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Synthesis and Reactivity of Zirconium Hydrazido Complexes Containing Aryloxide Ligation

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The reaction of $[(ArO)_2Zr(Me)_2]$ (ArO = 2,6-di-*tert*-butylphenoxide) with PhNHNHPh (1 equiv) leads to $[(ArO)_2Zr(Me)(\eta^2\text{-NPhNHPh})]$ (**1**) and 1 equiv of methane. Heating a C_6D_6 solution of **1** generates $[Zr\{OC_6H_3(Bu^t)C(CH_3)_2CH\}(OAr)(NPhNHPh)]$ (**2**) via cyclometalation of a *tert*-butyl group of the aryloxide ligand (^{1}H NMR). Addition of 4-pyrrollidinopyridine (>2 equiv, py′) to **1** results in the formation of the η^2-azobenzene complex $[(ArO)_2Zr(\eta^2\text{-}N_2Ph_2)(py')_2]$ (**3**) with the elimination of methane. Solutions of **3** in C_6D_6 slowly convert to the terminal imido complex $[(ArO)_2Zr({=}NPh)(py')_2]$ and free azobenzene. Reaction of **1** with organic isocyanides (1 equiv of RNC; R = Bu^t, 2,6-$Me_2C_6H_3$) produces a mixed hydrazido, iminoacyl complex $[(ArO)_2Zr(\eta^2\text{-NPhNHPh})(\eta^2\text{-MeCNR})]$, R = Bu^t (**4a**), 2,6-$Me_2C_6H_3$ (**4b**). Compound **4a** crystallizes in space group $P2_1/c$ with $a = 19.666(5)$ Å, $b = 12.166(3)$ Å, $c = 19139(3)$ Å, $\beta = 108.01(2)°$, and $Z = 4$. The solid state structure of **4a** shows both the hydrazido and iminoacyl groups to be η^2-bound to the metal with an PhN—NHPh distance of 1.47(2) Å and Bu^tN—CMe distance of 1.26(2) Å.

Introduction

The past few years have seen a renewed interest in the chemistry of early d-block metal complexes containing metal–nitrogen multiple bonds.[1–3] Some of these investigations have been prompted by the high reactivity demonstrated for the metal–imido functional group, as well as important catalytic and stoichiometric transformations in which metal amido complexes are implicated.[2,3] Transition metal hydrazido complexes have also received research attention mainly because they have been postulated as intermediates in the metal-mediated conversion of dinitrogen to ammonia.[4] Recent work by Bergman and co-workers has shown that η^2-bound hydrazido ligands can undergo a very rich cycloaddition reaction chemistry, through which new C–N bonds can be formed.[5]

To complement our work on the chemistry of group 4 metal–amido and –imido compounds,[6–9] we have investigated the reactivity of 1,2-diphenylhydrazine toward the bis(alkyl) complex $[(ArO)_2Zr(Me)_2]$ (ArO = 2,6-di-*tert*-butylphenoxide). Besides the synthesis of new hydrazido(1–) complexes, the work reported here demonstrates the stepwise fragmentation of hydrazine to eventually yield a phenyl imido complex of zirconium.[10]

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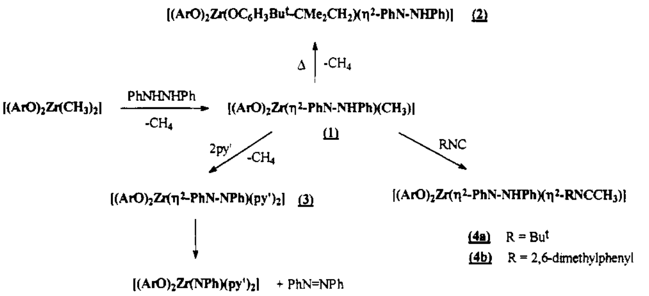
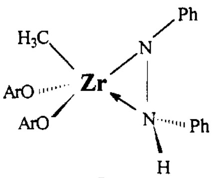
Scheme 1



