

Heteroleptic $[M(CH_2C_6H_5)_2(I)(THF)_3]$ Complexes (M = Y or Er): Remarkably Stable Precursors to Yttrium and Erbium T-Shaped Carbenes

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Heteroleptic dibenzyl yttrium and erbium iodides $[Ln(Bn)_2(I)(THF)_3]$ [Ln = Y(1), Er(2); Bn = $CH_2C_6H_5$] were prepared in high yields and are remarkable for their thermal stability and inertness toward ligand scrambling in Schlenk-type equilibria. A variable-temperature study of 1 revealed a dynamic process in solution attributed to the presence of three isomers, namely, cis-fac, cis-mer, and trans-mer, which were observed in a 0.11:1:0.05 ratio at 298 K, respectively. Only the isomer attributed as *cis-mer* was observed at 313 K. The synthetic utility of 1 and 2, which combines the potential benefits of protonolysis and salt elimination chemistry, was demonstrated by the facile synthesis of phosphorus-stabilized yttrium and erbium carbenes $[Ln(BIPM)(I)(THF)_2][Ln = Y(3);$ Er (4); BIPM = { $C(PPh_2NSiMe_3)$ }²⁻], which each contain unusual T-shaped carbene centers. DFT calculations on 3, BIPM, and Ph₃P=C=PPh₃ showed very similar frontier orbital compositions in all three examples. Although 3 and 4 are classified as carbene complexes, and NBO analysis is consistent with the BIPM ligand adopting the dipolar $N^-P^+-C^{2-}P^+-N^-$ resonance form, the possibility of categorizing **3** and **4** as captodative carbon(0) complexes of yttrium and erbium cannot be ruled out. Complexes 1-4 have been variously characterized by X-ray crystallography, multinuclear NMR spectroscopy, FTIR spectroscopy, room-temperature Evans method solution magnetic moments, and CHN microanalyses.

Introduction

The synthesis of organo-rare earth complexes continues to be of significant interest due to their high reactivities in synthetic transformations.¹ Salt elimination represents a convenient method to introduce ligands into the coordination sphere of rare earth metals, but it may be complicated by ligand redistribution reactions and alkali metal occlusion.² An attractive alternative to avoid such difficulties is to employ rare earth alkyls as starting materials. However, large coordination spheres, high Lewis acidities, and highly polar and labile rare earth—ligand bonds render the selective synthesis of rare earth alkyls a challenge.

Consequently, the synthesis of rare earth alkyls that are simple enough to be regarded as convenient starting materials is not always straightforward. For example, reaction of $LnCl_3$ salts with MeLi results in the formation of mixed-metal aggregates, e.g., $[Ln(Me)_6Li_3]$.³ Use of the more

sterically demanding Bu^t group results in "ate" complexes, e.g., $[Ln(Bu^t)_4]^{-.4}$ Even the bulky $(Me_3Si)_2CH^-$ group forms "ate" complexes when salt elimination methods are used, e.g., $[LiClLn{CH(SiMe_3)_2}_3]$,⁵ although the homoleptic $[Ln{CH(SiMe_3)_2}_3]$ complexes are available from rare earth aryloxides.⁶ Rare earth complexes of Trisyl, e.g., $(Me_3Si)_2$ - $(Me_2XSi)C^-$ (X = Me, OMe, NMe₂),⁷ are known but they are not usually employed as starting materials, as several steps are required to prepare them. Generally, the Me₃-SiCH₂⁻ group has risen to greater prominence,⁸ and even cationic species have been reported, but they are often

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⁽¹⁾ For a general review of the use of organo-rare earth metals in catalysis see: Molander, G.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161.

⁽²⁾ Piers, W. E.; Emslie, D. J. H. Coord. Chem. Rev. 2002, 233-234, 131.

^{(3) (}a) Schumann, H.; Müller, J.; Bruncks, N.; Lauke, H.; Pickardt, J. *Organometallics* **1984**, *3*, 69. (b) Schumann, H.; Müller, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 120. (c) Schumann, H.; Müller, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 276.

⁽⁴⁾ Wayda, A. L.; Evans, W. J. J. Am. Chem. Soc. 1978, 100, 7119.
(5) Atwood, J. L.; Lappert, M. F.; Zhang, H. J. Chem. Soc., Chem.

