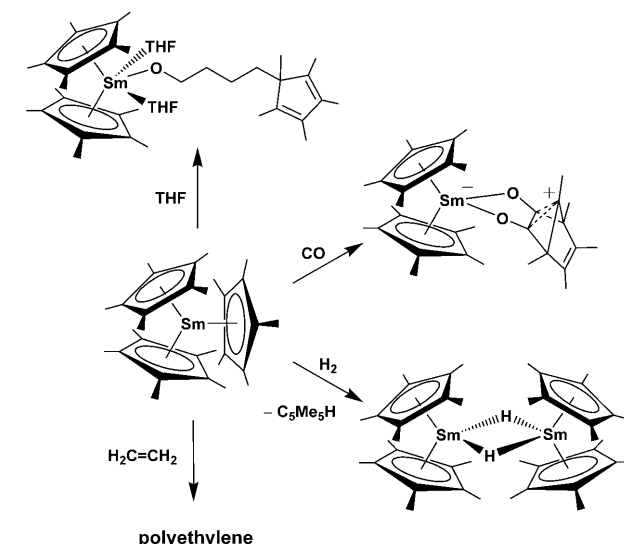
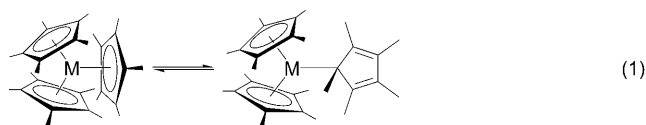


Tris(polyalkylcyclopentadienyl) Complexes: The Elusive $[(\eta^5\text{-C}_5\text{R}_5)_2\text{M}(\eta^1\text{-C}_5\text{R}_5)]$ Structure and Trihapto Cyclopentadienyl Coordination Involving a Methyl Substituent**

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Recent developments in metallocene chemistry have included the isolation of a series of sterically crowded complexes containing three η^5 -pentamethylcyclopentadienyl rings: $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{M}]$ (M = lanthanoide, actinoide, yttrium).^[1] Since the cone angle of $(\eta^5\text{-C}_5\text{Me}_5)^-$ had previously been estimated to be 142° ,^[2] or as large as 171° ^[3] and 188° ,^[4] the existence of these complexes was unexpected. Isolation of $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{M}]$ complexes, as well as the more crowded $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{AnX}]$, $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{ML}]$, and $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{ML}_2]$ species (An = actinoide),^[5] showed that the cone angle for $(\eta^5\text{-C}_5\text{Me}_5)^-$ could be reduced to 120° by moving the ligand further away from the metal. In each of these complexes, the metal–C($\eta^5\text{-C}_5\text{Me}_5$) distances are approximately 0.1 Å or more longer than any previously observed analogous distances.^[6]

Associated with the long distances in these tris(pentamethylcyclopentadienyl) complexes was unusual reactivity of the normally inert ancillary $(\eta^5\text{-C}_5\text{Me}_5)^-$ ligands. For example, $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{Sm}]$ was found to ring open THF,^[7] polymerize ethylene,^[1f] undergo insertion reactivity with CO,^[1b] and react by σ bond metathesis with dihydrogen (Scheme 1).^[1f] None of these reactions had previously been observed with the $(\eta^5\text{-C}_5\text{Me}_5)^-$ ligands, but they were common with alkyl lanthanoids.^[8] This led to the speculation that $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{M}]$ complexes could have access to a monohapto form, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}(\eta^1\text{-C}_5\text{Me}_5)]$, that engaged in these alkyl-like reactions [Eq. (1)]. Flexibility in the hapticity of cyclopentadienyl ligands is well known^[9] and has been theoretically analyzed.^[10] Examples include $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-C}_5\text{H}_5)]$,^[11] $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Zr}(\eta^1\text{-C}_5\text{H}_5)]$,^[12] $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}'(\eta^1\text{-C}_5\text{H}_5)_2]$ (M' = Ti,^[13] Hf^[14]),



Scheme 1. Reactivity of the sterically crowded $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{Sm}]$ complex.

