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Stabilization of Iridium(IV) by Monoanionic Dialkyldiarylguanidinato Ligands

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High-valent iridium has become an attractive target in recent years, mainly due to its role in C−H bond activation and oxygen atom transfer reactions.[1,2] Stable complexes of Ir^{IV} have found applications as one-electron oxidants for synthetic purposes and in mechanistic studies,[3] whereas transient Ir^{IV} species are involved in oxidatively induced C−H bond cleavage[4] and, more recently, in water oxidation chemistry.[5] Despite these developments, well-defined examples of Ir in the +IV oxidation state are still limited.[6] These include inorganic hexahalogeno complexes[7] and several organometallic compounds[2,8] with substituted phenyl or cyclopentadienyl ligands.

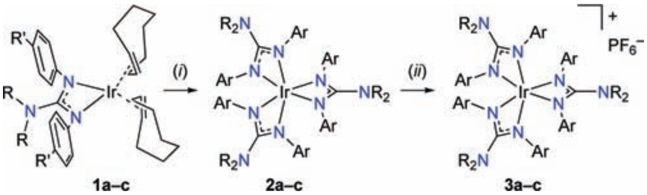
For a broader exploration of the chemistry of Ir^{IV}, however, the availability of complexes with multidentate ligands based on organic heteroatom-donor frameworks would be of great advantage, as has been the case for other high-valent transition metal centers.[9] Although a series of moderately stable complexes of the type $[Ir^{IV}X_4L_2]$ (where X = Cl, Br and L = N-, P-, or S-donor ligand) were described two decades ago, the corresponding complexes with more than two heteroatom donors could not be obtained.[10] Nevertheless, electrochemical studies of Ir^{III} complexes of phenylpyridine-derived[11] and corrolato ligands[12] suggest that high-valent analogues may be within reach. Intrigued by these reports, we decided to take advantage of the strongly electron-releasing character of *N*,*N*-dialkyl-*N*′,*N*′′-diarylguanidinato ligands, $\{ArNC(NR_2)NAr\}^-$,[13] and to investigate their potential for the stabilization of high-valent iridium. Herein, we report the synthesis and characterization of tris(guanidinato) complexes of Ir^{III} and Ir^{IV}, which feature coordination by six organic nitrogen donors, including the crystal structure of an Ir^{IV} complex.

The Ir^{III} complexes $[Ir\{ArNC(NR_2)NAr\}_3]$ (where R = Me, Ar = Ph (**2a**); R = Et, Ar = Ph (**2b**); and R = Me, Ar = 4-MeC_6H_4 (**2c**)) were synthesized by the reaction of the corresponding $[Ir\{ArNC(NR_2)NAr\}(coe)_2]$ complexes, **1a**−**c**, with the appropriate lithium guanidinates and dioxygen, as shown in Scheme 1 (coe = *cis*-cyclooctene). This reaction presumably proceeds through oxidation of the Ir^I center, dissociation of the labile alkene ligands, and coordination of the guanidinate anions. Surprisingly, **2a**−**c** are slightly air-sensitive, so the workup, which includes the separation from as yet unidentified byproducts, must be carried out under the exclusion of O_2. Compounds **2a**−**c** were isolated as racemic mixtures (Δ- and Λ-enantiomers), and their molecular composition was established by analytical and spectroscopic methods (cf. Supporting Information). The ^1H NMR spectra of each of these complexes indicate a symmetric N,N′-chelating binding mode for the bidentate guanidinato ligands and are consistent with coordination to a low-spin d^6 Ir^{III} center in the expected D_3 symmetric environment.