 ⁽⁵⁾ Atwood, J. L., Lappert, M. F., Zhang, H. J. Chem. Soc., Chem.
 Commun. 1988, 1308.
 (6) (a) Avent, A. G.; Caro, C. F.; Hitchcock, P. B.; Lappert, M. F.; Li,

⁽b) (a) Avent, A. G.; Caro, C. F.; Hitchcock, P. B.; Lappert, M. F.; Li, Z.; Wei, X.-H. *Dalton Trans.* **2004**, 1567. (b) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. J. Chem. Soc., Chem. Commun. **1988**, 1007.

⁽⁷⁾ Representative examples: (a) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. Organometallics 2007, 26, 2646. (b) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. J. Organomet. Chem. 2007, 692, 806.
(c) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. Organometallics 2006, 25, 2999. (d) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. Angew. Chem., Int. Ed. Engl. 1997, 36, 2815. (e) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. J. Am. Chem. Soc. 1994, 116, 12071.

^{(8) (}a) Schumann, H.; Freckmann, D. M. M.; Dechert, S. Z. Anorg. Allg. Chem. **2002**, 628, 2422. (b) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. Organometallics **2000**, 19, 228. (c) Schumann, H.; Müller, J. J. Organomet. Chem. **1978**, 146, C5. (d) Lappert, M. F.; Pearce, R. J. Chem. Soc., Chem. Commun. **1973**, 126.

stabilized with crown ethers, which may limit their applications.⁹ A simple one-step oxidative preparation of YbR₃ complexes ($R = CH_2SiMe_3$ or CH_2Bu^t) was reported, but this is currently limited to ytterbium.¹⁰



More recently, straightforward tribenzyls of Y,11 La,12 Sc,¹³ and Lu^{13a} have been reported, and they have already provided new synthetic routes to organo-rare earth complexes.¹⁴ These reports prompted us to report our improved synthesis of $[Y(Bn)_3(THF)_3]$ (1, Bn = CH₂C₆H₅),¹⁵ and we have subsequently extended this methodology across the rare earth series.¹⁶ We have used these and related trialkyls to prepare phosphorus-stabilized rare earth carbenes from H₂C(PPh₂NSiMe₃)₂ (H₂BIPM) and have investigated their reactivity, but while the desired complexes were isolated in good yields for yttrium and erbium (I and II), $^{15-17}$ the presence of an alkyl group limits the options for further synthetic transformations. The optimum scenario is represented by III, where a halide ligand provides maximum synthetic flexibility for derivatization. This is exemplified by our recent report of the first yttrium-gallium bond (IV).¹⁸ Complex IV was prepared by reacting [Ga(NAr- $CH_{2}K(tmeda)^{19} (Ar = 2, 6-diisopropylphenyl) with the pro$ duct (III) of the *in situ* reaction between $[K(Bn)]^{20}$ and [Y(HBIPM)(I)₂(THF)].¹⁸ Since preparation of the latter compound is surprisingly tedious, but double deprotonation of H₂BIPM by rare earth alkyls is facile, we targeted a heteroleptic dialkyl metal iodide, as this would bring the benefits of protonolysis chemistry but retain a halide ligand for maximum synthetic flexibility. Herein, we report the synthesis of dibenzyl yttrium and erbium iodides, which are remarkably stable, and demonstrate their synthetic utility by their reactions with H₂BIPM, which generates

(13) (a) Meyer, N.; Roesky, P. W.; Bambirra, S.; Meetsma, A.; Hessen, B.; Saliu, K.; Takats, J. *Organometallics* **2008**, *27*, 1501. (b) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363.

(14) Bambirra, S.; Perazzolo, F.; Boot, S. J.; Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 704.

(15) Mills, D. P.; Cooper, O. J.; McMaster, J.; Lewis, W.; Liddle, S. T. Dalton Trans. 2009, 4547.

(16) Wooles, A. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Dalton Trans.* **2009**, DOI: 10.1039/b911717b.

(17) Liddle, S. T.; McMaster, J.; Green, J. C.; Arnold, P. L. Chem. Commun. 2008, 1747.

(18) Liddle, S. T.; Mills, D. P.; Gardner, B. M.; McMaster, J.; Jones, C.; Woodul, W. D. *Inorg. Chem.* **2009**, *48*, 3520.

(19) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. J. Chem. Soc., Dalton Trans. **2002**, 3844.

