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Synthesis, Characterization, and O_2 Reactivity of Iridium(I) Complexes Supported by Guanidinato Ligands

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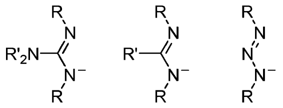
Mononuclear [Ir{ArNC(NR_2)NAr}(C_8H_{12})] complexes (where R = Me or Et; Ar = Ph, 4-MeC_6H_4, or 2,6-$Me_2C_6H_3$; and C_8H_{12} = 1,5-cyclooctadiene) were synthesized from the neutral *N*,*N*-dialkyl-*N*′,*N*′′-diarylguanidines via deprotonation and transmetalation. As confirmed by single-crystal structure determinations, the guanidinato(1−) ligands coordinate the low-valent d^8 Ir^I center in an N,N′-chelating binding mode, and the ^{13}C NMR chemical shifts of the alkene carbon atoms establish that these ligands function as stronger donors than related monoanionic, bidentate nitrogen-based ligands. In the reactions of the complexes with O_2, the observed reactivity trends correlate with the electronic and steric influences of the substituents of the guanidinato ligands.

Monoanionic nitrogen-donor ligands represent an important class of supporting ligands and have been widely used in the coordination chemistry of transition metals to impart diverse properties and reactivity. Prominent examples include poly(1-pyrazolyl)borate,[1] β-diiminate,[2] aminotroponiminate,[3] and amidinate[4] scaffolds. Because guanidinates are conceptually related to the latter three systems, they may be expected to be similarly well-suited as supports for reactive metal centers. Complexes of guanidinates are known for many metals and metalloids, in particular, for early transition metals and lanthanides in mid- to high-valent oxidation states.[5−9] The exceptional ability of guanidinate anions to stabilize electron-deficient metal centers can be ascribed to lone-pair donation from the nitrogen atom of the NR_2 group, which increases the electron density at the two donor atoms available for metal coordination and, thereby, makes this class of ligands stronger donors than the closely related amidinate and triazenide anions[10] (Scheme 1 and Chart 1). Consequently, if coordinated to a lower-valent metal center, guanidinato ligands confer greater oxidizability on the metal, as is evident, for example, from the redox potentials of $[Mo^{II}_2(\mu\text{-L})_4]$ complexes.[11,12] Guanidinato complexes of electron-rich transition-metal centers in oxidation states lower than +II are limited to only a few di- and tetranuclear complexes, which involve mainly coinage metals.[5,13,14]

Scheme 1. Resonance Structures of the Guanidinate Monoanion

Chart 1. Guanidinate, Amidinate, and Triazenide Anions



We have targeted Ir^I complexes of bidentate *N*,*N*-dialkyl-*N*′,*N*′′-diarylguanidinate anions, $\{ArNC(NR_2)NAr\}^-$, to explore the coordination ability of this ligand platform to transition metals in low oxidation states. Herein, we report

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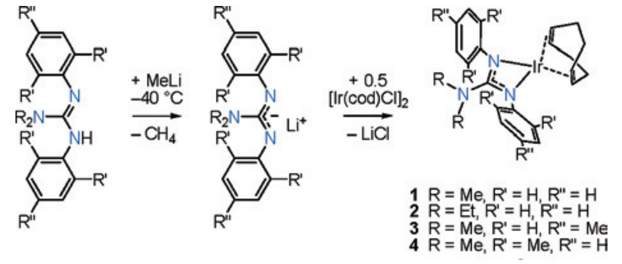
10.1021/ic801867r CCC: $40.75

Scheme 2. Synthesis of [Ir{ArNC(NR_2)NAr}(cod)] Complexes **1−4**



the synthesis and spectroscopic and structural characterization of a series of mononuclear [Ir{ArNC(NR_2)NAr}(cod)] complexes and evaluate the donor properties of the guanidinato ligands (cod = 1,5-cyclooctadiene). Several previously reported $[M^I(L)(cod)]^z$ complexes of Rh and Ir, where L is a di- or tridentate nitrogen- or oxygen-donor ligand, are known to react with dioxygen and undergo C−O bond formation under mild conditions.[15] In only two cases, however, the reactions take an atom-economic route that does not require additional reagents such as acids or sacrificial reductants.[15a,d] Also the new complexes presented here were found to react readily with dioxygen. In an effort to probe the utility of the guanidinate platform in tuning reactivity, we have investigated the effect of substituent variation (Ar and R) on the reactivity of these complexes.

