Synthesis and Reactivity of Dialkyl Lutetium Complexes Supported by a Novel Bis(phosphinimine)carbazole Pincer Ligand

Kevin R. D. Johnson and Paul G. Hayes*

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB, Canada, T1K 3M4

Received August 20, 2009

The synthesis of a novel bis(phosphinimine) ancillary ligand based on a carbazole framework is described (HL, 4a; HLP, 4b; Ph = phenyl, Pipp = para-isopropylphenyl). Protonolysis with Lu(CH2SiMe3)3(THF) afforded the corresponding lutetium dialkyl complexes (LuL(PPh(CH2SiMe3))2, 5a; LuL(Pipp(CH2SiMe3))2, 5b), which were thermally sensitive and rapidly underwent intramolecular metatative alkane elimination to generate LuL(PPh(CH2SiMe3))(THF), 6a, and LuL(Pipp(CH2SiMe3))- (THF), 6b, as highly reactive intermediates. Complexes 6a and 6b further decomposed, cleanly generating doubly metalated complexes LuL(PPh3)(THF), 7a, and LuL(Pipp3)(THF), 7b, respectively, as the thermodynamic products. Kinetic analysis of the decomposition of 5a revealed a first-order mechanism with activation parameters \( \Delta H^* = 19.2(1) \text{ kcal mol}^{-1} \) and \( \Delta S^* = -8.2(2) \text{ cal K}^{-1} \text{ mol}^{-1} \).

Compounds 4a, 4b, 6b, and 7b were characterized by single-crystal X-ray diffraction studies.

Introduction

Although organometallic chemistry of group 3 and lanthanide metals has received an increasing amount of attention over the past two decades, it still lags significantly behind that of the transition metals. This is in part due to the highly ionic nature of the lanthanides and reactivity issues such as ligand redistribution and “ate” complex formation. Largely these challenges can be overcome through the use of appropriate lanthanide precursors that incorporate sufficient steric bulk to saturate the coordination sphere of the metal or, alternatively, with ancillary ligands that impose a multidentate coordination mode. Despite this, the lack of adequate ancillaries for supporting these metals has drastically limited their applications in organometallic processes such as olefin polymerization, catalytic hydroamination, and \( \text{C–H} \) bond activation. While the cyclopentadienyl ligand system has been extremely influential in the development


of organolanthane chemistry, it is limited in the extent to which it can be electronically or sterically tuned. Thus, the development of more versatile ancillary ligands may provide access to metal complexes with unique structure, reactivity, and enhanced catalytic activity. Herein, we report the synthesis of a novel family of monoanionic carbazole-based pincer ligands and their ability to support well-defined mononuclear organometallic complexes.

Results and Discussion

Ligand Synthesis and Characterization. A novel monoa-
nionic ligand has been prepared whereby two phosphinimine donors have been installed at the 1 and 8 positions of a rigid 3,6-dimethylcarbazole (dmc) backbone. The presence of polar phosphinimine subunits is desirable, as they have been shown to provide ancillary ligands with enhanced capacity for electronic donation.10–12 Furthermore, the phosphinimine functionality allows for a high degree of sterically and electronic tunability through adjustment of R groups attached at the phosphorus and nitrogen atoms. In particular, the incorporation of sufficient steric bulk may assist in blocking Lewis bases such as tetrahydrofuran (THF) from binding to the metal center. The presence of sterically demanding groups can also help to reduce the potential for dimerization; however, the degree of incorporated bulk must be carefully selected so as to not completely inhibit reactivity at the metal center.

The high-yielding synthesis of the dmc-based ancillary is outlined in Scheme 1. From 1,8-dibromo-3,6-dimethylcar-
barazole,13 N-protection with tert-butoxy carbonyl afforded 1, which was lithiated and allowed to react with chlorodiphe-
nylphosphine to generate the corresponding diphosphine 2. Removal of the protecting group was efficiently achieved under thermal conditions14 (160 °C for 4.5 h), liberating deprotected compound 3. The synthesis of the desired proteo ligand (HL3, 4a; HL3pp, 4b; Ph = phenyl; Pipp = para-isopropylphenyl) was completed by reaction of 3 with an appropriate aryl azide under standard Staudinger conditions,15 installing the phosphinimine functionality with concomitant loss of N2. This four-step synthetic pathway is highly efficient with overall yields of 73% (4a) and 53% (4b).