(20) Schlosser, M.; Hartmann, J. Angew. Chem., Int. Ed. Engl. 1973, 12, 508.

Scheme 1. Synthesis of 1-4



phosphorus-stabilized rare earth carbenes that exhibit unusual T-shaped carbene centers.



Results and Discussion

We chose $[Y(I)_3(THF)_{3,5}]^{21}$ and $[K(Bn)]^{20}$ as reagents for the preparation of a dibenzyl complex because they are easy to prepare and the potassium iodide byproduct is too large to be occluded. Treatment of $[Y(I)_3(THF)_{3,5}]$ with 2 equiv of [K(Bn)] in THF at 0 °C for 4 h affords the anticipated potassium iodide precipitate. Filtration and removal of volatiles affords a brown oil in 62% yield, which was shown by ¹H NMR spectroscopy to be essentially pure and of the composition $[Y(Bn)_2(I)(THF)_3]$ (1) (Scheme 1). Complex 1 can be obtained as a microcrystalline solid by stirring the oil in hexane, or it can be recrystallized from THF. Complex 1 is thermally stable and surprisingly inert to ligand redistribution. Although the benzylic proton resonance of 1 is completely obscured by the β -methylene THF resonance in the ¹H NMR spectrum, the benzylic carbon, tentatively assigned as the cis-mer isomer V on the basis of the solid state structure (vide infra), is clearly observed in the ${}^{13}C{}^{1}H$ NMR spectrum at 55.10 ppm ($J_{YC} = 34.3 \text{ Hz}$). Interestingly, ${}^{13}C{}^{1}H$ NMR spectra of recrystallized or crude samples of 1 often exhibit two minor sets of resonances (~ 10 and $\sim 5\%$) at 298 K, consistent with presence of the cis-fac VI and transmer VII isomers in solution with those benzylic carbons resonating at 58.71 ppm ($J_{\rm YC}$ = 32.2 Hz) and 54.10 ppm $(J_{\rm YC} = 33.2 \text{ Hz})$. The presence of tribenzyl yttrium from Schlenk-type equilibria in solution was ruled out by careful comparison with an authentic sample.¹⁵ A variable-temperature ${}^{13}C{}^{1}H$ NMR study of 1 in d_8 -THF showed a *cis-fac*: cis-mer:trans-mer isomer ratio of 0.11:1:0.05 at 298 K and only the cis-mer isomer at 313 K, which returns to the

(21) Izod, K.; Liddle, S. T.; Clegg, W. Inorg. Chem. 2004, 43, 214.

⁽⁹⁾ Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. Chem. Rev. 2006, 106, 2404.

⁽¹⁰⁾ Niemeyer, M. Z. Anorg. Allg. Chem. 2000, 626, 1027.

^{(11) (}a) Carver, C. T.; Diaconescu, P. L. J. Am. Chem. Soc. 2008, 130, 7558. (b) Harder, S.; Ruspic, C.; Bhriain, N. N.; Berkermann, F.; Schürmann, M. Z. Naturforsch. B 2008, 63b, 267. (c) Zhang, W. -X.; Nishiura, M.; Mashiko, T.; Hou, Z. Chem.—Eur. J. 2008, 14, 2167. (d) Harder, S. Organometallics 2005, 24, 373.

⁽¹²⁾ Bambirra, S.; Meetsma, A.; Hessen, B. Organometallics 2006, 25, 3454.



Figure 1. Molecular structure of 1 (30% probability ellipsoids); hydrogen atoms and disordered THF components omitted for clarity. The molecular structure of 2 is very similar.

