* in this laboratory.[19,20] The structure of **5** was confirmed by an X-ray diffraction analysis (see Figure 1). Noteworthy aspects of the structure include an imide moiety that is planar at nitrogen (sum angles = 179°; Ir(1)–N = 2.031(10) Å; Ir(2)–N = 1.810(10) Å) and a very short Ir–Ir distance of 2.694(1) Å, indicating a metal–metal bond.[19]

Scheme I



Treatment of Cp*Ir≡N-*t*-Bu with 1 equiv of aniline resulted in the production of the black bridging imido dimer Cp*Ir(μ-NPh)$_2$IrCp* (**2**) (67% isolated yield), which has been characterized by X-ray diffraction. The X-ray structure (Figure 1) shows a pyramidal geometry at the nitrogen centers (Ir–N = 1.977(10) Å), a puckering of the Ir_2N_2 ring, and a short Ir–Ir distance (2.778(1) Å).

Imide transfer was observed upon addition of 2 equiv of PMe_3 to **2**. This resulted in the formation of PhN=PMe_3 (**6**)[21] (75% yield by ^{1}H NMR) and the green complex Cp*Ir(PMe_3)(μ-NPh)-IrCp* (**7**) (75% yield by ^{1}H NMR; 25% isolated yield). An intermediate in this reaction was observed by ^{1}H NMR spectroscopy during the course of the reaction. This species could not be isolated, but its formulation as the PMe_3 adduct of **2**, Cp*(PMe_3)Ir(μ-NPh)$_2$IrCp* (**8a**), is supported by its ^{1}H NMR spectrum. This suggests a mechanism involving initial coordination of phosphine followed by imide transfer to produce the phosphinimine PhN=PMe_3. In light of this observation, it is reasonable to assume that the reaction of **1** with phosphine proceeds through a similar intermediate (**8b**) (Scheme I), although this complex was not observed spectroscopically.

No changes in the spectral characteristics of **2** were observed upon treatment with 1 equiv of H_2O. However, addition of 2 equiv of PMe_3 to this mixture of **2** and H_2O afforded PMe_3 adduct **7** (99% yield by ^{1}H NMR) and O=PMe_3; no PhN=PMe_3 was detected. This reaction proceeds at an elevated rate in the presence of H_2O; it is complete after 24 h at room temperature. We rationalize these results by assuming an equilibrium between bis(imido) complex **2** and the analogous oxo complex Cp*Ir(μ-NPh)(μ-O)IrCp* (**3**) in which $K_{eq} \ll 1$ (Scheme I). Imido–oxo dimer **3** then transfers an oxygen atom faster than it or the bis(imido)

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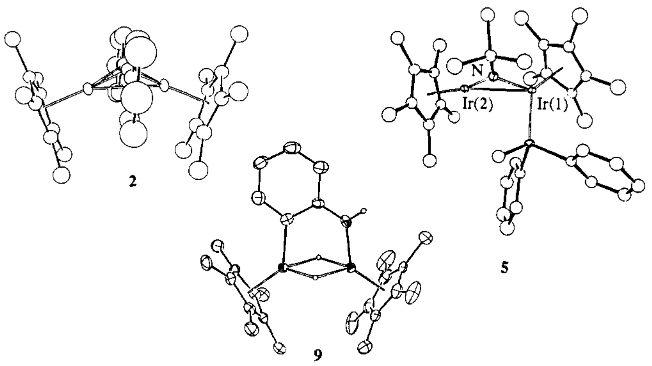

Figure 1. ORTEP diagrams from crystal structures of Cp*Ir(μ-NPh)$_2$IrCp* (**2**), Cp*Ir(μ-N-*t*-Bu)Ir(PPh$_2$Me)Cp* (**5**), and Cp*Ir(μ-NH(*o*-C$_6$H$_4$))(μ-H)$_2$IrCp* (**9**).

complex **2** transfers an imide moiety and thus favors the **2** → **3** → **8c** → **7** route over the direct **2** → **7** pathway. Oxo transfer to phosphine has been shown to be faster than imide transfer with at least one other oxo–imido complex.[2]

Treatment of a benzene solution of **2** with gaseous hydrogen[22] at 60 °C resulted in loss of aniline and the formation of a complex in 56% yield formulated as Cp*Ir(μ-NH(*o*-C$_6$H$_4$))(μ-H)$_2$IrCp* (**9**) (see Scheme I). The structure of this complex was confirmed by an X-ray diffraction study (Figure 1). The hydride positions were located,[23] and their observed symmetry (and thus, chemical equivalence) is further supported by the ^{1}H NMR spectrum of **9**, which gives magnetically equivalent hydride resonances even upon cooling to −90 °C. Compound **9**, which contains a ligand that might be described as a dinuclear N–H and C–H activated aniline, is the apparent result of reduction of a bridging iridium imide followed by intramolecular C–H activation by the adjacent iridium center. The addition of H$_2$ to metal–nitrogen bonds has been observed only very rarely.[24–28]

In summary, we have prepared a new series of bridging iridium bis(imido) and imido–oxo complexes through exchange reactions with H$_2$O and aniline, and these compounds have been found to act as imido and oxygen group transfer agents. A bridging arylimido complex was found to undergo hydrogenolysis to give free aniline and a bridging hydride complex. These results serve to broaden the scope of known reactions of bridging imide complexes and raise the possibility that bridging species may be viable intermediates in catalytic imido group transfer reactions.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **2**, **5–8a**, and **9**; X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional and anisotropic thermal parameters, intramolecular distances and angles) for **2**, **5** and **9** (19 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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(22) H$_2$ (2.0 atm) was added at room temperature.

(23) Peaks were observed in the difference Fourier map corresponding to reasonable positions for the two hydride ligands and the N–H proton. These three were included in structure factor calculations, and their positional and isotropic thermal parameters were refined. The *R* value for all accepted data was 3.53%. Additional data from the X-ray structure determination are provided as supplementary material.

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