Single crystals of 4a suitable for an X-ray diffraction study were readily obtained upon recrystallization from a benzene solution layered with pentane at ambient temperature. The molecular structure of 4a is illustrated in Figure 1 as a thermal ellipsoid plot. Ligand 4a was designed to chelate metals in a tridentate motif with N1, N2, and N3 occupying a common plane with the aromatic dmc backbone. In the solid state, N1 indeed lies approximately within the same plane as the dmc backbone (N1–P1–C1–C12 torsion angle of –11.1(4)°). However, N3 lies significantly out of this plane with an N3–P2–C8–C9 torsion angle of 68.4(4)°. The rotation of the P2–N3 arm out of the plane of the dmc backbone is likely due to steric interactions between the two N-phenyl groups on the phosphinimine moiety. It is possible that in the solid state N1 lies within the plane of the dmc backbone due to the hydrogen-bonding interaction that exists between it and H2C. The distance between the donor and acceptor nitrogen atoms in the N2–H2C···N1 interaction in 4a is 2.789(5) Å.

Similar to 4a, single crystals of 4b were obtained from a concentrated benzene solution layered with pentane. The molecular structure of 4b, as determined from an X-ray diffraction experiment, is depicted in Figure 2. Analogous to that described for 4a, ligand 4b has one nitrogen donor (N1) lying in the same plane as the dmc backbone and one (N3) out of the plane. The N1–P1–C1–C12 and N3–P2–C8–C9 torsion angles of 7.8(2)° and –70.7(2)°, respectively, correspond well with that observed for 4a. In comparison to that of 4a, the N3 group in 4b is rotated about 2° further out of plane from the aromatic backbone, while the N1 group is approximately 2° closer to the plane of the dmc backbone. This small, but statistically relevant difference may be attributed to the presence of the isopropyl groups in the para positions of the N-aryl rings of 4b, which create slightly greater steric repulsion between the N-aryl rings. It is notable that only minor differences in the geometry of 4a and 4b are observed, a fact that correlates well with


the identical reaction rates of ligand metalation observed for complexes 5a and 5b (vide infra).

Proteo ligands 4a and 4b are both C$_2$v symmetric on the NMR time scale. Each ligand exhibits a sharp singlet (δ = 5.41, 4a; δ = 11.7, 4b) in its $^{31}$P{1H} NMR (CDCl$_3$) spectrum. The 1H NMR spectrum of 4a (CDCl$_3$) has a single methyl resonance at δ = 2.44, a broad NH peak at δ = 11.8, and an expectedly complicated aromatic region. Similarly, the 1H NMR spectrum of 4b (CDCl$_3$) displays a singlet at δ = 2.45 corresponding to the symmetric methyls of the dmc backbone and a broad NH signal at δ = 11.7. The 1H NMR spectrum of 4b also features isopropyl resonances at δ = 2.74 (sp, CH$_3$) and δ = 1.17 (d, CH$_3$) in addition to a well-defined AB spin pattern (δ = 6.74, d; δ = 6.64, d) corresponding to protons on the N-aryl rings.