Results and Discussion

The complex [(ArO)$_2$ZrMe$_2$] (ArO = 2,6-di-*tert*-butylphenoxide) reacts slowly with 1 equiv of 1,2-diphenylhydrazine in hydrocarbon solvents at ambient temperature to generate a new compound [(ArO)$_2$Zr(Me)(η^2-NPh-NHPh)] (1) with elimination of 1 equiv of methane (Scheme 1). Characterization of the product by NMR (^{1}H and ^{13}C) spectroscopy indicated that simple substitution of one methyl group by a hydrazido(1−), [NPh-NHPh], ligand had taken place. In the ^{1}H NMR spectrum of 1, two sets of aryloxide resonances were observed, indicating the presence of two nonequivalent ArO ligands. The hydrazido proton (ZrNPhN*H*Ph) was found to resonate as a sharp singlet at δ 6.35 ppm, considerably downfield of the δ 4.65 ppm found for 1,2-diphenylhydrazine. This downfield chemical shift combined with the observation of nonequivalent aryloxide ligands indicates that the hydrazido ligand is η^2-bound to the metal. Facile rotation of the hydrazido ligand will not result in the aryloxide ligands becoming equivalent. This can only happen if dissociation and inversion of the NHPh nitrogen atom occurs (see I). An absorption band at 3254 cm^{-1} in the infrared spectrum of 1 was assigned to the $\bar{\nu}$(NH) stretch vibration of the remaining NH group.



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The addition of a second equivalent of 1,2-diphenylhydrazine to 1 showed no reaction at room temperature, but heating the mixture (110 °C, minutes) resulted in the formation of aniline and azobenzene. Over a further period of time the generated aniline reacted with 1, forming the bis(amido) complex [(ArO)$_2$Zr(NHPh)$_2$],[9] eliminating PhNHNHPh and methane. The formation of this bis(amido) complex precludes further disproportionation of 1,2-diphenylhydrazine.

On the basis of the reported chemistry of the zirconocene complexes [Cp$_2$Zr(Me)(NHPhNPh)],[5] thermolysis of [(ArO)$_2$Zr(Me)(η^2-NHPhNPh)] (1) was expected to yield an η^2-azobenzene derivative and 1 equiv of methane. However, heating at 90 °C a C$_6$D$_6$ solution of 1 showed (^{1}H NMR) cyclometalation of an aryloxide—*tert*-butyl group leading to a new complex (2) (Scheme 1). The collapse of the methyl peak (Zr–Me) was accompanied by the appearance of an AB pattern (δ 3.70 and 3.95 ppm), and a number of new aliphatic resonances, consistent with the presence of a cyclometalated 2,6-di-*tert*-butylphenoxide ligand.[11] The addition of 4-pyrrolidinopyridine (py′; ≥2 equiv) to 1 led to highly colored solutions from which a bright red precipitate (3) was isolated. This product was not thoroughly characterized. We propose it to be the η^2-azobenzene complex [(ArO)$_2$Zr(η^2-PhNNPh)(py′)$_2$] (3) on the basis of its ^{1}H NMR spectrum which is very similar to a titanium analog.[8a] Complex 3 proved to be thermally unstable and decomposed in solution over a few hours at 25 °C with formation of a new zirconium complex along with free azobenzene (Scheme 1). The zirconium compound was determined to be the previously reported terminal imido complex [(ArO)$_2$Zr═NPh(py′)$_2$],[9] from its highly characteristic ^{1}H NMR spectrum.[8] The formation of a metal—imido compound by cleavage of the N—N bond of an η^2-azobenzene ligand was previously observed for the titanium complex [(Ar′O)$_2$Ti(η^2-PhNNPh)(py′)$_2$] (Ar′O = 2,6-diisopropylphenoxide).[6b,12]

