room-temperature ^{13}C NMR spectrum, at the fast-exchange limit, exhibits $^{3}J_{O^{13}C-Rh-O-^{119}Sn}$ (see Figure 3), consistent with an *intra*-molecular dynamic rearrangement process. Studies to distinguish between an associative (five-coordinate rhodium) or dissociative (three-coordinate rhodium) intramolecular exchange mechanism are in progress.

The thermogravimetric analysis of **3** under nitrogen shows an onset of weight loss at approximately 160 °C, which is complete by approximately 200 °C and corresponds to a 55% loss in weight. X-ray powder diffraction data taken after the residual black powder is heated to 325 °C indicate the presence of crystalline Rh together with material that either is amorphous or has a small particle size. After the sample is heated to 1039 °C, the only crystalline phases observed are Rh and SnO_2 (cassiterite) (see supplementary material). The weight loss observed at 200 °C corresponds to loss of the organic fragments, but we note that the surface area of this powder is extremely low (4 m^2/g, as determined by nitrogen adsorption).[13] In comparison, thermogravimetric analysis of $[Sn(OEt)_4]_n$ reveals that, although the onset of weight loss is at approximately the same temperature as **3** (160 °C), weight loss is not complete until ~300 °C.[14] When the thermal decomposition (300 °C) of **3** was conducted on a larger scale, ethanol, 1,3-cyclooctadiene, 1,5-cyclooctadiene, and *cis*-cyclooctene were isolated as the major condensable volatile byproducts,[15] together with minor products such as acetaldehyde. Previously, the thermal decomposition of metal alkoxides has generally resulted in the formation of alcohol and alkene.[16] Further studies to determine the mechanism of decomposition of **3** and its derivatives and the catalytic activity of **3** and **4** dispersed on high surface area supports are in progress.[17]

Acknowledgment. We thank the UNM/NSF Center for Micro-Engineered Ceramics and Sandia National Laboratories for supporting this work, Dr. Dan Doughty of Sandia National Laboratories for helpful discussions, Eva Quesnell for typing the manuscript, the NSF Chemical Instrumentation Program for the purchase of an NMR spectrometer, the Johnson-Matthey Precious Metals loan program for generous support, and Greg Johnson for measuring the surface area.

Supplementary Material Available: Single-crystal X-ray diffraction data for **1** [Table S1 (atomic coordinates and thermal parameters), Tables S2 and S3 (bond lengths and angles), Tables S4 and S5 (anisotropic thermal parameters and H atom coordinates)], thermogravimetric analysis of **3** (Figure S1), X-ray powder diffraction data for **3** heated to 325 °C (Figure S2) and 1000 °C (Figure S3), ^{1}H NMR spectrum of byproducts trapped at −196 °C from pyrolysis of **3** at 300 °C (Figure S4), and ^{1}H and ^{13}C NMR spectra of fractionated volatile byproducts (Figures S5 and S6) (12 pages); observed and calculated structure factors (Table S6) (29 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Five-Coordinate Aryl–Imido Derivatives of Zirconium(IV)

The last few years have seen a dramatic increase of interest in the structure, bonding, and reactivity of terminal imido compounds of the transition metals.[1-5] Particular attention has recently been focused upon the chemistry of the group 4 metal–imido bond.[6-8] The work of Bergman et al.[6] and Wolczanski et al.[7] has shown that alkyl- or silylimido derivatives of zirconium are very reactive, even being able to activate carbon–hydrogen bonds. We wish to communicate here our isolation and characterization of five coordinate, terminal arylimido derivatives of zirconium and to also comment upon the bonding in these molecules.

The tetrabenzyl compound $Zr(CH_2Ph)_4$ reacts with 2,6-diisopropylaniline ($H_2NC_6H_3Pr^{i}_{2}$-2,6; ≥4 equiv) in benzene solution to produce the yellow, homoleptic arylamido complex [$Zr(NHC_6H_3Pr^{i}_{2}$-2,6$)_4$] (**1**) in high yield.[9] Crystals of **1** can be obtained from hexane solution. Upon addition of 4-pyrrolidinopyridine (py′; ≥2 equiv) to hydrocarbon solutions of **1**, elimination of 1 equiv of $H_2NC_6H_3Pr^{i}_{2}$-2,6 takes place with formation of the arylimido complex [$Zr(NC_6H_3Pr^{i}_{2}$-2,6$)(NHC_6H_3Pr^{i}_{2}$-2,6$)_2(py')_2$] (**2**) (Scheme I).[10] The ^{1}H NMR spectrum of **2** in C_6D_6 shows two sharp sets of isopropyl resonances in the ratio 2:1. Hence, rapid proton transfer between amido and imido nitrogen atoms is not taking place in solution.