Organolutetium Reactivity. Complexation with lutetium was readily achieved via the alkane elimination reaction of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 4a or 4b (Scheme 2). When equimolar quantities of 4 and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ were reacted in cold (−78 °C) toluene-$d_8$, the corresponding dialkyl metal complexes LuL$^{Ph}$Ph$_2$(CH$_2$SiMe$_3$)$_2$, 5a, and LuL$^{Pipp}$Pipp$_2$(CH$_2$SiMe$_3$)$_2$, 5b, began to cleanly form as highly thermally sensitive compounds. Upon warming the solution to 0 °C, complete conversion to dialkyl 5 was achieved, as evidenced by consumption of the sparingly soluble proteo ligand and formation of a clear yellow solution. Accordingly, when the reaction was monitored in situ, the generation of 1 equiv of tetramethylsilane was observed by $^1$H NMR spectroscopy. Due to the thermal sensitivity of dialkyl species 5a and 5b, neither complex could be isolated as a pure solid. All attempts to do so resulted in samples contaminated with the thermodynamic decomposition product 7 (vide infra). However, both complexes were quantitatively generated
The $^1$H NMR spectra of 5 in toluene-$d_8$ exhibit diagnostic methyl and methylene resonances upfield of 0 ppm for the protons of the trimethylsilylmethyl groups (5a, 271.3 K: $\delta$ = -0.06 (CH$_3$), -0.79 (CH$_2$); 5b, 249.1 K: $\delta$ = -0.01 (CH$_3$), -0.72 (CH$_2$)). Upon cooling solutions of 5a or 5b below -60 °C the two trimethylsilylmethyl moieties become inequivalent with splitting of the methylene resonances, indicating a reduction in molecular symmetry from $C_2$ to $C_s$. In the $^{31}$P{$^1$H} NMR spectra (toluene-$d_8$), a significant downfield shift of the phosphine functionality is observed upon complexation with lutetium (5a, 271.3 K: $\delta$ = 29.4; 5b, 249.1 K: $\delta$ = 29.4). As the phosphine functionality is highly sensitive to its coordination environment, the large downfield shift is indicative of complexation with the electropositive lutetium center.$^{10-12}$ In addition, the sharp single resonance in the $^{31}$P{$^1$H} NMR spectrum corroborates that the ancillary is bound to lutetium in a $\kappa^3$-coordination mode. Although 2 equiv of THF are present in the in situ-generated reaction mixture, it appears that the dialkyl lutetium complex is five-coordinate with no THF donors bound to the metal. Specifically, toluene-$d_8$ solutions of 5 at temperatures between -40 and 0 °C (the range in which 5 is relatively thermally stable) exhibit resonances in the $^1$H and $^{13}$C{$^1$H} NMR spectra consistent with free THF.

At temperatures above 0 °C, toluene solutions of 5 undergo two sequential intramolecular metatative alkane eliminations whereby both alkyl groups are liberated as RH through a $\sigma$-bond metathesis pathway with the ortho C–H bonds of the adjacent P-phenyl rings. Upon monitoring the decomposition of 5 by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy, the formation of an asymmetric intermediate with $C_1$ symmetry was observed (Scheme 3). This transient species, assigned as monometalated complex 6, then undergoes a second intramolecular $\sigma$-bond metathesis process with a phenyl group from the other phosphinine phosphorus (vide infra), releasing a second equivalent of tetramethylsilane. The final $C_2$ symmetric products 7a and 7b are the result of a rare double-metatation process. These $\kappa^2$-bound lutetium diaryl species consist of two six-membered metallacycles complete with bridging phenyl rings.

The loss of symmetry in the final thermodynamic products, 7a and 7b, compared to the initial dialkyl complexes (5a and 5b), was difficult to ascertain through $^1$H NMR spectroscopy due to overlapping signals in the aromatic region of the spectrum. However, $^{11}$C{$^1$H} NMR spectroscopy proved to be diagnostic in this regard. The metalated ipso carbon attached directly to lutetium is highly deshielded and resonates far downfield as a doublet of doublets at $\delta$ = 204.6 (dd, $^2$J$_{PC}$ = 41.2 Hz, $^4$J$_{PC}$ = 1.1 Hz, 7a) and $\delta$ = 204.7 (dd, $^2$J$_{PC}$ = 40.9 Hz, $^4$J$_{PC}$ = 1.2 Hz, 7b). Such values correspond well with the shifts reported for other neutral lutetium aryl species such as LuPh$_3$(THF)$_2$ ($\delta$ = 198.7, benzene-$d_6$),$^{16}$ Lu(p-tol)$_2$(THF)$_2$ ($\delta$ = 195.2, benzene-$d_6$),$^{16}$ Lu(C$_8$H$_7$-$p$-Et)$_3$(THF)$_2$ ($\delta$ = 194.2, benzene-$d_6$),$^{16}$ (Cp*)$_2$LuPh ($\delta$ = 198.5, cyclohexane-$d_1$)$_2$,$^{17}$ and Lu(o-C$_8$H$_7$CH$_2$NMe$_2$)$_3$ ($\delta$ = 196.7, benzene-$d_6$).$^{18}$