$[(\eta^1\text{-C}_5\text{Me}_4\text{R})_3\text{Ga}]$,^[15] and polymeric $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Sc}(\mu\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{H}_5)]_x$.^[16] However, it was unclear if such an η^5 to η^1 transformation could occur in these crowded $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{M}]$ complexes.

Numerous efforts have been made since $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{Sm}]$ was first discovered^[1d] to obtain spectroscopic evidence on the existence of a $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}(\eta^1\text{-C}_5\text{Me}_5)]$ complex.^[17] No evidence was obtained by low-temperature spectroscopy and reactions with bases designed to trap a $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}(\eta^1\text{-C}_5\text{Me}_5)\text{L}]$ complex suitable for crystallization led to base adducts $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{ML}]$ ^[5d–f] and $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{ML}_2]$,^[5f,g] that only contained η^5 -rings in the solid state.

We now report the first structurally characterizable example of an $[(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{M}(\eta^1\text{-C}_5\text{Me}_4\text{R})]$ complex (R = Me, H). The discovery arose from investigations of the $(\text{C}_5\text{Me}_4\text{H})^-$ chemistry of Sc^{3+} designed to make the first reduced dinitrogen complex of scandium.^[18] The $(\text{C}_5\text{Me}_4\text{H})^-$ ligand was chosen instead of $(\text{C}_5\text{Me}_5)^-$ due to the small size of scandium. The value of exploring $(\text{C}_5\text{Me}_4\text{H})^-$ vs. $(\text{C}_5\text{Me}_5)^-$ has recently been impressively shown with zirconium.^[19] The tetraphenylborate complex, $[(\text{C}_5\text{Me}_4\text{H})_2\text{Sc}\{(\mu\text{-Ph})\text{BPh}_3\}]$, used as a precursor to $[(\text{C}_5\text{Me}_4\text{H})_2\text{Sc}\{(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)\}]$ ^[18] is also a viable precursor to $[(\text{C}_5\text{Me}_4\text{H})_3\text{Sc}]$ through the most common synthetic route to $[(\text{C}_5\text{Me}_5)_3\text{M}]$ complexes, namely reaction of a tetraphenylborate salt of a metallocene with an alkali metal cyclopentadienide.^[1a–c,e,f] When this reaction was

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conducted with the scandium and $(C_5Me_4H)^-$ combination, it provided evidence on the previously elusive [bis(pentahapto)](monohapto) orientation for three cyclopentadienyl rings.

Examination of the coordination mode of the $(C_5Me_4H)^-$ ligand with a slightly different combination of metal and ligand sizes, the larger metals lutetium and yttrium with $(C_5Me_5)^-$, provided yet another new structural type of tris(polyalkylcyclopentadienyl) complex and a new mode of trihapto coordination for a cyclopentadienyl ring. Given the many decades of study of cyclopentadienyl chemistry by scores of groups around the world, it was surprising to find a new option for coordination by this classical ligand.

KC_5Me_4H reacts with $[(C_5Me_4H)_2Sc]\{(\mu-Ph)BPh_3\}$ ^[18] within 1 h to form yellow crystals, **1**, with an elemental analysis consistent with $[(C_5Me_4H)_3Sc]$ in 80% yield. The 1H and ^{13}C NMR spectra of **1** showed a single type of $(C_5Me_4H)^-$ environment in solution down to $-80^\circ C$ in toluene, but X-ray crystallography revealed that in the solid state, **1** had a [bis(pentahapto)](monohapto) metallocene structure, $[(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)]$ [**1**; Eq. (2), Figure 1].

