

In conclusion, we report the isolation of the unusual RTE^- anion where R is thienyl, which may be the first member of a large class of stable anions. This can be used to prepare a new silver telluride cluster $[\text{Ag}_4(\text{TeR})_6]^{2-}$, which is only the second homoleptic metal organotelluride structurally characterized.

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Supplementary Material Available: Complete listings of crystallographic information, atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for compounds I and II, another view of molecule II, and a complete description of the disorder problem in molecules I and II and the attempts made to resolve it (14 pages); listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

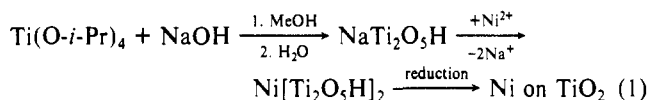
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Synthesis and Characterization of the Mixed-Metal Alkoxides $[\text{((L}_2\text{)Rh)}_2\text{Sn(OEt)}_6]$, Where $\text{L}_2 = 1,5\text{-Cyclooctadiene (COD) (3) and (CO)}_2\text{ (4)}$, and the Conversion of 3 to Rh and SnO₂ under Mild Conditions

There has been growing interest in the marriage of classical organometallic and inorganic chemistry for the synthesis of soluble molecular species as models for late-transition-metal catalysts on metal oxide supports.¹ In one approach, a variety of polyoxo-anion-supported organometallic fragments have been prepared.² However, less attention has been directed toward the design of new chemical routes for the preparation of supported catalysts themselves.³ An example of the existing routes to these catalysts is given as follows:^{3a}



As part of our strategy to prepare new mixed-metal alkoxide compounds⁴ containing a catalytically important transition metal,

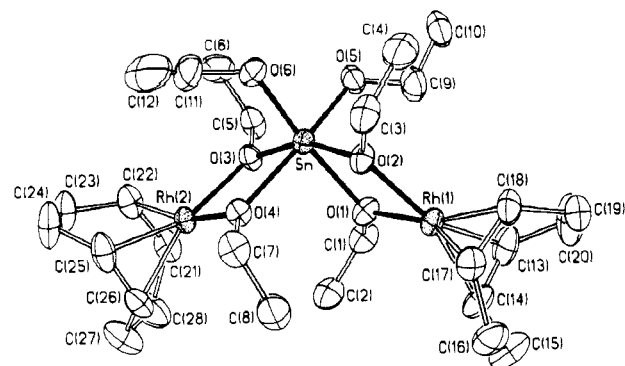
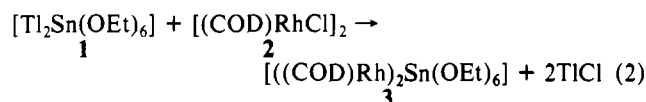


Figure 1. ORTEP plot of $[\text{((COD)Rh)}_2\text{Sn(OEt)}_6]$, showing the atom-numbering scheme. Relevant bond distances (\AA): Rh(1)-O(1) = 2.059 (4), Rh(1)-O(2) = 2.082 (4), Rh(2)-O(3) = 2.063 (5), Rh(2)-O(4) = 2.065 (4), Sn-O(1) = 2.098 (3), Sn-O(2) = 2.075, Sn-O(3) = 2.082 (4), Sn-O(4) = 2.103 (4), Sn-O(5) = 1.979 (5), Sn-O(6) = 1.980 (4), Rh(1)-C = 2.080 (6) (average), Rh(2)-C = 2.078 (average). Relevant bond angles (deg): O(1)-Rh-O(2) = 74.4 (1), O(3)-Rh(2)-O(4) = 74.6 (2), O(1)-Sn-O(2) = 73.7 (1), O(3)-Sn-O(4) = 73.4 (2), O(5)-Sn-O(6) = 90.4 (2).

we report here the synthesis and characterization of the new rhodium-tin alkoxide compounds $[\text{(L}_2\text{(Rh))}_2\text{Sn(OEt)}_6]$, where $\text{L}_2 = 1,5\text{-cyclooctadiene (3) and (CO)}_2\text{ (4)}$, and the conversion of 3 to Rh and SnO₂.