Organometallics, Vol. 28, No. 21, 2009

Kinetic Analysis. The decomposition from derivative 5a to 6a was quantitatively monitored by $^{31}$P{H} NMR spectroscopy and revealed to be first order in the dialkyl species. The reaction progress at 293.5 K (from $t = 1760$ s to $t = 15,500$ s) is depicted in Figure 3 as a stacked plot of $^{31}$P{H} NMR spectra. As can be seen from the plot, the decreasing concentration of 5a (δ 29.4) is accompanied by the growth of two broad peaks resonating at δ 27.5 and 22.7 for asymmetric intermediate 6a. Within 4 h at this temperature complex 6a gradually converts exclusively to thermodynamic product 7a (δ 25.6).

The reaction was followed over a broad range of temperatures (282.4 to 326.9 K; Figure 4a), with observed $t_{1/2}$ values ranging from 5690 to 44.7 s (Table 1). Construction of an Eyring plot (Figure 4b) allowed for extraction of the
activation parameters, $\Delta R^f = 19.2(2)$ kcal·mol$^{-1}$ and $\Delta S^f = -8.2(2)$ cal·K$^{-1}$·mol$^{-1}$, for the metatlas process. These values correspond to that expected for a highly ordered four-transformed center state and agree well with others reported for intramolecular $\sigma$-bond metathesis reactions.  

Kinetic data for the conversion of 6a to 7a was not ascertained due to problems in accurately determining the concentration of 6a over the course of decomposition. Such difficulty stemmed from the broad peaks for 6a in the $^{31}$P-$^1$H NMR spectra, which could not be reproducibly integrated due to the low signal-to-noise ratio. In addition, certain temperature ranges gave rise to an overlap of resonances for 6a and 7a. As such, the sum of the concentration of 6a and 7a could be readily determined at those temperatures; however, it was not always possible to establish the concentration of each individual species without introducing significant error.

At 295.7 K, metalation of 5a proceeds at a rate of 5.89 × $10^{-4}$ s$^{-1}$, while that for 5b was found to be 5.98 × $10^{-4}$ s$^{-1}$ (Table 1). The high degree of correlation between these two rates suggests that the presence of the isopropyl groups in the para positions of the N-aryl rings of 5b does not significantly alter reactivity. This result was anticipated, as the incorporation of isopropyl groups on 5b was intended solely for the purposes of (a) increasing solubility, (b) increasing crystallinity, and (c) providing more diagnostic $^1$H NMR resonances for the N-aryl ring compared to that available for 5a. Furthermore, the solid state structures of proto ligands, 4a and 4b, which were used to prepare 5a and 5b, were essentially isostructural (vide supra).

**Solid State Structures.** In order to unambiguously establish that the C–H bond activation of the ancillary ligand occurred through the ortho carbon of the phenyl rings on phosphorus, single-crystal X-ray diffraction studies were performed. Crystals of 6b were serendipitously obtained from an in situ-generated solution of 5b in a 4:1 mixture of toluene and THF at ~35 °C over the course of ~1 week. As 5b slowly decomposed at this temperature, intermediate 6b selectively crystallized out of solution. Under these dynamic and highly variable conditions the single crystallinity of 5b was of low quality, and repeated attempts to grow higher quality crystals of this unstable intermediate were unsuccessful. Despite the challenges encountered with crystal quality, a reliable set of low-intensity single-crystal data was obtained for complex 6b. Such data were sufficient for unambiguously establishing the connectivity of the structure; however, no meaningful comments on the metrical parameters can be made at this time.