A simple phenylimido derivative of zirconium can be obtained by initial reaction of the compound [$Zr(OC_6H_3Bu^{t}_{2}$-2,6$)_2(CH_3)_2$] with aniline followed by addition of 4-pyrrolidinopyridine (Scheme I). The intermediate bis(phenylamido) complex [$Zr(OC_6H_3Bu^{t}_{2}$-2,6$)_2(NHPh)_2$] (**3**)[11] has also been isolated prior to its conversion to the phenylimido complex [$Zr(NPh)(OC_6H_3Bu^{t}_{2}$-2,6$)_2(py')_2$] (**4**).[12]

Both of the arylimido compounds **2** and **4** have been structurally characterized (Figures 1 and 2).[13] The molecular structures of

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(9) Anal. Calcd for $ZrN_4C_{48}H_{72}$ (**1**): C, 72.40; H, 9.11; N, 7.04. Found: C, 72.07; H, 9.45; N, 7.40. ^{1}H NMR (C_6D_6, 30 °C): δ 6.98 (s, Zr–N*H*); 3.26 (septet, C*H*Me_2), 1.18 (d, CHMe_2).

(10) Anal. Calcd for $ZrC_{54}H_{77}N_7$ (**2**): C, 70.85; H, 8.48; N, 10.71. Found: C, 70.43; H, 8.58; N, 10.30. ^{1}H NMR (C_6D_6, 30 °C): δ 6.90 (s, Zr–N*H*); 3.92 (septet, imido C*H*Me_2), 3.77 (septet, amido C*H*Me_2), 1.29 (d, imido CHMe_2), 1.43 (d, amido CHMe_2), 8.87 (d, 2,6-H py′), 5.62 (d, 3,5-H py′), 2.32 (m, α-CH_2–py′), 1.07 (m, β-CH_2–py′).

(11) Anal. Calcd for $ZrN_2O_2C_{40}H_{54}$, (**3**): C, 70.02; H, 7.93; N, 4.08. Found: C, 68.96; H, 8.40; N, 3.86. ^{1}H NMR (C_6D_6, 30 °C): δ 7.33 (s, Zr–N*H*Ph), 1.44 (s, *Bu*^{t}), 6.6–7.2 (m, aromatics).

(12) Anal. Calcd for $ZrN_5O_2C_{52}H_{71}$ (**4**): C, 70.22; H, 8.05; N, 7.87. Found: C, 70.26; H, 8.47; N, 7.48. ^{1}H (C_6D_6, 30 °C): δ 1.38 (s, *Bu*^{t}), 8.33 (d, 2,6-H py′), 5.02 (d, 3,5-H py′), 1.80 (m, α-CH_2–py′), 0.65 (m, β-CH_2–py′), 6.5–7.3 (m, aromatics).

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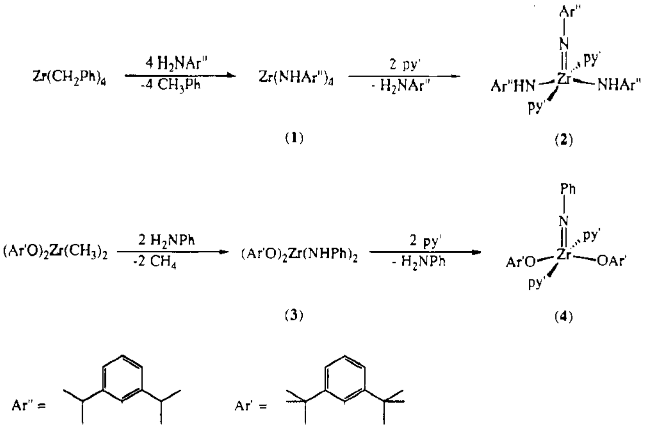
Scheme I