Table 1. Selected Bond Lengths and Angles for 1-4

	1	1	
Y(1) - C(1)	2.431(3)	Y(1) - C(8)	2.461(3)
Y(1) - I(1)	3.0981(3)	Y(1) - O(1)	2.3303(16)
Y(1) - O(2)	2.4723(17)	Y(1)-O(3)	2.3178(18)
		2	
Er(1) - C(1)	2.440(4)	Er(1) - C(8)	2.413(4)
Er(1) - I(1)	3.0821(3)	Er(1) - O(1)	2.308(2)
$\operatorname{Er}(1) - O(2)$	2.309(2)	Er(1) - O(3)	2.461(2)
	ŝ	3	
Y(1) - C(1)	2.356(3)	Y(1) - I(1)	3.0667(4)
Y(1) - N(1)	2.382(3)	Y(1) - N(2)	2.367(3)
C(1) - P(1)	1.641(3)	C(1) - P(2)	1.640(3)
P(1) - N(1)	1.620(3)	P(2) - N(2)	1.623(3)
P(1) - C(1) - P(2)	172.5(2)	Y(1) - C(1) - P(1)	93.55(14)
Y(1) - C(1) - P(2)	93.34(15)	., ., .,	
	4	4	
Er(1) - C(1)	2.322(2)	Er(1) - I(1)	3.0737(2)
Er(1) - N(1)	2.3636(17)	Er(1) - N(2)	2.3794(18)
C(1) - P(1)	1.640(2)	C(1) - P(2)	1.640(2)
P(1) - N(1)	1.6240(19)	P(2) - N(2)	1.6221(18)
P(1)-C(1)-P(2)	171.72(15)	Er(1) - C(1) - P(1)	93.42(10)
Er(1) - C(1) - P(2)	94.37(10)		

isomeric mixture on cooling back to 298 K. Unfortunately, no definite conclusions could be drawn from EXSY spectra because of the low quantities of VI and VII present coupled with the low isotopic abundance of ¹³C and the relatively small temperature window of 15 K; consequently, and because numerical line shape analysis was not practical, it is not realistic to extract thermodynamic parameters. However, a comparison of 0.02 and 0.04 M solutions showed almost identical isomer ratios and dynamic behavior, which implies the exchange is unimolecular in nature. The observation of isomers in solution, even on samples recrystallized several times, is noteworthy, as this is seldom observed in rare earth chemistry.²²

Colorless crystals of 1 were grown from a solution in THF. The molecular structure is illustrated in Figure 1, and selected bond lengths are listed in Table 1. The yttrium center adopts a distorted octahedral *cis-mer* geometry. Multihapto yttrium-benzyl interactions are not observed in the solid state $[Y(1)\cdots C(2) \text{ and } Y(1)\cdots C(9) = 3.177 \text{ and } 3.273 \text{ Å},$ respectively]. The Y(1)-C(1) and Y(1)-C(8) bond lengths of



Figure 2. Molecular structure of 3 (30% probability ellipsoids). Hydrogen atoms and disordered THF components are omitted for clarity. The structure of 4 is very similar.



Figure 3. Kohn–Sham orbital representations of (a) HOMO of **3**; (b) HOMO–1 of **3**; (c) HOMO of **5**; (d) HOMO–1 of **5**; (e) HOMO of **6**; (f) HOMO–1 of **6**.

2.431(3) and 2.461(3) Å, respectively, are at the lower and higher end of the range of reported yttrium-benzyl bond distances,²³ and the difference between them may reflect a *trans*-effect from the iodide ligand. The Y(1)–I(1) bond distance of 3.0981(3) Å is unremarkable.²¹

Encouraged by the successful and straightforward preparation of **1**, we sought to extend the synthetic protocol to a heavier rare earth metal. The erbium analogue $[Er(Bn)_2-(I)(THF)_3]$ (**2**) was prepared from $[Er(I)_3(THF)_{3,5}]^{21}$ and $[K-(Bn)]^{20}$ as a microcrystalline solid in 85% yield (Scheme 1). Pink single crystals of **2** were grown from a solution in THF layered with hexane and were found to be isostructural to **1**;

^{(22) (}a) Jones, C.; Stasch, A.; Woodul, W. D. *Chem. Commun.* **2009**, 113. (b) Beaini, S.; Deacon, G. B.; Delbridge, E. E.; Junk, P. C.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2008**, 4586.

⁽²³⁾ As evidenced from a search of the Cambridge Structural Database (CSD version 1.11, date 07/08/2009): (a) Allen, F. H. Acta Crystallogr. Sect. B 2002, 58, 380. (b) Allen, F. H.; Kennard, O. Chem. Des. Autom. News 1993, 8, 31.