The addition of 1 equiv of (cyclooctadiene)rhodium(I) chloride dimer⁵ to $[\text{Ti}_2\text{Sn(OEt)}_6]^{4a}$ in THF at room temperature results in smooth precipitation of thallium(I) chloride, according to eq 2.⁶ After filtration, removal of the volatile components in vacuo,



extraction, and crystallization from *n*-pentane at -30°C , pale yellow crystals that analyzed correctly as $[\text{((COD)Rh)}_2\text{Sn(OEt)}_6]$ (3) were isolated in 90.8% yield.⁷ In toluene-*d*₈ solution at room temperature, 3 exhibits only one type of ethoxide and cyclooctadiene ligand, as determined by ¹H and ¹³C NMR spectroscopy. Upon cooling, however, the ¹H NMR ethoxide ligand resonances begin to broaden at 233 K, and the cyclooctadiene resonances begin to broaden at 193 K. Unfortunately, temperatures low enough to freeze out the exchange process could not be reached, so the thermodynamically preferred conformation of this com-

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- (6) To a solution of 2.0 g (2.5 mmol) of $[\text{Ti}_2\text{Sn(OEt)}_6]$ in THF was added a THF solution of 1.24 g (2.5 mmol) of $[(\text{COD)RhCl}]_2$ with rapid stirring. A white precipitate was immediately formed. After being stirred for 2 h, the solution was filtered, and the volatile components were removed in vacuo to give a yellow oil, which was taken up in *n*-pentane. The resultant solution was filtered and evaporated to dryness to give a pale yellow solid. Recrystallization from *n*-pentane at -30°C gave crystals suitable for X-ray diffraction.
- (7) $[\text{((COD)Rh)}_2\text{Sn(OEt)}_6]$: mp 82-84 $^\circ\text{C}$; ¹H NMR (C_6D_6 , 20 $^\circ\text{C}$, 250 MHz) 3.97 (q, 7 H, ²*J*_{19Sn-1H} = 52 Hz, 12 H, OCH_2CH_3), 3.69 (s, br, 4 H, $-\text{CH}=\text{CH}-$), 2.17 (m, 4 H, $=\text{CH}-\text{CH}_2-$), 1.59 (t, 18 H, OCH_2CH_3), 1.41 ppm (m, 4 H, $=\text{CH}-\text{CH}_2-$); ¹³C{¹H} NMR (C_6D_6 , 20 $^\circ\text{C}$, 62.9 MHz) 73.9 (d, ¹*J*_{103Rh-13C} = 15 Hz, $-\text{CH}=\text{CH}-$), 60.9 (s, ²*J*_{19Sn-13C} = 27 Hz, OCH_2CH_3), 30.6 (s, $=\text{CH}-\text{CH}_2-$), 20.8 ppm (s, ²*J*_{119Sn-13C} = 16 Hz); ¹¹⁹Sn NMR (C_6D_6 , 20 $^\circ\text{C}$, 93.3 MHz) -529.5 ppm (s); IR (KBr disk) 2951.7 (s), 2878.0 (s), 1471.0 (m), 1435.0 (m), 1380.4 (s), 1299.0 (m), 1153.0 (m), 1089.5 (s), 1033.0 (s), 961.3 (m), 884.1 (s), 840.1 (s), 558.2 (s), 452.1 (s), 540.0 (s), 525.9 (s), 498.0 cm^{-1} (s). Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_6\text{Rh}_2\text{Sn}$: C, 41.46; H, 6.71. Found: C, 41.76; H, 6.96 (monomeric in benzene solution).