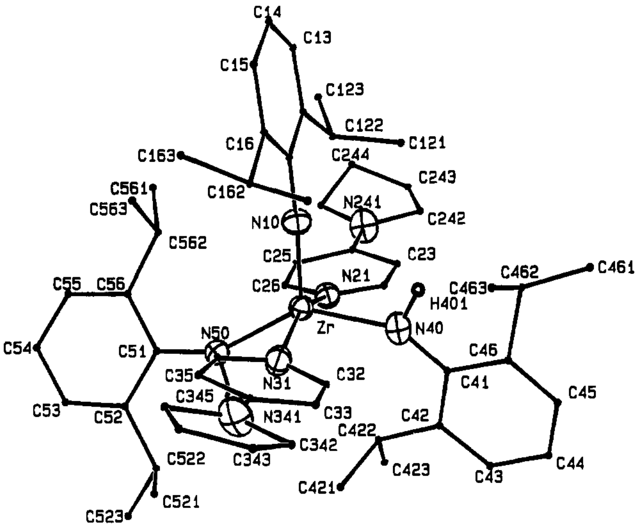


Figure 1. ORTEP view of **2**. Selected bond distances (Å) and angles (deg): Zr–N(10) = 1.868 (3); Zr–N(21) = 2.358 (3); Zr–N(31) = 2.381 (3); Zr–N(40) = 2.134 (4); Zr–N(50) = 2.150 (3); N(10)–Zr–N(21) = 99.6 (1); N(10)–Zr–N(31) = 100.4 (1); N(10)–Zr–N(40) = 100.9 (1); N(10)–Zr–N(50) = 117.7 (1); Zr–N(10)–C(11) = 174.9 (3); Zr–N(40)–C(41) = 148.0 (3); Zr–N(50)–C(51) = 152.5 (3).

2 and **4** can be seen to be closely related, and best described as distorted square-pyramidal with an axial arylimido function. In both strucures the py' ligands are mutually trans with py'–Zr–py' angles of 160.0 (1) and 160.1 (3)°. In the imido, amido compound (**2**) the (imido)N–Ar–N(amido) angles are 100.9 (1) and 117.7 (1)°, while in **4** the corresponding angles to the aryloxide oxygen atoms are 106.1 (3) and 108.4 (3)°. The metal–ligand bond distances in these compounds are worthy of special comment. Compound **2** allows a comparison of zirconium bonding to amine (pyridine), amido, and imido nitrogen ligands within the same molecule. A contraction of 0.5 Å in bond lengths is observed on moving from the neutral donor pyridine to the formally diionic imido group. By far the most interesting parameters in these two compounds are the zirconium–imido bond lengths of 1.868 (3) and 1.844 (9) Å for **2** and **4**, respectively. The only previously reported alkylimido derivative of zirconium, $Cp_2Zr(NBu^t)(thf)$[6], was found to have a Zr–N bond distance of 1.826 (4) Å. This "long"[6] distance was ascribed to the electronic saturation present in the metallocene compound. However, the Zr–N(imido) distances in **2** and **4** are even longer. One possible explanation for these long bonds would argue that the molecular geometry of these five-coordinate compounds precludes the full formation of the two π-bonds between the metal and the imido nitrogen. A simple analysis of an idealized square-pyramidal geometry with an axial imido group coincident with the z axis would involve the two π-bonds being formed by overlap of the empty metal d_{xz} and d_{yz} atomic orbitals with the filled imido nitrogen p_x and p_y orbitals. The two trans amido groups in **2** have the potential for π-donation into one of these atomic orbitals on the metal, thus competing with π-donation from the imido nitrogen. However, the arylamido groups in **2** are both oriented coplanar with the Zr–N(imido) bond, hence precluding π-donation into the metal d_{xz} orbital. An EHMO calculation on the idealized molecule $[Zr(NH)(NH_2)_2(NH_3)_2]$ using the structural parameters of **2** shows that the molecular geometry of **2** does not preclude the formation of two π-bonds to the imido nitrogen atom.[14] The Zr–NPh distance in **4** can be compared with the Ti–NPh distance of 1.719 (3) Å found for the structurally similar titanium imido complex $[Ti(NPh)(OC_6H_3Pr^i{}_2\text{-}2,6)_2(py')_2]$.[8b] The increase in M–NPh distances on moving from titanium to zirconium is comparable in magnitude to increases seen on moving from first- to second-row elements for group 5–7 metal imido and oxo compounds.[1] Hence it would appear that the distances observed for these terminal arylimido derivatives of zirconium are not unusual. Clearly a larger database of compounds will be needed before definitive conclusions can be made.[16]