Table 2. Crystallographic Data for 1–4

	1	2	3	4
formula	C ₂₆ H ₃₈ IO ₃ Y	C ₂₆ H ₃₈ ErIO ₃	C44 25H60IN2O2P2Si2Y	C39H54ErIN2O2P2Si2
fw	614.37	692.72	985.87	995.12
cryst size, mm	0.81 imes 0.27 imes 0.25	$0.52 \times 0.45 \times 0.42$	0.33 imes 0.11 imes 0.06	0.27 imes 0.26 imes 0.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	8.4422(5)	8.4244(6)	22.2321(15)	12.6861(4)
b, Å	21.3091(13)	21.3331(14)	10.4676(7)	17.9166(5)
<i>c</i> , Å	14.9695(9)	14.9588(10)	22.5947(15)	19.2882(6)
β , deg	104.035(2)	104.078(2)	101.744(2)	96.902(2)
$V, Å^3$	2612.6(3)	2607.6(3)	5148.1(6)	4352.3(2)
Z	4	4	4	4
$\rho_{\rm calcd}, {\rm g} {\rm cm}^{-3}$	1.562	1.765	1.272	1.519
μ, mm^{-1}	3.437	4.426	1.874	2.799
no. of reflections measd	15963	16106	25216	27 317
no. of unique reflns, R_{int}	4590, 0.0190	5975, 0.0316	9030, 0.0370	9946, 0.0197
no. of reflns with $F^2 > 2\sigma(F^2)$	4169	5769	6635	8763
transmn coeff range	0.42-0.24	0.24-0.20	0.90-0.57	0.58 - 0.49
$R, R_{w}^{a}(F^{2} > 2\sigma)$	0.0291, 0.0631	0.0303, 0.0804	0.0409, 0.0929	0.0211, 0.0511
R, R_{w}^{a} (all data)	0.0252, 0.0648	0.0314, 0.0811	0.0595, 0.0987	0.0274, 0.0546
S^{a}	1.036	1.113	0.980	1.026
parameters	298	281	496	448
max., min. diff map, e $Å^{-3}$	0.57, -0.43	2.01, -1.91	0.74, -0.59	0.93, -0.48

^{*a*} Conventional $R = \sum ||F_0| - |F_c|| / \sum |F_0|$; $R_w = \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 |^{1/2}$; $S = \sum w(F_o^2 - F_c^2)^2 / \text{no. data - no. params})^{1/2}$ for all data.

selected bond lengths are compiled in Table 1. With 1 and 2 in hand, we tested their synthetic utility in reactions with H_2BIPM .

Compounds 1 and 2 react smoothly with H₂BIPM at room temperature to give facile access to the doubly deprotonated carbene complexes [Ln(BIPM)(I)(THF)₂] (Ln = Y, 3; Er, 4) as colorless and pink crystals in 68% and 81% yields, respectively (Scheme 1). The ³¹P{¹H} NMR spectrum of 3 exhibits a doublet at 3.48 ppm (${}^{2}J_{YP} = 12.96$ Hz) and the ¹³C{¹H} NMR spectrum of 3 exhibits a triplet of doublets at 60.28 ppm ($J_{PC} = 207.30$; $J_{YC} = 5.03$ Hz), which is similar to that observed in related yttrium-BIPM complexes.¹⁵⁻¹⁸

Crystalline samples of 3 and 4 suitable for X-ray diffraction were obtained from toluene. The molecular structure of 3 is illustrated in Figure 2, and selected bond lengths and angles for 3 and 4 are tabulated in Table 1. Since the structures of 3 and 4 are very similar, we confine our discussion to 3. The yttrium center is distorted from an octahedral geometry by the bite angle of the BIPM ligand [133.86(9)°]. Of principal interest is the nearly perfect T-shaped geometry at C(1) ($\sum \angle = 359.4(2)^{\circ}$); indeed the YN₂P₂C ring adopts a rare, essentially planar geometry, whereas a boat conforma-tion is more usual for BIPM.²⁴ We suggest this is due to the softer iodide rendering the yttrium center more Lewis acidic than in the corresponding alkyls (I and II), so the carbene is drawn closer to the yttrium center, resulting in the planar configuration. The Y(1)-C(1) bond length of 2.356(3) Å is ~ 0.05 Å shorter than in I, and, while short, it is not the shortest reported to date (range of 2.339-2.632 Å).²³ In **3** the P-N and endocyclic P-C bonds are longer and shorter, respectively, compared to H₂BIPM,²⁵ and the exocyclic P-C bonds are ~ 0.01 Å longer.