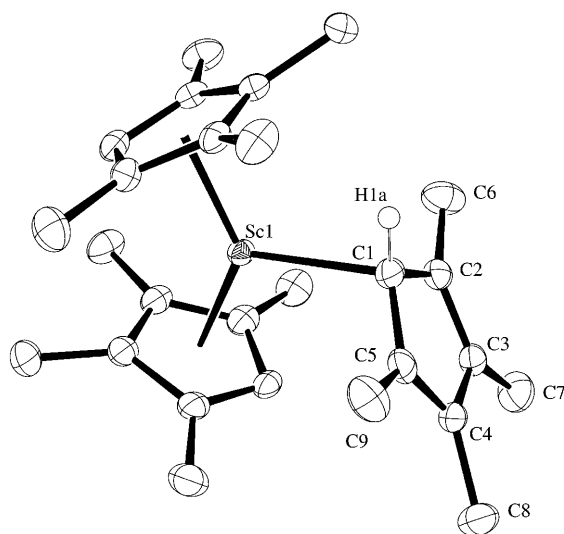
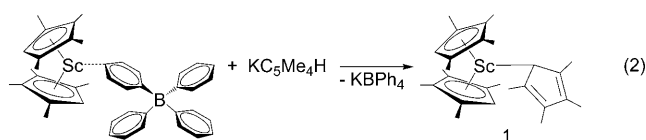


Figure 1. Thermal ellipsoid plot of $[(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)]$ (**1**) drawn at the 50% probability level. There are two independent molecules of **1** in the unit cell. The second independent molecule of **1** and hydrogen atoms except for H1a are omitted for clarity.

The X-ray diffraction data (see Supporting Information) of **1** clearly showed the monohapto nature of the C1–C5 ring. The 1.380(2) Å C4–C5 and 1.388(2) Å C2–C3 distances are shorter than the other three 1.427(2)–1.443(2) Å C–C distances in the ring, which is consistent with a localized diene structure. The 2.374(2) Å Sc1–C1 distance is much longer than the 2.243(11), 2.278(2), and 2.286(4) Å Sc–C(alkyl)

single bonds in $[(C_5Me_5)_2ScMe]$,^[20] $[(C_5Me_5)_2ScCH_2CMe_3]$,^[21] and $[(C_5Me_5)_2ScCH_2SiMe_3]$,^[22] respectively, but it is shorter than the 2.423(2)–2.544(2) Å range of Sc–C($\eta^5-C_5Me_4H$) distances in **1**. C1 is clearly the main contact with scandium in the η^1 -ring since the scandium distances to C2, C5, C6, and C9 are all $>2.945(2)$ Å. The 2.171 Å average Sc–(C_5Me_4H ring centroid) distance is longer than the 2.130 Å value in $[(C_5Me_4H)_2Sc]\{(\mu-Ph)BPh_3\}$ and identical to the 2.171 Å analogue in $[(C_5Me_5)_2ScMe]$.

Since the $(C_5Me_4H)^-$ ligand provided the long sought $[(\eta^5-C_5R_5)_2M(\eta^1-C_5R_5)]$, its coordination in other crowded metallocenes was explored. Since the tris(tetramethylcyclopentadienyl) complexes of the next largest rare earth metal, Lu, and Y (eight-coordinate ionic radii: Lu, 0.977; Y, 1.019; Sc, 0.870 Å),^[23] had normal $[(\eta^5-C_5Me_4H)_3M]$ structures,^[24] the synthesis of slightly more crowded $[(C_5Me_5)_2M(C_5Me_4H)]$ complexes was sought. Accordingly, KC_5Me_4H was reacted with the appropriate $[(C_5Me_5)_2M]\{(\mu-Ph)_2BPh_2\}$ complexes^[16,25] and $[(\eta^5-C_5Me_5)_2M(\eta^3-C_5Me_4H)]$ complexes (M = Lu, **2**; Y, **3**) were isolated. X-ray crystallography showed that both of these compounds were isomorphous and had an unusual cyclopentadienyl coordination mode in the solid state [Eq. (3), Figure 2].