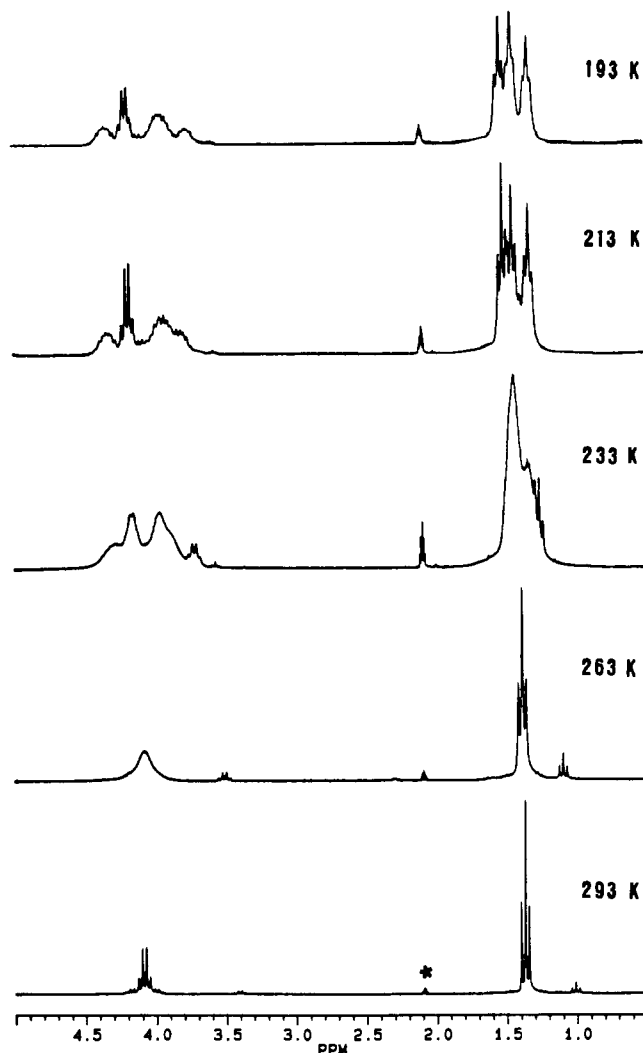


Figure 2. Variable-temperature ^1H NMR spectra of **4**. (* marks the protio impurity of the solvent. There is a small amount of ethanol impurity present at ~ 1.0 and ~ 3.4 ppm.)

pound *in solution* could not be established.

A solid-state X-ray structural analysis of crystalline **3**⁸ confirmed its identity and showed that each $[(\text{COD})\text{Rh}]^+$ cation is coordinated to two ethoxide ligands to produce a molecule with approximate C_2 molecular symmetry. An ORTEP plot of **3** is shown in Figure 1, together with the relevant bond lengths and angles. Of the six ethoxide ligands coordinated to tin, two cis pairs are coordinated to Rh(1) and Rh(2), resulting in a distortion of the octahedral coordination environment for tin ($\text{O}(3)\text{--Sn--O}(4) = 73.4(2)^\circ$ and $\text{O}(1)\text{--Sn--O}(2) = 73.7(1)^\circ$) and distortion of the square-planar coordination environment of Rh ($\text{O}(3)\text{--Rh}(2)\text{--O}(4) = 74.6(2)^\circ$ and $\text{O}(1)\text{--Rh}(1)\text{--O}(2) = 74.4(1)^\circ$). The tin-oxygen and rhodium-oxygen distances are in the range expected.^{4a,c,9} The bridging alkoxide oxygen atoms are approximately planar, and the sums of their angles are close to 360° .¹⁰ The angle between