DFT studies of I and II showed that the carbene centers contain a nonbonding pair of electrons due to the YN_2P_2C ring boat conformation.^{15,17} Since the carbene centers in **3**

and **4** bind in-plane, the potential for C-Y π -bonding is maxmized. We therefore carried out DFT calculations on the full structure of **3** and, for comparison, the BIPM dianion (**5**) and the carbodiphosphorane Ph₃PCPPh₃ (**6**) (see Supporting Information for further details). The latter was included due to the similarity of the valid heteroallene resonance forms $R_3P^+-C^{2-}-P^+R_3 \leftrightarrow R_3P^+-C^-=PR_3 \leftrightarrow R_3P=C=PR_3$ for **3**, **5**, and **6**. In each case the key features of the available X-ray structures are reproduced well by the calculations with bond lengths typically overestimated by 0.03 Å.²⁶

The natures of the HOMO and HOMO-1 Kohn-Sham orbitals for each calculation (Figure 3) show little change in the gross nature of the two carbon-based frontier orbitals. The orbitals are composed as follows: 3, HOMO 53.7% C_p, 2% Y, 5.9% P, HOMO-1 58.0% C_p, 3.2% Y, 2% P; 5, HOMO 60.3% C_p, 12.6% P, HOMO-1 56.1% C_p, 13.2% P; 6, HOMO 60.7% C_p, 16.7% P, HOMO-1 51.2% C_p, 10.1% C_s, 13.8% P. The trends from the NBO analyses for 3, 5, and 6 (see Supporting Information) are clear-cut: (i) the central carbon atom of the carbene ligand carries a negative charge between -1.32 and -1.58; (ii) the phosphorus centers carry a positive charge between +1.32 and +1.61; (iii) the nitrogen atoms in 3 and 5 possess a negative charge between -1.48and -1.56. The P-C and P-N bond orders are consistently > 1, which reflects a polarization of the central carbon and nitrogen lone pairs toward phosphorus, although true multiple bonds are clearly not manifested. NBO analyses show C-P σ -bonds with ~60% carbon 2sp and ~40% phosphorus $3sp^3$ character and frontier orbitals of π -symmetry with $\sim 90\%$ carbon 2p and $\sim 10\%$ phosphorus 3pd compositions for 3, 5, and 6. The latter values indicate that negative hyperconjugation is minimal in these systems.²⁷ NBO analysis of the Y-C interaction reveals a highly polarized interaction with 95% carbon 2p and 5% yttrium 4d contributions to this bond. This is consistent with

^{(24) (}a) Cantat, T.; Mézailles, N.; Auffrant, A.; Le Floch, P. Dalton Trans. 2008, 1957. (b) Jones, N. D.; Cavell, R. G. J. Organomet. Chem.
2005, 690, 5485. (c) Cavell, R. G.; Kamalesh Babu, R. P.; Aparna, K. J. Organomet. Chem. 2001, 617–618, 158.

⁽²⁵⁾ Appel, R.; Ruppert, I. Z. Anorg. Allg. Chem. 1974, 406, 131.

^{(26) (}a) Hardy, G. E.; Kaska, W. C.; Chandra, B. P.; Zink, J. I. J. Am. Chem. Soc. **1981**, 103, 1074. (b) Hardy, G. E.; Zink, J. I.; Kaska, W. C.; Baldwin, J. C. J. Am. Chem. Soc. **1978**, 100, 8001. (c) Vincent, A. T.; Wheatley, P. J. J. Chem. Soc., Dalton Trans. **1972**, 617.

⁽²⁷⁾ Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. Angew. Chem., Int. Ed. 2006, 45, 8038.

Coulombic attraction between these centers within the BIPM ligand in the dipolar $N^-P^+-C^{2-}-P^+-N^-$ resonance form, which has now emerged as the most accurate description of the bonding within other early metal BIPM complexes.^{15,17,24,28} However, given the close similarity between the frontier orbitals and atomic charges of **3** and **6**, the intriguing possibility of categorizing **3** and **4** as captodative carbon(0) complexes of yttrium and erbium should not be dissmissed.²⁹