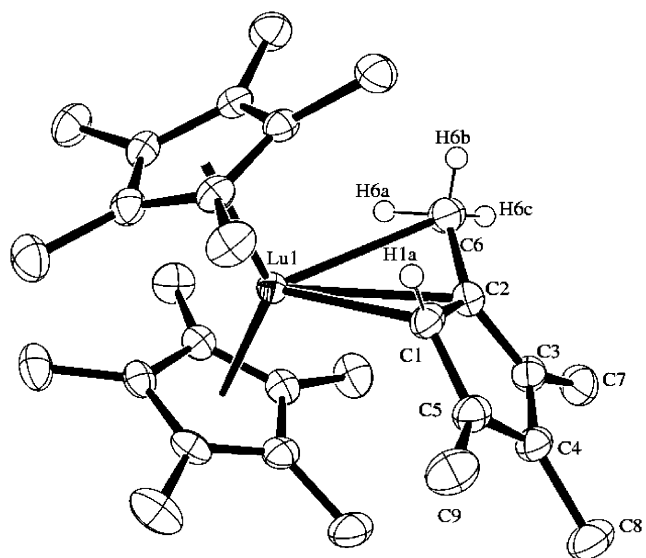
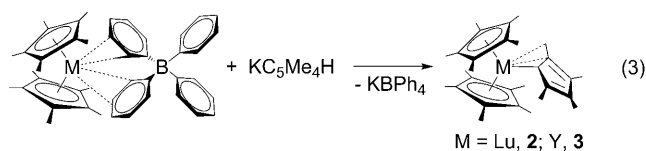


Figure 2. Thermal ellipsoid plot of $[(\eta^5-C_5Me_5)_2Lu(\eta^3-C_5Me_4H)]$ (**2**) drawn at the 50% probability level. There are two independent molecules of **2** in the unit cell. The second independent molecule of **2** and hydrogen atoms except for H1a, H6a, H6b, and H6c are omitted for clarity.

As shown in Figure 2, the three carbon atoms closest to Lu are the CH ring carbon, C1, its adjacent ring carbon, C2, and its attached methyl carbon, C6. Since the structures of **2** and **3**

are isomorphous and the bond distances just vary by the difference in their ionic radii (see Supporting Information), only the data on **2** will be used in the structural discussion.

The trihapto C1–C5 ring in **2** has a localized diene structure similar to the monohapto C1–C5 ring in **1**: the 1.380(3) Å C4–C5 and 1.397(3) Å C2–C3 distances are shorter than the other three 1.424(3)–1.446(3) Å C–C distances in the ring. The primary contact of the C1–C5 ring with Lu is through the 2.468(2) Å Lu–C1 linkage. This distance is 0.094 Å longer than the Sc–C1 analogue in **1** which matches the 0.107 Å difference in ionic radii.^[23] The Lu–C1 distance is similar to that of the 2.423(3) Å Lu–C(terminal Me) distance in $[(C_5Me_5)_2LuMe]_n$.^[25] However, in contrast to **1**, two other carbon atoms are oriented toward the metal through 2.737(2) Å Lu–C2 and 2.851(2) Å Lu–C6 distances. The latter distances are significantly longer than Lu–C1 as well as the 2.552(2)–2.654(2) Å Lu–C(C₅Me₅) distances, but they are much shorter than any other Sc–C(η^1 -C₅Me₄H) distances in **1** (2.945(2)–3.954(2) Å). The trihapto arrangement in **2** differs not only from the conventional trihapto cyclopentadienyl coordination that involves three ring carbons, but also from that in allyl complexes. The closest allyl examples in the literature are $[(\eta^5-C_5Me_5)_2Lu(\eta^3-C_3H_5)]$ (**4**; Lu–C(allyl) 2.545(5), 2.548(4), and 2.549(5) Å)^[26] and the *ansa*-allyl-cyclopentadienyl dianion in $[(\eta^5-C_5Me_5)_2Y\{(\eta^5-C_5Me_4CH_2-C_5Me_4CH_2-\eta^3)\}]$ (**5**; Y–C(allyl) 2.450(2), 2.699(2), and 2.990(2) Å).^[27] The structure of **2** could also be considered as dihapto-cyclopentadienyl coordination with an agostic methyl interaction. Agostic interactions are well known in rare earth complexes containing two (η^5 -C₅Me₅)[–] ligands and alkyl or amide ligands such as $[(C_5Me_5)_2M\{CH(SiMe_3)_2\}]$ ^[28] and $[(C_5Me_5)_2M\{N(SiMe_3)_2\}]$ (M = lanthanoid, Y).^[5g,28a]