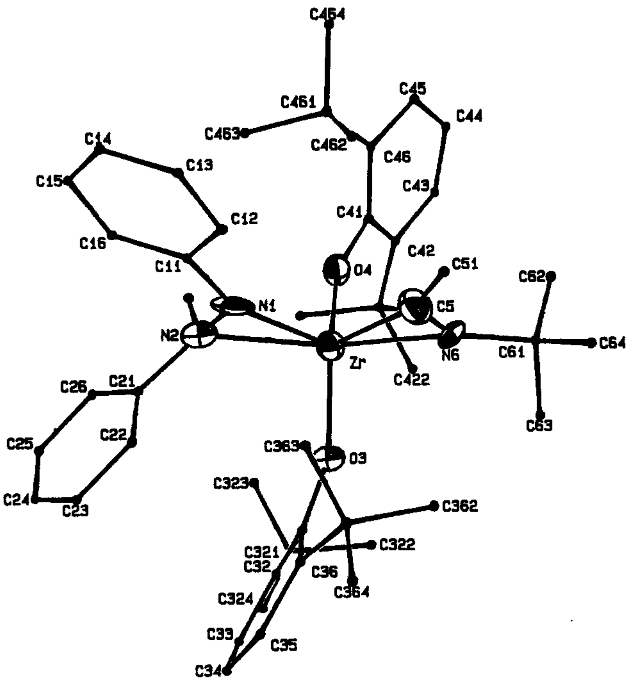

Figure 1. ORTEP view of [Zr(OAr)$_2$(η^2-NPhNHPh)(η^2-Bu^t-CNCH$_3$] (4a).

Addition of 1 equiv of organic isocyanides RNC to solutions of 1 led to the formation of the η^2-iminoacyl derivatives [(ArO)$_2$Zr(η^2-RNCMe)(η^2-NPhNHPh)] (R = Bu^t, **4a**; R = 2,6-dimethylphenyl, xy, **4b**) by migratory insertion of the isocyanide into the Zr–C(methyl) bond of 1 (Scheme 1). Two nonequivalent aryloxide ligands are observed in the ^{1}H NMR spectra of **4a** and **4b** while the η^2-CN binding of the iminoacyl ligand is indicated ligand is indicated by the downfield resonance of the η^2-RNCMe carbon at δ 238.0 ppm (**4a**) and 247.1 ppm (**4b**).[13] Crystals of 4a suitable for an X-ray diffraction study were grown from a concentrated hexane solution at ambient temperature. The results of this analysis confirmed the η^2-binding of both the iminoacyl and hydrazido ligands in the solid state.

Solid State Structure of [(ArO)$_2$Zr(η^2-Bu^{t}NCMe)(η^2-NPhNHPh)] (4a). An ORTEP view of the complex [(ArO)$_2$Zr(η^2-Bu^{t}NCMe)(η^2-NPhNHPh)] (**4a**) is shown in Figure 1, while Figure 2 shows a view of the central coordination sphere. Some pertinent bond distances and angles are collected in Table 1. Although formally six-coordinate, this molecule can be best described as distorted tetrahedral with both η^2-bound ligands occupying single coordination sites. In this respect compound **4a** is related

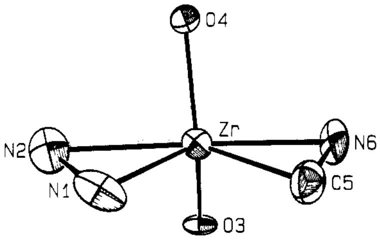

Figure 2. ORTEP view of the central coordination sphere of (**4a**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4a

Zr–O(3)	2.004(8)	Zr–C(5)	2.18(1)
Zr–O(4)	2.015(9)	N(1)–N(2)	1.47(2)
Zr–N(1)	2.08(1)	N(2)–H(2)	0.77(7)
Zr–N(2)	2.36(1)	N(6)–C(5)	1.26(2)
Zr–N(6)	2.19(1)		
O(3)–Zr–O(4)	142.4(3)	Zr–O(3)–C(31)	160.6(7)
O(3)–Zr–N(1)	104.0(4)	Zr–O(4)–C(41)	155.6(7)
O(3)–Zr–N(2)	94.5(4)	Zr–N(2)–H(2)	133(6)
O(3)–Zr–N(6)	94.0(4)	Zr–N(6)–C(5)	72.7(8)
O(3)–Zr–C(5)	102.5(5)	Zr–C(5)–C(51)	155(1)
N(1)–Zr–C(5)	96.1(5)	Zr–N(6)–C(61)	153(1)
N(2)–Zr–N(6)	166.7(5)		