Summary and Conclusions

In summary, utilizing readily available reagents we have prepared heteroleptic dibenzyl yttrium (1) and erbium (2) iodides. Both 1 and 2 are accessible as thermally stable crystalline solids in high yields, and they each exhibit remarkable stability with respect to ligand scrambling. The potential widespread utility of 1 and 2 in rare earth chemistry was demonstrated by their successful use in the synthesis of yttrium (3) and erbium (4) carbene derivatives that exhibit unusual T-shaped carbon geometries. We are currently seeking to extend the synthesis of 1 and 2 across the whole rare earth series and are investigating the reactivity of 3 and 4, and we will describe these experiments in subsequent publications.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles, and stored under nitrogen. The compounds $[LnI_3(THF)_n]$,²¹ [K(Bn)],²⁰ and H₂-BIPM²⁵ were prepared according to published procedures. ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectra were recorded on a

¹H, ¹³C, ³¹P, and ²⁵Si NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, 162.0, and 79.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (¹H, ¹³C, and ²⁹Si) and external 85% H₃PO₄ (³¹P). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental microanalyses were carried out by Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Preparation of [Y(Bn)₂(I)(THF)₃] (1). THF (30 mL) was added to a precooled (0 °C) mixture of PhCH₂K (1.30 g, 10.00 mmol) and [YI₃(THF)_{3,5}] (3.61 g, 5.00 mmol), and the resultant beige mixture was stirred at this temperature for 4 h. The mixture was filtered and volatiles were removed *in vacuo* to afford **1** as a brown oil of sufficient purity for further reaction. A pale beige powder was obtained by stirring the oil in hexane (30 mL) overnight, followed by filtration of the supernatant solution and drying *in vacuo*. Yield: 1.60 g, 62%. Colorless crystals were grown at 5 °C overnight from a saturated THF solution. Yield: 1.17 g, 45%. Anal. Calcd for C₂₆H₃₈IO₃Y: C, 50.83; H, 6.23. Found: C, 50.71; H, 6.22. ¹H NMR (*d*₈-THF, 298 K): δ 1.81 (m, 12H, OCH₂CH₂ and CH₂Ph), 3.66 (m, 8H, OCH₂CH₂), 6.44 (t, ³J_{HH} = 6.80 Hz, 2H, *p*-Ar-CH), 6.88 (m, ³J_{HH} = 7.20 Hz, 6H, *m*-Ar-CH) and 6.93 (d, ³J_{HH} = 7.20 Hz, 4H, *o*-Ar-CH). ¹³C{¹H} NMR (*d*₈-THF, 298 K): δ 25.40 (OCH₂CH₂), 55.10 (d, ${}^{1}J_{YC}$ = 34.3 Hz, CH₂Ph), 67.61 (OCH₂-CH₂), 115.88 (Ar-C), 123.62 (Ar-C), 127.61 (Ar-C) and 153.22 (*ipso*-Ar-C). IR ν /cm⁻¹ (Nujol): 1586 (m), 1213 (m), 1014 (m), 904 (m), 852 (br, m), 794 (m), 745 (m), 703 (w), 675 (w).

Preparation of [Er(Bn)₂(I)(THF)₃] (2). This was prepared by the same general method as 1, with PhCH₂K (0.78 g, 6.00 mmol) and [ErI₃(THF)_{3.5}] (2.40 g, 3.00 mmol), and was isolated as an orange-pink microcrystalline solid. Yield: 1.77 g, 85%. Pink crystals were grown at 5 °C overnight from a THF solution layered with hexane. Yield: 0.53 g, 26%. Anal. Calcd for C₂₆H₃₈IO₃Er: C, 45.08; H, 5.53. Found: C, 44.99; H, 5.46. μ_{eff} (Evans method, 298 K, THF): 9.34 μ_{B} . IR ν/cm^{-1} (Nujol): 1586 (s), 1297 (w), 1260 (w), 1212 (s), 1177 (m), 1014 (m), 910 (br, s), 855 (br, s), 795 (m), 746 (m), 703 (m), 536 (w).