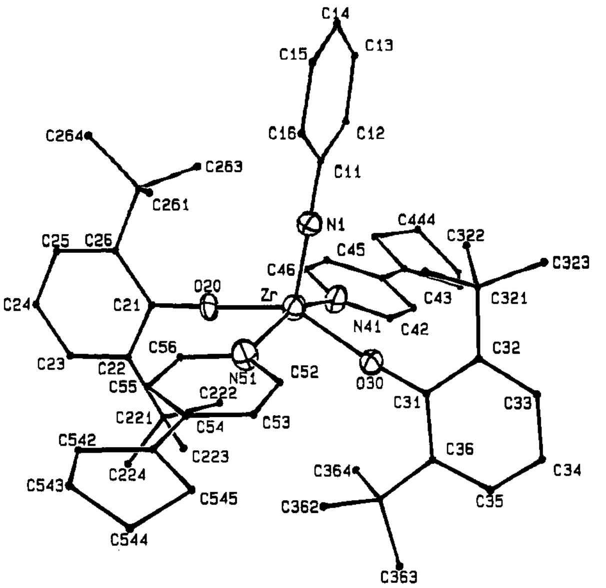


Figure 2. ORTEP view of **4**. Selected bond distances (Å) and angles (deg): Zr–N(1) = 1.844 (9); Zr–O(20) = 2.030 (6); Zr–O(30) = 2.047 (7); Zr–N(41) = 2.359 (9); Zr–N(51) = 2.366 (9); N(1)–Zr–N(41) = 97.1 (4); N(1)–Zr–N(51) = 102.8 (4); N(1)–Zr–O(20) = 106.1 (3); N(1)–Zr–O(30) = 108.4 (3); Zr–N(1)–C(11) = 175.5 (8); Zr–O(20)–C(21) = 173.7 (7); Zr–O(30)–C(31) = 174.4 (7).

Unlike previously reported terminal imido derivatives of zirconium, compounds **2** and **4** exhibit little reactivity. Thermolysis of the phenylimido complex (**4**) does not lead to cyclometalation of the 2,6-di-*tert*-butylphenoxide ligands[15] while no H/D exchange

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(13) Crystals of both **2** and **4** obtained from toluene solution contained three molecules of toluene per zirconium. Hence, samples for crystallography were handled under a mother liquor of toluene. Drying of the samples under vacuum results in complete (**2**) or partial (**4**) loss of solvent from the crystals. Crystal data at −102 °C for $ZrN_7C_{75}H_{101}$ (**2**): $a = 13.473$ (4) Å, $b = 14.445$ (3) Å, $c = 17.981$ (3) Å, $\alpha = 82.78$ (1), $\beta = 76.59$ (2), $\gamma = 87.51$ (2)°, $Z = 2$, $d_{calcd} = 1.172$ g cm^{-3} in space group $P\bar{1}$. Of the 8835 unique data collected, $4.0° \le 2\theta \le 45°$, the 6536 data with $I > 3.0\sigma(I)$ were used in the final refinement to yield $R = 0.066$, $R_w = 0.082$. Data for $ZrO_2N_5C_{73}H_{95}$ (**4**) at −64 °C: $a = 25.101$ (1) Å, $b = 10.145$ (2) Å, $c = 25.721$ (2) Å, $Z = 4$, $d_{calcd} = 1.182$ g cm^{-3} in space group $Pna2_1$. Of the 4799 unique data collected, the 2691 data with $I > 3.0\sigma(I)$ were used in the final refinement to yield R = 0.053, $R_w = 0.061$.

(14) The five-coordinate organoimido compounds $Nb(OC_6H_3Ph_2\text{-}2,6)_3({=}NMe)(HNMe_2)$, 1.720 (5) Å, and $W({=}NPh)(NMe_2)_4$, 1.758 (5) Å do not have excessively long metal–N (imido) distances; see: (a) Chesnut, R. W.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1988**, *24*, 752. (b) Berg, D. M.; Sharp, P. R. *Inorg. Chem.* **1987**, *26*, 2959.

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(16) The zirconium–imido complex $[(Bu^t{}_3SiNH)_2Zr(NS{:}Bu^t{}_3)(thf)]$ was a Zr–N(imido) distance of 1.974 (6) Å: Wolczanski, P. T., personal communication.

is observed between the amido NH bonds of **2** and C_6D_6 after days at 100 °C in a sealed tube. Both five-coordinate arylimido compounds do not react with 3-hexyne.[6]

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Supplementary Material Available: Description of the experimental procedure for the X-ray structural determination and tables of crystallographic data, positional parameters and isotropic thermal parameters, anisotropic thermal parameters, complete bond distances, and complete bond angles for **2** and **4** (57 pages); tables of structure factors for **2** and **4** (40 pages). Ordering information is given on any current masthead page.