Electrochemical measurements revealed that **2a**−**c** can be oxidized at unusually low potentials. The cyclic voltammogram of **2a**, for example, displays two distinct one-electron redox events at potentials of −0.27 and 0.73 V [$E_{1/2} = (E_{pa} + E_{pc})/2$] with respect to the $[FeCp_2]/[FeCp_2]^+$ redox couple (Figure 1). The first electron transfer is a reversible, diffusion-controlled process, whose ΔE_p values do not differ significantly for scan rates ranging from 0.05 to 0.5 V·s^{-1} ($\Delta E_p = E_{pa} - E_{pc}$). Because both free guanidine, $PhN{=}C(NMe_2)NHPh$, and lithium guanidinate, $Li\{PhNC(NMe_2)NPh\}$, are irreversibly oxidized at much more positive potentials (≈ 0.66 and 0.49 V, respectively), the first redox event in **2a** may be assigned to a metal-centered electron-transfer process. The second step is quasi-reversible and may be attributable to either a metal-centered or a ligand-centered process. Voltammograms similar to those for **2a** were obtained for **2b** and **2c**, but the first redox step occurred at lower potentials, i.e., −0.33 V for **2b** and −0.41 V for **2c**, in line with the increasing electron donation from the guanidinato ligand[13] to the Ir center (**2a** < **2b** < **2c**). By comparison, the Ir^{III}/Ir^{IV} redox potentials of **2a**−**c** are significantly less positive than those of many other Ir^{III} complexes (≥0.21 V vs $[FeCp_2]/[FeCp_2]^+$).[10,14a] Even complexes with very electron-rich ligand sets such as cyclometalated tris(2-pyridylphenyl),[11,14b] corrolato,[12] and tris(dithiocarbamato) complexes,[15] which all provide a trianionic environment around the Ir center akin to the tris(guanidinato) complexes **2a**−**c**, exhibit higher potentials (0.07−0.91 V vs $[FeCp_2]/[FeCp_2]^+$).

Chemical oxidation of **2a** in dichloromethane solution with $[FeCp_2]PF_6$ produced $[Ir\{PhNC(NMe_2)NPh\}_3]PF_6$, **3a** (Scheme 1), with absorption bands in the vis−near-IR region [$\lambda_{max} = 540$ (ϵ =

Scheme 1. Synthesis of Ir^{III} and Ir^{IV} Compounds **2a**−**c** and **3a**−**c**[a]



[a] **a**, R = Me, R′ = H; **b**, R = Et, R′ = H; **c**, R = R′ = Me; Ar = 4-C_6H_4R'; (*i*) 3 equiv of $Li\{ArNC(NR_2)NAr\}$, O_2; (*ii*) 1 equiv of $[FeCp_2]PF_6$.

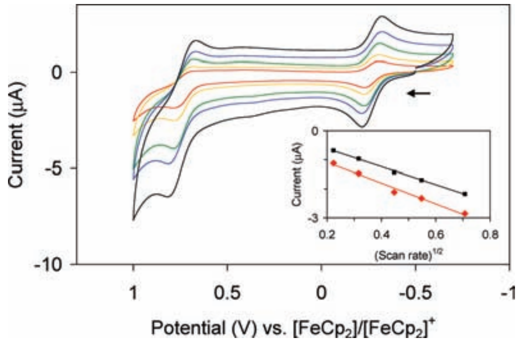


Figure 1. Cyclic voltammograms of 0.1 mM **2a** in CH_2Cl_2 (0.1 M NBu_4ClO_4) at scan rates of 0.05, 0.1, 0.2, 0.3, and 0.5 V·s^{-1}. Inset: Plot of anodic peak current, i_{pa}, versus square root of scan rate for the first (■, black; $R^2 = 0.9982$) and second oxidation (◆, red; $R^2 = 0.9861$).