Preparation of [Y(BIPM)(I)(THF)₂] (3). A solution of H₂C-(PPh₂NSiMe₃)₂ (1.12 g, 2.00 mmol) in toluene (15 mL) was added dropwise to a suspension of 1 (1.23 g, 2.00 mmol) in toluene (15 mL) at -78 °C. The mixture was allowed to slowly warm to room temperature with stirring over 18 h. Volatiles were removed *in vacuo*, and the resulting pale yellow solid was recrystallized from toluene (1.50 mL) to afford **3** as colorless crystals. Yield: 1.13 g, 68%. Anal. Calcd for C₃₉H₅₄IN₂O₂P₂. Si₂Y: C, 51.09; H, 5.94; N, 3.06. Found: C, 51.07; H, 5.78; N, 3.13. ¹H NMR (*d*₈-THF, 298 K): δ 0.12 (s, 18H, NSi(CH₃)₃), 1.82 (m, 8H, OCH₂CH₂), 3.68 (m, 8H, OCH₂CH₂), 7.21 (t, ³J_{HH} = 7.20 Hz, 8H, *m*-Ar-CH), 7.31 (t, ³J_{HH} = 7.20 Hz, 4H, *p*-Ar-CH) and 7.48 (dd, ³J_{HH} = 7.20 Hz, 8H, *o*-Ar-CH). ¹³C{¹H} NMR (*d*₈-THF, 298 K): δ 3.91 (NSi(CH₃)₃), 25.43 (OCH₂CH₂), 60.28 (td, ¹J_{PC} = 207.30 Hz, ¹J_{YC} = 5.03 Hz, YCP₂), 67.39 (OCH₂CH₂), 127.07 (Ar-C), 129.12 (Ar-C), 131.09 (Ar-C) and 141.81 (t, ¹J_{PC} = 47.80 Hz, *i*-Ar-C). ³¹P{¹H} NMR (*d*₈-THF, 298 K): δ 3.48 (d, ²J_{YP} = 12.96 Hz, NPC). ²⁹Si{¹H} NMR (*d*₈-THF, 298 K): δ -3.05 (virtual t, ²J_{PSi} = 3.98 Hz, NS*i*-(CH₃)₃). IR ν/cm⁻¹ (Nujol): 1260 (w), 1241 (w), 1105 (s), 1088 (m), 1066 (s), 832 (s), 725 (m), 521 (m).

Preparation of [Er(BIPM)(I)(THF)₂] (4). This compound was prepared by the same general method as **3**, with **2** (1.83 g, 2.64 mmol) and H₂C(PPh₂NSiMe₃)₂ (1.48 g, 2.64 mmol), and was isolated as pink crystals. Yield: 1.82 g, 81%. Anal. Calcd for C₃₉H₅₄ErIN₂O₂ P₂Si₂Er: C, 47.07; H, 5.47; N, 2.82. Found: C, 46.97; H, 5.54; N, 2.73. μ_{eff} (Evans method, 298 K, THF): 7.18 μ_{B} . IR ν/cm^{-1} (Nujol): 2360 (w), 1261 (m), 1081 (br, m), 1022 (m), 800 (m), 691 (w), 667 (w).

X-ray Crystallography. Crystal data for compounds 1-4 are given in Table 2, and further details of the structure determinations are in the Supporting Information. Bond lengths and angles are listed in Table 1. Crystals were examined variously on Bruker AXS SMART 1000 or APEX CCD area detector diffractometers using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ A). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semiempirical absorption corrections based on symmetry-equivalent and repeat reflections were applied. The structures were solved variously by direct methods and were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{iso}(H)$ was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Highly disordered solvent molecules of crystallization in 3 could not be modeled and were treated with the Platon SQUEEZE procedure.³⁰ Programs were Bruker AXS SMART (control) and SAINT (integration),³¹ and

^{(28) (}a) Orzechowski, L.; Jansen, G.; Lutz, M.; Harder, S. *Dalton Trans.* **2009**, 2958. (b) Orzechowski, L.; Harder, S. *Organometallics* **2007**, 26, 2144. (c) Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676.

⁽²⁹⁾ Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürster, A. Nat. Chem. 2009, 1, 295.

⁽³⁰⁾ Spek, A. L. *Platon SQUEEZE*; University of Utrecht: The Netherlands, 2000.

⁽³¹⁾ Bruker SMART and SAINT; Bruker AXS Inc.: Madison, WI, 2001.

SHELXTL was employed for structure solution and refinement and for molecular graphics. $^{\rm 32}$

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Supporting Information Available: Variable-temperature NMR study of 1, details of the DFT calculations, including calculated coordinates and energies of 3, 5, and 6, and X-ray crystallography of 1–4. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

⁽³²⁾ Sheldrick, G. M. SHELXTL. Acta Crystallogr., Sect. A 2008, 64, 112.