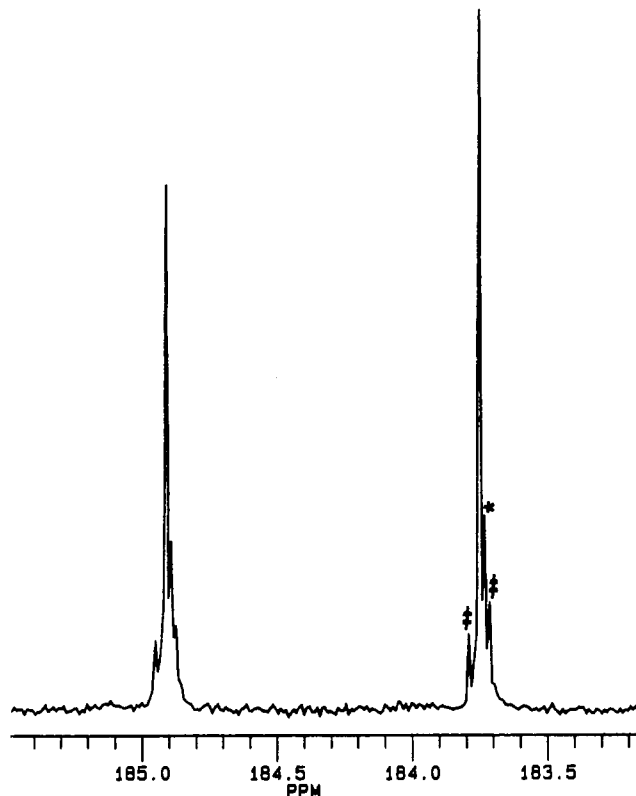
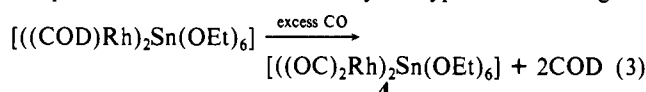


Figure 3. ^{13}C NMR spectrum of $[(\text{O}^*\text{C})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$ (where $^*\text{C} = 99\%$ ^{13}C enriched) recorded at 293 K. ^{119}Sn satellites are marked #, and * indicates the resonances due to the $^{18}\text{O}^{13}\text{C}$ isotopomer present.

the cis terminal ethoxide ligands is 90.4° , and the Sn-O(5)-C(9) and Sn-O(6)-C(11) angles of 125.4 and 125.6° are as expected for terminal tin alkoxide ligands.^{4c} Other structural features of this molecule are unremarkable.

To gain further insight into the solution dynamic process, the COD ligands of **3** were replaced by carbonyl ligands according to eq 3.¹¹ In solution, **4** exhibits only one type of ethoxide ligand



at room temperature, as determined by ^1H NMR spectroscopy. Upon cooling, the ^1H NMR resonances broaden, and the low-temperature limiting spectrum *can* be obtained, as shown in Figure 2. At -80°C , three types of alkoxide ligands of equal intensity were observed consistent with a structure analogous to that adopted by **3** in the solid state. In the -60°C ^{13}C NMR spectrum, one of the methylenic ethoxide carbon resonances exhibits a $^2J_{^{119}\text{Sn}\text{--O}\text{--}^{13}\text{C}}$ coupling constant of 40 Hz, consistent with a terminal ethoxide ligand, while the other two exhibit couplings of <30 Hz in the range expected for doubly bridging ethoxide ligands.¹² Furthermore, when 99% ^{13}C -enriched CO is used to prepare **4**, the

(8) Crystal data for **3**: irregular crystals ($0.27 \times 0.30 \times 0.33$ mm) grown from *n*-pentane at -30°C ; $\text{C}_{28}\text{H}_{54}\text{O}_6\text{Rh}_2\text{Sn}$, monoclinic, $P2_1/n$, $a = 10.8895(15)$ Å, $b = 18.3805(27)$ Å, $c = 17.0229(2)$ Å, $\beta = 105.501(10)^\circ$, $V = 3283.2(7)$ Å³, $Z = 4$, $D(\text{calc}) = 1.641$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 17.5$ cm⁻¹, $T = 294$ K. Of 7637 data that were collected on a Nicolet R₃ instrument, using Mo K α radiation ($\lambda = 0.71073$ Å) and employing a graphite monochromator, and that were corrected for absorption ($4^\circ \leq 2\theta \leq 54^\circ$) (SHELXTL), 7161 were independent, and 4906 with $F_o \geq 5\sigma(F_o)$ were observed. At convergence, with all non-hydrogen atoms anisotropic and all hydrogen atoms idealized, $R_F = 4.00\%$, $R_w = 4.34\%$, $\text{GOF} = 1.145$, $\Delta(\rho) = 0.73$ e Å⁻³, and $N_o/N_v = 14.7$.