In solution at room temperature, **2** and **3** exhibit two (C₅Me₅)[–] resonances in their ¹H NMR spectra. This indicates that the (C₅Me₄H)[–] ligand maintains asymmetric coordination in solution such that the (C₅Me₅)[–] ligands differ. At 85 °C in *p*-[D₁₀]xylene, the two (C₅Me₅)[–] resonances in **2** begin to coalesce and at 135 °C, the two resonances have fully merged into a single peak at 2.00 ppm (*E*_a = 72 kJ mol^{–1}, **2**; 73 kJ mol^{–1}, **3**).^[29] For the (C₅Me₄H)[–] ligand in the ¹H NMR spectra of **2** and **3**, only two methyl resonances are observed. Hence, in solution it appears that there is a process that equilibrates the two sides of the (C₅Me₄H)[–] ring such that coordination can alternate between the (C1, C2, and C6) set and (C1, C5 and C9). Consistent with this, the solid-state structures of **2** and **3** contain two independent molecules in the unit cell that differ in terms of which set of three carbons is closest to the metal. The η^3 coordination mode in solution is further supported by the ¹³C NMR spectrum of **3** which contains a doublet assignable to C1 (confirmed by HMQC) that has *J*_{Y–C} = 12 Hz. This coupling constant is lower than the 25–37 Hz range previously observed for *J*_{Y–C} in other complexes containing Y–C(alkyl) single bonds,^[27,28,30] which is reasonable considering the longer Y–C1 distance in **3** and its bonding motif. No coupling was observed between yttrium and C2, C6, C5, and C9 presumably because of the dynamic nature of the complex.

The structures of **1**–**3** indicate that tris(polyalkylcyclopentadienyl) complexes can access structures in which the

cyclopentadienyl ligands are not always pentahapto, the only coordination mode previously observed in the solid state for rare earth $[(C_5R_5)_3M]$ complexes. The structure of **1** matches the ligand arrangement proposed to explain the pseudo-alkyl reactivity of $[(C_5Me_5)_3M]$ complexes. The fact that the NMR spectrum of **1** shows none of the asymmetry of the solid-state structure suggests that in solution the monohapto coordination mode may only be transitory. However, the solid-state structure shows this arrangement is energetically accessible under the proper conditions.

The structures of **2** and **3** show that transitory intermediate structures accessible from tris(polyalkylcyclopentadienyl) complexes need not necessarily be the classical coordination modes previously identified for (C₅R₅)[–] ligands. They also show that saturated methyl groups in substituted cyclopentadienyl ligands can occupy coordination positions analogous to unsaturated methylene carbons in allyl ligands. Evidently the coordination chemistry of the cyclopentadienyl ring continues to expand.