to the series of bis(η^2-iminoaryl) compounds [$(ArO)_2M(\eta^2\text{-}RNCR')_2$] (M = Ti, Zr, Hf).[14,15] However, structural studies of the bis(η^2-iminoacyl) complexes show them to adopt a structure in which the CN units of the iminoacyl groups are arranged in a head to tail fashion parallel with each other.[14] In contrast the solid state structure of **4a** (Figure 1) shows the η^2-iminoacyl and η^2-hydrazido(1–) ligands to be nearly coplanar with each other with the iminoacyl carbon adjacent to the amido nitrogen of the NPhNHPh ligand. The Zr–C(5) and Zr–N(6) distances of 2.18(1) and 2.19(1) Å are both slightly shorter than those reported for the bis(η^2-iminoacyl) compound [$(ArO)_2Zr(\eta^2\text{-}Bu^tNCCH_2Ph)_2$],[14] cf. corresponding distances of 2.228(3) and 2.221(3) Å. The Zr–N(1) distance of 2.08(1) Å is slightly longer than typical for dialkylamido ligands bound to Zr(IV),[14] whereas the Zr–N(2) distance of 2.36(1) Å is very similar to Zr–N(pyridine) distances, i.e. is representative of a dative bond.[13-16] The C–N distance of 1.26(2) Å is typical of η^2-iminoacyl groups[13] while the N(1)–N(2) distance of 1.47(2) Å is as expected for a nitrogen–nitrogen single bond. The bonding parameters for the aryloxide ligands are unexceptional.[17]

Table 2. Crystal Structure Determination Data for 4a

formula	$ZrO_2N_3C_{46}H_{65}$
fw	783.27
space group	$P2_1/c$ (No. 14)
a, Å	19.666(5)
b, Å	12.166(3)
c, Å	19.139(3)
β, deg	108.01(2)
Z	4
V, Å^3	4354(3)
d(calcd), c/cm^3	1.195
cryst size, mm	0.40 × 0.38 × 0.31
cryst color	colorless
temp, °C	20
monochromator	graphite
rad wavelength (λ, Å)	Mo Kα (0.710 73)
linear abs coeff, cm^{-1}	1.83
abs correction	empirical[20]
trans factors: min, max	0.56, 1.00
diffractometer	Enraf-Nonius CAD4
scan method	ω–2θ
takeoff angle, deg	2.95
scan rate, deg/min	2–16
2θ range, deg	4.00–45.00
no. of unique data	5986
no. of data with $F_0 > 3.00\sigma(I)$	2237
no. of variables	248
$R(F)$	0.071
$R_w(F)$	0.075
weighting factor (ρ)	0.040
goodness of fit	1.651
largest Δ/σ	0.00

Experimental Section

All operations were carried out under a dry nitrogen atmosphere using a Vacuum Atmospheres glovebox or standard Schlenk techniques. The compounds 1,2-diphenylhydrazine and 4-pyrrolidinopyridine were purchased from Aldrich and purified by vacuum sublimation. The organic isocyanides were obtained from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded either on a Varian Associates Gemini-200 spectrometer or a General Electric QE-300 spectrometer. In all cases chemical shifts were reported in units of parts per million referenced against TMS. Microanalysis and crystallographic studies were carried out in-house at the Purdue University Chemistry Department.

Synthesis of [(2,6-ArO)$_2$Zr(Me)(η^2-NPhNHPh)] (1). To a benzene solution containing 1.57 g (2.95 mmol) of [$(ArO)_2Zr(Me)_2$], (ArO = 2,6-di-*tert*-butylphenoxide) was added 1 equiv (0.54 g) of 1,2-diphenylhydrazine. Stirring of the reaction mixture was continued for 12 h before removal of the solvent under vacuum. Purification by recrystallization from a toluene/hexane mixture resulted in 0.85 g of crystalline product (42% based upon Zr). Anal. Calcd for $C_{41}H_{56}N_2O_2Zr$: C, 70.34; H, 8.06; N, 4.00. Found: C, 70.67; H, 8.44; N, 3.62. ^{1}H NMR (C_6D_6, 30 °C): δ 0.78 (s, Zr*Me*), 1.46 (s), 1.50 (s, *Bu*^{t}), 6.35 (s, NPhN*H*Ph), 6.8–7.4 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 31.6, 31.7 (CMe$_3$), 35.4 (CMe$_3$), 46.4 (ZrMe), 161.9, 162.2 (*ipso*-OAr). IR spectrum (Nujol mull): $\bar{\nu}$(NH) = 3254 cm^{-1} (w).