A thermal ellipsoid plot of 6b is depicted in Figure 5. The solid state structure confirms that the ligand is bound to lutetium in a κ$^4$-fashion, bonding through three nitrogen atoms, as well as via an ortho carbon of one P-phenyl ring. One trimethylsilylmethyl group remains attached to lutetium as well as one THF donor, giving rise to a structure with distorted octahedral geometry. This structural information corroborates the postulated intermediate in the conversion of dialkyl complex 5b to diaryl species 7b (Scheme 3). Due to the very small (~10 mg) crop of crystals obtained from the crystallization of 6b, insufficient material was available for further characterization.


In contrast to the unstable nature of 6b, diaryl lutetium 7b can easily be prepared on a multigram scale. Reaction of 4b with Lu(CH₂SiMe₃)₃(THF)₂ in benzene for 18 h at ambient temperature generated 7b, which was isolated as a pure yellow crystalline solid. Recrystallization from a benzene solution layered with pentane at ambient temperature afforded large needles of 7b, which were suitable for X-ray diffraction. It was found that complex 7b crystallized with two independent molecules in the asymmetric unit, in addition to a variety of solvent molecules. These independent structures, 7b and 7b', are enantiomers of one another and are depicted as thermal ellipsoid plots in Figure 6a and b, respectively.

At ～1.61 Å, complexes 7b and 7b' exhibit P–N bonds that are elongated relative to that of the free ligand (average P–N = 1.575 Å). Such lengthening is indicative of strong donation from the phosphinimine functionality to the metal center; however, such a distance is still consistent with a formal phosphorus–nitrogen double bond.¹¹ The Lu–Caryl contacts in 7b and 7b' range from 2.425(8) Å in 7b' to 2.472(8) Å in 7b. These values fall within the normal range for neutral Lu–Caryl bonds.¹¹a,b,18,21 Complexes 7b and 7b' both exhibit distorted octahedral geometry at the lutetium center, with the ancillary ligand occupying five of the six coordination sites. The sixth site composing the octahedron is occupied by the THF donor. No attempt has yet been made to remove or exchange the coordinated Lewis base. Future work will explore such processes and investigate the exciting possibility that 7b may serve as a low-valent (Lu(I)) synthon (via metalation reversal promoted by reaction with reagents of the form H₂ER or H₂SiR₂ (E=N, P; R=sterically bulky group)).²²

Concluding Remarks

In summary, the synthesis and characterization of a versatile family of pincer ligands, which represent a new versatile family of pincer ligands, which represent a new

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere with the rigorous exclusion of oxygen and water using standard glovebox (MBraun) or high vacuum line techniques, unless specified otherwise. The solvents THF, diethyl ether, dichloromethane (DCM), pentane, benzene, and toluene were dried and purified using a solvent purification system (MBraun) and stored in evacuated 500 mL bombs over sodium benzenophenone ketyl (THF and ether), CaH₂ (DCM), or “titaneocene” (pentane, benzene, and toluene). Deuterated solvents were dried over sodium benzenophenone ketyl (benzene-d₆ and toluene-d₆) or CaH₂ (DCM), degassed via three freeze–pump–thaw cycles, distilled under vacuum, and stored in glass bombs under argon. Unless otherwise specified, all solvents required for air-sensitive manipulations were introduced directly into the reaction flasks by vacuum transfer with condensation at ～78 °C. For air-stable manipulations, the solvents THF, diethyl ether, DCM, and n-hexane were purchased from EMD Chemicals and used without further purification. Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (Ultrashield) spectrometer (¹H 300.138 MHz, ¹³C–¹H 75.468 MHz, ³¹P{¹H} 121.495 MHz) and referenced relative to either SiMe₄ through the residual solvent resonance(s) for ¹H and ¹³C–¹H or external 85% H₃PO₄ for ³¹P{¹H}. All NMR spectra were recorded at ambient temperature (295 K) unless specified otherwise. FT–IR spectra were recorded on a Bruker ALPHA FT infrared spectrometer with Platinum ATR sampling. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. Phenyl azide,²³ 1,8-dibromo-3,6-dimethylcarbazole,¹³ and Lu(2H₃SiMe₃)₃(THF)²⁴ were prepared according to literature procedures. The compound 4-isopropylphenyl azide was prepared according to a modified literature procedure.²³ Chlorodiphenylphosphine was purchased from Strem Chemicals and used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. All other reagents were obtained from Aldrich Chemicals or Alfa Aesar and used as received.