Experimental Section

$[(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)]$ (**1**): In an argon glovebox, KC₅Me₄H (40 mg, 0.25 mmol) was added to a stirred yellow slurry of $[(C_5Me_4H)_2Sc]\{(\mu-Ph)BPh_3\}$ (152 mg, 0.251 mmol) in 10 mL of benzene. After the mixture was stirred for 1 h, the orange slurry was centrifuged, filtered, and the solvent was removed under reduced pressure to yield **1** as a bright orange crystalline solid (84 mg, 82 %). Yellow crystals of **1** were grown from toluene at –35 °C. ¹H NMR (500 MHz, [D₆]benzene, 298 K): δ = 5.62 (s, 3H, C₅Me₄H), 2.09 (s, 18H, C₅Me₄H), 1.71 ppm (s, 18H, C₅Me₄H). ¹³C NMR (126 MHz, [D₆]benzene, 298 K): δ = 125.9 (C₅Me₄H), 120.6 (C₅Me₄H), 111.0 (C₅Me₄H), 13.5 (C₅Me₄H), 12.7 ppm (C₅Me₄H). ¹H NMR (500 MHz, [D₈]toluene, 298 K): δ = 5.55 (s, 3H, C₅Me₄H), 2.07 (s, 18H, C₅Me₄H), 1.69 ppm (s, 18H, C₅Me₄H). ¹³C NMR (126 MHz, [D₈]toluene, 298 K): δ = 125.5 (C₅Me₄H), 120.1 (C₅Me₄H), 110.7 (C₅Me₄H), 13.0 (C₅Me₄H), 12.3 ppm (C₅Me₄H). ⁴⁵Sc NMR (145 MHz, [D₈]toluene, 298 K): δ = 227 ppm (*v*_{1/2} = 3300 Hz). IR: $\tilde{\nu}$ = 3096w, 3075w, 3033w, 2975m, 2904s, 2858s, 2726w, 1662w, 1548w, 1481m, 1432m, 1331w, 1266m, 1106w, 1024m, 974w, 834s, 808s, 728w, 670vs, 623s, 613s cm^{–1}. Anal. calcd for C₂₇H₃₉Sc: C 79.37, H 9.62; found: C 79.40, H 9.80.

$[(\eta^5-C_5Me_5)_2Lu(\eta^3-C_5Me_4H)]$ (**2**): KC₅Me₄H (203 mg, 1.27 mmol) was added to a stirred white slurry of $[(C_5Me_5)_2Lu]\{(\mu-Ph)_2BPh_3\}$ (303 mg, 0.396 mmol) in benzene (7 mL). After stirring for 18 h, the yellow slurry was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a pale yellow solid. The solid was stirred in hexane (15 mL) for 30 min, centrifuged, filtered, and the hexane was removed under reduced pressure to yield a bright yellow solid (190 mg, 85 %). Crystals of **2** were grown from benzene at 25 °C. ¹H NMR (500 MHz, [D₆]benzene, 298 K): δ = 5.39 (s, 1H, C₅Me₄H), 2.29 (s, 6H, C₅Me₄H), 1.91 (s, 15H, C₅Me₅), 1.73 (s, 6H, C₅Me₄H), 1.70 ppm (s, 15H, C₅Me₅). ¹³C NMR (126 MHz, [D₆]benzene, 298 K): δ = 119.6 (C₅Me₄H), 119.2 (C₅Me₅), 117.6 (C₅Me₄H), 85.7 (C₅Me₄H), 15.3 (C₅Me₄H), 12.7 (C₅Me₄H), 12.0 (C₅Me₅), 10.9 ppm (C₅Me₅). ¹H NMR (500 MHz, *p*-[D₁₀]xylene, 298 K): δ = 5.40 (s, 1H, C₅Me₄H), 2.32 (s, 6H, C₅Me₄H), 2.06 (s, 15H, C₅Me₅), 1.83 (s, 15H, C₅Me₅), 1.82 ppm (s, 6H, C₅Me₄H). IR: $\tilde{\nu}$ = 2956s, 2906s, 2857s, 2726w, 2605m, 2454w, 2387w, 1598w, 1545w, 1485m, 1439s, 1401m, 1381s, 1275m, 1136m, 1105w, 1062w, 1023m, 946w, 800w, 708w, 681m, 636s, 610s, 561m cm^{–1}. Anal. calcd for C₂₉H₄₃Lu: C 61.47, H 7.65; found: C 60.90, H 7.97.