The neutral guanidines ArN═C(NR_2)NHAr [where R = Me, Ar = Ph; R = Et, Ar = Ph;[16a] R = Me, Ar = 4-MeC_6H_4; and R = Me, Ar = 2,6-$Me_2C_6H_3$] were synthesized from the corresponding thioureas, ArHNC(S)NHAr, and the appropriate amines, HNR_2, according to literature methods for related compounds.[16] As shown in Scheme 2, treatment with MeLi and subsequent transmetalation using $[\{Ir(cod)\}_2(\mu\text{-}Cl)_2]$ under an inert atmosphere furnished the yellow Ir^I complexes of the anionic guanidinates, [Ir{ArNC(NR_2)NAr}(cod)], **1−4**. Complexes **1−4** are well soluble in nonpolar organic solvents such as toluene, diethyl ether, and *n*-pentane but only sparingly soluble in acetonitrile. The ^1H NMR spectra of each of these complexes are consistent with a guanidinato-$\kappa^2 N,N'$ and an η^4-cod ligand coordinated to a d^8 Ir^I center in a square-planar environment. On the basis of the molecular ion peaks observed by electron impact mass spectrometry, **1−4** are identified as mononuclear complexes (cf. the Supporting Information).

Yellow single crystals of **2** and **4** were grown from concentrated *n*-pentane solutions upon standing at −30 °C. The solid-state molecular structures of both compounds were determined from crystallographic analyses and confirm the mononuclear nature of **2** and **4** (Figure 1 and Supporting Information).[17] The Ir−N and Ir−C distances are in the ranges of 2.069(2)−2.099(2) and 2.095(3)−2.122(3) Å, respectively, which agree well with the values of related complexes.[17b,c,18,19] Because of the acute bite angles of the chelating guanidinato ligands (N1−Ir−N2 = 63.68(9)° for **2** and 63.72(9)° for **4**), the metal centers adopt a distorted square-planar coordination geometry. The structural analysis also reveals important intraligand parameters that provide insight into the bonding of the guanidinato ligands. Remarkably, the C−N distances in the planar CN_3 core of each complex are nearly identical, 1.346(4)−1.361(4) Å for **2** and 1.335(4)−1.354(4) Å for **4**. These parameters indicate a high degree of π-electron delocalization over the CN_3 core, implicating a significant contribution of the iminium/diamide resonance structure (Scheme 1, structure **II**). In accordance with the sp^2 hybridization expected for efficient lone-pair donation into the CN_3 unit, the N3 atoms adopt a trigonal-planar geometry with bond angle sums of 359.9(5)° (**2**) and 359.8(4)° (**4**). In contrast, the N1 and N2 atoms are more pyramidalized, with bond angle sums ranging from 346.0(3) to 352.5(3)°. Although the C−N3−C and N1−C1−N2 planes are slightly twisted with respect to each other [25.6(1)° for **2** and 18.7(3)° for **4**], presumably because of minor steric interactions between the NR_2 alkyl and the NAr aryl groups, the conjugation of N3 and C1 p orbitals is apparently not disrupted.

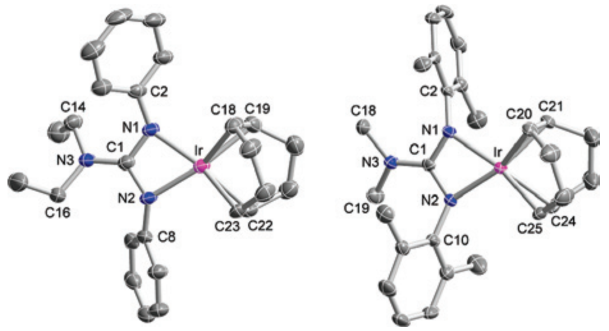


Figure 1. Molecular structures of **2** (left) and **4** (right), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Color key: pink = Ir, blue = N, gray = C.

The intraligand structural features of **2** and **4** are unusual because complexes of guanidinato(1−) ligands typically display more localized bonding with a longer C−N bond to the noncoordinated nitrogen atom and shorter ones to the metal-coordinated nitrogen atoms.[5,9b,11,13,14,20] Thus, the bonding in those guanidinate systems is best described by a relatively larger contribution of the amine/amidinate resonance structures (**I** and **III**). On the other hand, the greater extent of delocalization

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observed for **2** and **4** is precedent in complexes of Ti^{IV},[21] Zr^{IV},[7] and Nb^{V}.[8] It has been argued that significant involvement of the lone pair of the NR_2 nitrogen atom is due to the ligands' coordination to an electron-deficient metal center. In this context, the observations made here for low-valent d^8 Ir^I complexes may seem surprising. Presumably, the π-acceptor alkene ligand enhances the electron-releasing character of the guanidinato ligand and thus facilitates participation of the NR_2 lone pair in CN_3 π bonding.