Synthesis of [(ArO)$_2$Zr(η^2-Bu^{t}NCMe)(η^2-NPhNHPh)] (4a). To a benzene solution of 1.36 g (1.97 mmol) of [$(2,6\text{-}Bu^t_2C_6H_3O)_2Zr(Me)(\eta^2\text{-}NPhNHPh)$] (1) was slowly added 1 equiv (0.16 g) of *tert*-butyl isocyanide. The resulting mixture was stirred for 1 h before the solvent was removed under vacuum. Recrystallization of the resulting crude product from hexane gave orange crystals in modest yields (*ca.* 40% based on Zr). Anal. Calcd for $C_{46}H_{65}O_2N_3Zr$: C, 70.54; H, 8.36; N, 5.36. Found: C, 70.62; H, 8.70; N, 5.13. ^{1}H NMR (C_6D_6, 30 °C): δ 1.09 (s, *Bu*^{t}NC), 1.40 (s), 1.45 (OAr–*Bu*^{t}), 2.71 (s, Bu^{t}NC*Me*), 5.90 (s, NPhN*H*Ph), 6.5–7.4 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 24.0 (Bu^{t}NC*Me*), 29.9 (*Me*$_3$CNCMe), 62.3 (Me$_3$*C*NCMe), 32.2, 32.6 (OAr–C*Me*$_3$), 36.0 (OAr, *C*Me$_3$), 162.6, 163.0 (Zr–O–*C*), 236.0 (Bu^{t}N*C*Me). IR spectrum (Nujol mull): ν(NH) = 3250 cm^{-1} (w), ν(CN) = 1582 cm^{-1} (w).

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Synthesis of [$(ArO)_2Zr(\eta^2$-xyNCMe)(η^2-NPhNHPh)] (4b). The same general procedure used for **4a** except using 2,6-dimethylphenyl isocyanide (xync) yielded complex **4b**. ^{1}H NMR (C_6D_6, 30 °C): δ 1.56 (s, *Me*$_2$), 1.43 (s), 1.48 (s) (*Bu*^{t}), 2.32 (s, xyNC*Me*), 6.45 (s, NPhN*H*Ph), 6.55–7.35 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 20.4 (xyNC*Me*), 19.9 (Me$_2$), 32.4, 32.6 (C*Me*$_3$), 34.8 (Bu^t, CMe$_3$), 162.5, 162.8 (Zr–O–*C*), 247.1 (xyN*C*Me). IR spectrum (Nujol mull): ν(NH) = 3260 cm^{-1} (w).

Selected Spectroscopic Data. The following compounds were identified in solution by their ^{1}H NMR spectra (C_6D_6, 30 °C): [(ArO)Zr($OC_6H_3Bu^tCMe_2CH_2$)(η^2-NPhNHPh)] (**2**) [δ 1.38 (s), 1.40 (s), 1.47 (s, *Bu*^{t}); 1.50 (s), 1.57 (s, *Me*); 3.70 (d), 3.95 (d) (Zr=CH$_2$, ^2J = 14.4 Hz); 6.35 (s, NPhN*H*Ph), 6.50–7.40 (m, aromatic–protons); [$(ArO)_2Zr(\eta^2$-PhNNPh)(py′)$_2$] (**3**) [δ 1.63 (s, *Bu*^{t}), 8.80 (d, *ortho* protons of py′), 5.50 (d, *meta* protons of py′), 7.50 (dd, *ortho* protons of η^2-azobenzene)].

X-ray Crystal Structure Analysis of 4a. Crystal data and data collection parameters are given in Table 2. Further details of the structure determination are given in the supplementary material.

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Supplementary Material Available: Textual presentation of experimental details and tables of crystal data, atom positions, anisotropic thermal parameters, bond angles and distances, and atomic multiplicities for **4a** (25 pages). Ordering information is given on any current masthead page.

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