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(10) The sums of the angles are as follows: $\text{O}(4) = 360.0^\circ$, $\text{O}(3) = 358.3^\circ$, $\text{O}(2) = 356.5^\circ$, $\text{O}(1) = 359.7^\circ$.

(11) $[(\text{CO})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$: ^1H NMR (C_6D_6 , 20°C , 250 MHz) 4.10 (q, 7 Hz, $^3J_{^{119}\text{Sn}\text{--}^1\text{H}} = 44$ Hz, 12 H, $-\text{OCH}_2\text{CH}_3$), 1.35 ppm (t, 18 H, $-\text{OCH}_2\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C , 62.9 MHz) 185.6 (d, $^1J_{^{103}\text{Rh}\text{--}^{13}\text{C}} = 73$ Hz, $^3J_{^{119}\text{Sn}\text{--}^{13}\text{C}} = 4.1$ Hz, $-\text{CO}$), 65.04 (s, br), 57.94 (s, $-\text{OCH}_2\text{CH}_3$), 18.55 ppm (s, $-\text{OCH}_2\text{CH}_3$). $[(^{13}\text{C}^{18}\text{O})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$: 183.79 ppm (d, $^1J_{^{103}\text{Rh}\text{--}^{13}\text{C}} = 74$ Hz, $^{-13}\text{C}^{18}\text{O}$). $[(\text{CO})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$: $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_6 , -80°C , 62.9 MHz) 184.4 (d, $^1J_{^{103}\text{Rh}\text{--}^{13}\text{C}} = 73$ Hz, $^3J_{^{119}\text{Sn}\text{--}^{13}\text{C}} = 4.1$ Hz, $-\text{CO}$), 67.37 (s), 66.94 (s), 60.10 ppm (s, $^2J_{^{119}\text{Sn}\text{--}^{13}\text{C}} = 40$ Hz, $-\text{OCH}_2\text{CH}_3$), $-\text{OCH}_2\text{CH}_3$ obscured by $-\text{CD}_3$ peak of toluene- d_6 . $[(^{13}\text{C})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$: IR (C_6D_6 solution, KBr windows) 3235.0 (m), 2966.5 (s), 2859.1 (m), 2388.8 (m), 2271.6 (s), 2073.8 (s), 1999.1 (s), 1618.2 (s), 1453.1 (m), 1380.7 (s), 1330.6 (s), 1161.9 (m), 1092.4 (s), 1057.0 (s), 889.1 (s), 810.2 (s), 665.0 (w), 505.9 cm⁻¹ (s). $[(\text{CO})_2\text{Rh})_2\text{Sn}(\text{OEt})_6]$: IR (C_6D_6 solution, KBr windows) 3235.0 (m), 2966.9 (s), 2858.5 (m), 2388.8 (m), 2273.1 (s), 2075.3 (s), 2005.0 (s), 1617.8 (s), 1453.2 (s), 1381.4 (m), 1330.3 (s), 1162.3 (m), 1091.1 (s), 1057.0 (s), 888.8 (m), 814.0 (s), 667 (9) cm⁻¹ (w).