10.1021/ja9033445 CCC: $40.75

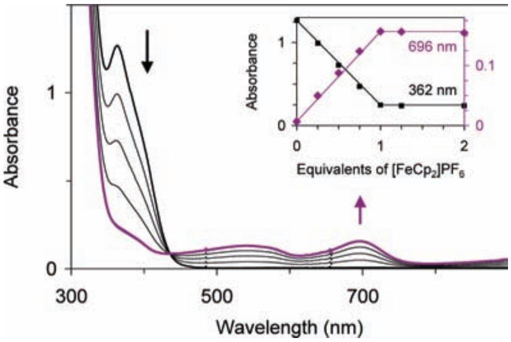


Figure 2. Oxidation of 0.1 mM **2a** (—, black) to **3a** (—, violet) in CH_2Cl_2 by addition of $[FeCp_2]PF_6$ in increments of 0.25 equiv as monitored by electronic absorption spectroscopy (path length, 0.5 cm). Inset: Corresponding changes of the absorbance at 362 (■, black) and 696 nm (◆, violet).

$2800\ M^{-1}\cdot cm^{-1}$) and 696 nm (3100)]. As shown in Figure 2, incremental addition of $[FeCp_2]PF_6$ demonstrated that 1 equiv is required for maximal formation of **3a**, and the isosbestic point in this conversion indicates that **3a** was formed directly from **2a**. On a larger scale, **3a**−**c** were generated and isolated as dark violet solids in nearly quantitative yields and analytically pure form. The complex cations, $[Ir\{ArNC(NR_2)NAr\}_3]^+$, were identified by ESI-MS. As expected for odd-electron species, the ^1H NMR spectra of **3a**−**c** are featureless.

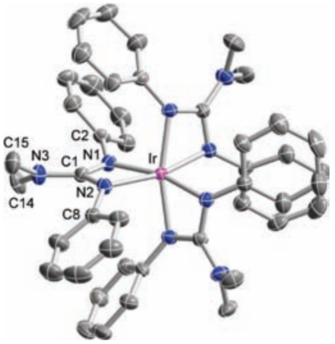


Figure 3. Molecular structure of the complex cation of **3a**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Color key: pink = Ir, blue = N, gray = C.

A crystallographic analysis on a single crystal of **3a**, grown by vapor diffusion of *n*-pentane into a dichloromethane solution at −30 °C, confirmed the formation of $[Ir\{PhNC(NMe_2)NPh\}_3]PF_6$ (Figure 3 and Supporting Information). The Ir−N distances of 2.040(3) and 2.064(3) Å agree well with those in $[IrCl_4(phen)]$.[10b] The intraligand C−N and C−C distances are comparable to those of related guanidinato complexes of Ir^I and Ir^{III}.[13,16] In contrast, the C−C distances in Ir^{III} semiquinonato complexes display bond alternation, clearly indicating ligand radical character.[17] The crystal structure thus provides evidence for the assignment of **3a** as an Ir^{IV} rather than an Ir^{III}-ligand-radical species. In agreement with this assignment, the 77 K EPR spectrum of **3a** in frozen solution is consistent with the presence of a low-spin d^5 Ir^{IV} center.[18]

In summary, we have prepared and characterized rare examples of air-sensitive coordinatively saturated Ir^{III} complexes. Oxidation of these compounds led to the isolation of stable tris(guanidinato)iridium(IV) complexes, in which the Ir center is exclusively coordinated by nitrogen-donor ligands. These results underscore the exceptional ability of the *N*,*N*-dialkyl-*N*′,*N*″-diarylguanidinate anions to stabilize transition metals in high oxidation states and suggest them as excellent ancillary ligands for new high-valent Ir complexes that may be tailored to effect useful transformations. Current efforts are directed at the identification of the even further oxidized species detected in our electrochemical studies.

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Supporting Information Available: Experimental procedures, characterization data of **2a**−**c** and **3a**−**c**, details of the crystal structure determination (Tables S1−S3, PDF), and CIF of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The EPR spectrum exhibits a large *g* anisotropy ($g_\perp = 2.38$ and $g_\parallel = 1.87$) and a broad line width (peak-to-peak separation ≈ 300 G), indicative of localization of the unpaired electron predominantly in a metal-based orbital.

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