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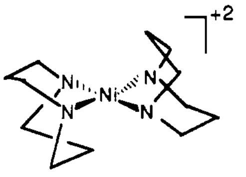
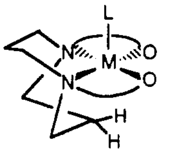
Sterically Protected Nickel(II) in a N_2S_2 Donor Environment: 1,5-Bis(mercaptoethyl)-1,5-diazacyclooctane and Its Methylated Derivative

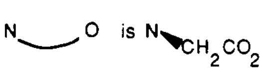
The macrocyclic diazacyclooctane ligand, DACO,[1] offers several attractive features as a framework for ligand development: an exceptionally strong ligand field, unique conformational requirements (aptly demonstrated in the $(DACO)_2Ni^{II}$ complex ion),[2a,b] and the potential for further functionalization. Such functionalization led to the synthesis of 1,5-diazacyclooctane-1,5-diacetato, DACODA, derivatives of Co and Ni for which the chair/boat configurations of the Ni–N($CH_2CH_2CH_2$)N rings resulted in the first recognized examples of agostic C–H interactions in classical coordination complexes.[3,4] In the case of M = Co, a unique heterolytic C–H bond cleavage followed the oxidation of Co(II) to Co(III).[4]



(DACO)$_2$ Ni(II) [2a,b]

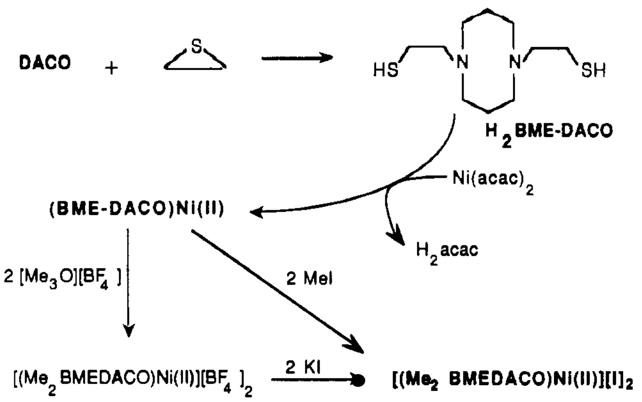


(DACODA)M(II) [3,4]



This interesting chemistry prompted our investigation of DACO modified with sulfur ligation sites for the following purposes: such donor environments for Ni^{2+} are expected to be important as prototypes for the active site in nickel-containing hydrogenases,[5] the ligand field and presumably the redox properties of Ni may be systematically tuned by variation of additional axial ligand(s), and, on the basis of precedents from organometallic chemistry[6] and recent similar bioinorganic model chemistry,[7] we reason that the flap-over ring could provide a sterically protected metal coordination site capable of supporting interactions of small molecules, such as H_2 or CO_2, or a highly reactive metal hydride functionality. (Although there are no known biomolecules containing metal hydrides, there are growing allegations of their feasibility as intermediates in reaction pathways,[7-10] and examples of well-characterized "organometallic" nickel hydrides are legend.)[11] The synthesis of 1,5-bis(mercaptoethyl)-1,5-diazacyclooctane, BME-DACO, and the complexes (BME-DACO)Ni^{II} and $[Me_2BME\text{-}DACONi][I]_2$ is reported herein. The latter is the first reported structure of the well-studied sulfur alkylation of Busch-type N_2S_2 complexes[12] and answers an old question of whether the thioether produced is Ni-coordinated.

Scheme I



The BME-DACO ligand is obtained as its thiol (Scheme I), via reaction of diazacyclooctane[13] with ethylene sulfide,[14] and used in situ. Addition of 1:1 equiv of the thiol to nickel acetylacetonate yields a yellow-brown toluene solution from which a purple powder (40–60% yield based on DACO) precipitates on standing overnight. The complex is readily soluble in water, acetonitrile, and methanol and less so in THF and acetone, in all yielding purple, air-stable solutions. Crystalline material, formulated as $Ni(C_{10}H_{20}N_2S_2)$ according to elemental analysis,[15a] is produced on layering pentane over an acetone solution of (BME-DACO)Ni^{II}. Diamagnetism is inferred from sharp resonances in the complex ^1H NMR spectrum, which differ substantially from that of the free ligand.[16] Broad bands of λ_{max} = 602, 500, and 346 nm (sh

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(15) Elemental analysis (Galbraith Laboratories): (a) Calcd for $NiN_2S_2C_{10}H_{20}$ (found): C, 41.3 (40.8); H, 6.92 (6.90); N, 9.62 (9.42). (b) Calcd for $NiN_2S_2C_{12}H_{26}I_2$ (found): C, 25.1 (24.9); H, 4.56 (4.66); N, 4.87 (4.90). (c) Calcd for $NiN_2S_2C_{12}H_{26}Br_2$ (found): C, 31.7 (31.7); H, 5.32 (5.56); N, 5.68 (5.67).

(16) ^1H NMR (CD_3OD), δ (ppm): 3.23, m (4 H); 3.13, m (2 H); 2.62, t (3 H); 2.51, m (4 H); 2.08, m (2 H); 1.82, m (4 H).

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