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room-temperature ^{13}C NMR spectrum, at the fast-exchange limit, exhibits $^3J_{\text{O}^{13}\text{C}-\text{Rh}-\text{O}^{119}\text{Sn}}$ (see Figure 3), consistent with an intramolecular 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 m²/g, as determined by nitrogen adsorption).¹³ In comparison, thermogravimetric analysis of $[\text{Sn}(\text{OEt})_4]_n$ 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 by-products,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

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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), ^1H NMR spectrum of byproducts trapped at -196 °C from pyrolysis of **3** at 300 °C (Figure S4), and ^1H 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 $\text{Zr}(\text{CH}_2\text{Ph})_4$ reacts with 2,6-diisopropylaniline ($\text{H}_2\text{NC}_6\text{H}_3\text{Pr}_i^2-2,6$; ≥ 4 equiv) in benzene solution to produce the yellow, homoleptic arylimido complex $[\text{Zr}(\text{NHC}_6\text{H}_3\text{Pr}_i^2-2,6)_4]$ (**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 $\text{H}_2\text{NC}_6\text{H}_3\text{Pr}_i^2-2,6$ takes place with formation of the arylimido complex $[\text{Zr}(\text{NC}_6\text{H}_3\text{Pr}_i^2-2,6)(\text{NHC}_6\text{H}_3\text{Pr}_i^2-2,6)(\text{py}')_2]$ (**2**) (Scheme I).¹⁰ The ^1H 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 $[\text{Zr}(\text{OC}_6\text{H}_3\text{Bu}_i^2-2,6)_2(\text{CH}_3)_2]$ with aniline followed by addition of 4-pyrrolidinopyridine (Scheme I). The intermediate bis(phenylimido) complex $[\text{Zr}(\text{OC}_6\text{H}_3\text{Bu}_i^2-2,6)_2(\text{NHPh})_2]$ (**3**)¹¹ has also been isolated prior to its conversion to the phenylimido complex $[\text{Zr}(\text{NPh})(\text{OC}_6\text{H}_3\text{Bu}_i^2-2,6)_2(\text{py}')_2]$ (**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 $\text{ZrN}_4\text{C}_{48}\text{H}_{72}$ (**1**): C, 72.40; H, 9.11; N, 7.04. Found: C, 72.07; H, 9.45; N, 7.40. ^1H NMR (C_6D_6 , 30 °C): δ 6.98 (s, Zr-NH); 3.26 (septet, CHMe_2), 1.18 (d, CHMe_2).
- (10) Anal. Calcd for $\text{ZrC}_{54}\text{H}_{77}\text{N}_7$ (**2**): C, 70.85; H, 8.48; N, 10.71. Found: C, 70.43; H, 8.58; N, 10.30. ^1H NMR (C_6D_6 , 30 °C): δ 6.90 (s, Zr-NH); 3.92 (septet, imido CHMe_2), 3.77 (septet, amido CHMe_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, $\alpha\text{-CH}_2\text{-py}'$), 1.07 (m, $\beta\text{-CH}_2\text{-py}'$).
- (11) Anal. Calcd for $\text{ZrN}_2\text{O}_2\text{C}_{46}\text{H}_{54}$ (**3**): C, 70.02; H, 7.93; N, 4.08. Found: C, 68.96; H, 8.40; N, 3.86. ^1H NMR (C_6D_6 , 30 °C): δ 7.33 (s, Zr-NHPh), 1.44 (s, Bu^i), 6.6-7.2 (m, aromatics).
- (12) Anal. Calcd for $\text{ZrN}_3\text{O}_2\text{C}_{52}\text{H}_{71}$ (**4**): C, 70.22; H, 8.05; N, 7.87. Found: C, 70.26; H, 8.47; N, 7.48. ^1H (C_6D_6 , 30 °C): δ 1.38 (s, Bu^i), 8.33 (d, 2,6-H py'), 5.02 (d, 3,5-H py'), 1.80 (m, $\alpha\text{-CH}_2\text{-py}'$), 0.65 (m, $\beta\text{-CH}_2\text{-py}'$), 6.5-7.3 (m, aromatics).