To assess the donor strength of the guanidinato ligands in **1**−**4**, we turned to ^{13}C NMR spectroscopy to gauge the extent of Ir-to-cod π back-bonding. Complexes **1**−**4** exhibit ^{13}C NMR resonance signals for the alkene carbon atoms in the range of 58.8−61.0 ppm. These are upfield-shifted compared to the corresponding signals in Ir^I(cod) complexes of dicoordinating tris(pyrazolyl)borato and β-diketiminato ligands, which appear in the range of 63.2−66.7 ppm.[18,19] Lower $\delta(^{13}C_{C=C})$ values reflect increased π back-donation into the alkene π^* orbitals caused by increased electron density at the metal center. Therefore, the dialkyldiarylguanidinates may be considered stronger donors than κ^2-binding tris(pyrazolyl)borates and β-diketiminates. They are still weaker donors than tris(pyrazolyl)borate-κ^3 and cyclopentadienyl ligands (54.1 and 45.5−53.1 ppm).[18,22]

In solution, complexes **1**−**4** react readily with dioxygen, as indicated by the disappearance of their characteristic absorption features in the UV−vis region (Figure 2). For example, at 0 °C, the half-life of **1** in a toluene solution saturated with O_2 is ca. 20 min. Mono- and dioxygenated products were identified by electrospray ionization mass spectrometry. The masses and isotope distribution patterns of the peaks at $m/z = 554$ and 570 are consistent with $\{\mathbf{1} + O - H\}^+$ and $\{\mathbf{1} + 2O - H\}^+$, respectively, and the reaction of **1** with isotope-enriched $^{18}O_2$ shows that the oxygen atoms are derived from O_2 ($m/z = 556$ and 574).[23] The m/z value of the monooxygenated product agrees with the formulation as an oxocyclooctenyl complex. An example of an oxocyclooctenyl complex with a different ancillary ligand was previously reported to form in the reaction of an Ir^I complex with H_2O_2 via an intermediate iridaoxetane.[24] In contrast, other Ir^I(cod) and Rh^I(cod) complexes that react with O_2 afford metallaoxetanes that rearrange to hydroxycyclooctenediyl complexes.[15]

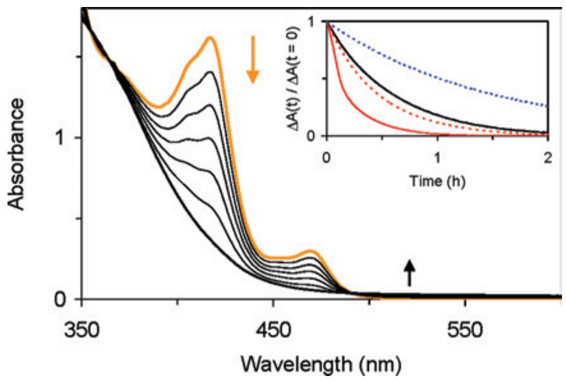

Figure 2. Reaction of 2 mM **1** (orange solid line) in toluene with O_2 at 0 °C as monitored by electronic absorption spectroscopy (path length, 0.5 cm). Inset: Time courses of the reactions of **1** (black solid line; λ, 417 nm), **2** (red dashed line; λ, 418 nm), **3** (red solid line; λ, 410 nm), and **4** (blue dashed line; λ, 423 nm) with O_2.

Interestingly, while complexes **2**−**4** reacted with O_2 similarly to **1**, the rates of the reactions varied with the substituents on the guanidinato ligand. Under the same conditions, the half-lives of the Ir^I complexes increase in the order **3** < **2** < **1** < **4** (Figure 2, inset; $t_{1/2} = 400$ s, 1100 s, 1300 s, and 1 h). Thus, both methyl substitution in the para position of the benzene rings (**3**) and extension of the alkyl substituents of the NR_2 group (**2**) have an accelerating effect on the O_2 reaction, whereas methyl groups in the ortho position of the benzene rings (**4**) have a decelerating effect. The higher reactivity of **2** and **3** compared to that of **1** can be explained by increased electron donation from the guanidinato ligand to the Ir^I center and consequent destabilization of the low oxidation state. In the case of **4**, the steric influences of the *o*-methyl groups appear to exceed their electronic influences and may be responsible for the slower rate. Clearly, the Ir^I centers in **1**−**3** are somewhat more exposed than that in **4**, and the methyl groups of the latter may limit access to the metal center (Figure S1 in the Supporting Information). It also may be possible that the differences in sterics lead to different reaction pathways.

In summary, we have prepared and characterized mononuclear complexes of a low-valent d-block metal center coordinated by bidentate guanidinato(1−) ligands and thus expanded the scope of this ligand platform in transition-metal chemistry. Spectroscopic evidence suggests that the *N*,*N*-dialkyl-*N′*,*N″*-diarylguanidinates employed here function as stronger donors than other monoanionic, nitrogen-based scaffolds, such as tris(pyrazolyl)borates-κ^2 and β-diketiminates, when bound to the Ir^I(cod) unit. While complexes **1**−**4** differ only in the methyl substitution pattern, the trends observed for the half-lives of their reactions with O_2 illustrate the potential that the guanidinato(1−) platform has to offer for facile modulation of the reactivity of transition-metal complexes.

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Supporting Information Available: Experimental procedures, characterization data of all compounds, details of the crystal structure determinations (Figure S1 and Tables S1−S4), and CIF files of **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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