$[(\eta^5-C_5Me_5)_2Y(\eta^3-C_5Me_4H)]$ (**3**): Following the procedure for **2**, KC₅Me₄H (62 mg, 0.39 mmol) reacts with $[(C_5Me_5)_2Y]\{(\mu-Ph)_2BPh_3\}$ (260 mg, 0.383 mmol) to yield a bright yellow solid

(131 mg, 71%). Crystals of **3** were grown from toluene at -35°C . ^1H NMR (500 MHz, $[\text{D}_6]\text{benzene}$, 298 K): δ = 5.65 (s, 1 H, $\text{C}_5\text{Me}_4\text{H}$), 2.28 (s, 6 H, $\text{C}_5\text{Me}_4\text{H}$), 1.89 (s, 15 H, C_5Me_5), 1.75 (s, 6 H, $\text{C}_5\text{Me}_4\text{H}$), 1.68 ppm (s, 15 H, C_5Me_5). ^{13}C NMR (126 MHz, $[\text{D}_6]\text{benzene}$, 298 K): δ = 126.7 ($\text{C}_5\text{Me}_4\text{H}$), 120.2 (d, $^1J_{\text{YC}} = 1\text{ Hz}$, C_5Me_5), 119.7 (d, $^1J_{\text{YC}} = 1\text{ Hz}$, C_5Me_5), 114.3 ($\text{C}_5\text{Me}_4\text{H}$), 89.8 (d, $^1J_{\text{YC}} = 12\text{ Hz}$, $\text{C}_5\text{Me}_4\text{H}$), 14.8 ($\text{C}_5\text{Me}_4\text{H}$), 12.9 ($\text{C}_5\text{Me}_4\text{H}$), 11.9 (C_5Me_5), 10.7 ppm (C_5Me_5). ^1H NMR (500 MHz, $p\text{-}[\text{D}_{10}]\text{xylene}$, 298 K): δ = 5.67 (s, 1 H, $\text{C}_5\text{Me}_4\text{H}$), 2.31 (s, 6 H, $\text{C}_5\text{Me}_4\text{H}$), 2.04 (s, 15 H, C_5Me_5), 1.83 (s, 6 H, $\text{C}_5\text{Me}_4\text{H}$), 1.81 ppm (s, 15 H, C_5Me_5). IR: $\tilde{\nu}$ = 2952s, 2906s, 2857s, 2725m, 2610m, 2457w, 2393w, 1491w, 1439s, 1382s, 1330w, 1284w, 1258w, 1138m, 1105w, 1062w, 1022m, 944w, 788m, 730w, 705w, 654s, 643s, 625m, 605s, 563w cm^{-1} . Anal. calcd for $\text{C}_{29}\text{H}_{43}\text{Y}$: C 72.48, H 9.02; found: C 72.37, H 9.73.

Crystallographic data for **1**: $\text{C}_{27}\text{H}_{39}\text{Sc}$, $P2_1/c$, $M = 408.54$, $a = 16.9583(9)$, $b = 17.2189(9)$, $c = 17.1638(9)\text{ \AA}$, $\beta = 112.7633(7)$, $V = 4621.5(4)\text{ \AA}^3$, $T = 148(2)\text{ K}$, $Z = 8$, $R1 = 0.0368$, $wR2 = 0.1025$.

Crystallographic data for **2**: $\text{C}_{29}\text{H}_{43}\text{Lu}$, $P\bar{1}$, $M = 566.60$, $a = 10.0535(4)$, $b = 14.3590(5)$, $c = 17.8772(6)\text{ \AA}$, $\alpha = 91.9550(4)$, $\beta = 91.4539(4)$, $\gamma = 100.5306(4)^{\circ}$, $V = 2534.46(16)\text{ \AA}^3$, $T = 173(2)\text{ K}$, $Z = 4$, $R1 = 0.0166$, $wR2 = 0.0427$.

Crystallographic data for **3**: $\text{C}_{29}\text{H}_{43}\text{Y}$, $P\bar{1}$, $M = 480.54$, $a = 10.0376(4)$, $b = 14.3585(5)$, $c = 17.7416(6)\text{ \AA}$, $\alpha = 92.3586(4)$, $\beta = 90.3582(4)$, $\gamma = 99.8809(4)^{\circ}$, $V = 2516.71(16)\text{ \AA}^3$, $T = 93(2)\text{ K}$, $Z = 4$, $R1 = 0.0292$, $wR2 = 0.0727$.

CCDC 788557 (**1**), 788558 (**2**), and 788559 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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