4-Isopropylphenyl Azide. Aqueous 5 M HCl (125 mL) was added dropwise to a clear dark red solution of 4-isopropylamine (10.0 g, 74.2 mmol) in THF (100 mL) at 0 °C. The red-brown solution was stirred for 15 min, following which a solution of NaNO₂ (5.63 g, 81.6 mmol) in H₂O (65 mL) was added dropwise over 20 min. Urea (0.708 g, 11.8 mmol) was added as a solid to remove excess nitrous acid. A solution of Na₂S (5.65 g, 87.0 mmol) in H₂O (50 mL) was added very slowly at 0 °C, after which the solution was stirred at this temperature for a further 2 h. The product was extracted into Et₂O (3 x 100 mL), and the organic layer was washed with 1 x 100 mL of 1 M HCl, dried over MgSO₄, and concentrated in vacuo to give a dark red liquid. The product was purified by filtration through a silica column (20 cm), eluting with hexane. The hexane was removed under the eluent by rotational evaporation, leaving PPnN₃ as a canary yellow liquid. Yield: 10.4 g (86.7%).¹³ ¹H NMR (CDCl₃): δ 7.21 (d, 2H, J = 8.4 Hz, Ar–H), 6.96 (d, 2H, J = 8.4 Hz, Ar–H), 2.90 (sp, 1H, J = 6.9 Hz, CH), 1.24 (d, 6H, J = 6.9 Hz, CH₃), 2.93 ppm.¹³C–¹H NMR (CDCl₃): δ 145.9, 137.5, 127.9, 119.1 (Ar–Cs), 33.7 (CH), 24.2 (CH₃). IR (neat): 2960 (m), 2128 (s), 2092 (s), 1457 (s), 1222 (m). 19F NMR (CDCl₃): δ –63.6 ppm.¹⁴

Concluding Remarks

In summary, the synthesis and characterization of a versatile family of pincer ligands, which represent a new platform for stabilizing low-coordinate, electronically unsaturated organometallic species, have been described. These carbazole-based ligands have been utilized to prepare monomeric base-free dialkyllutetium complexes. Although these highly electrophilic complexes are thermally sensitive and undergo a rare double-metalative mechanism with the ortho C–H bonds of the P-phenyl rings, it is likely that minor structural modifications will yield complexes that are sufficiently stable to allow full exploration of their organometallic chemistry. As such, we are currently reducing the steric bulk around the peripheral edge of the ligand. It is anticipated that replacement of the phenyl groups attached to phosphorus with a less bulky moiety will dampen undesired metalation pathways.


The spectroscopic analysis of this compound agrees with previously published data for the fully characterized product.[26]

1.8-Dibromo-3,6-dimethyl-9-BOC-carbazole (1). An intimate mixture of 1.8-dibromo-3,6-dimethylcarbazole (0.468 g, 1.33 mmol) and dimethylaminopyridine (0.171 g, 1.40 mmol) was dissolved in 30 mL of dichloromethane to give a clear yellow solution. An excess of di-tert-butoxycarbonyl (0.479 g, 2.19 mmol) was added via syringe at ambient temperature. The clear red reaction mixture was stirred for 18 h, generating a yellow solution. The reaction was quenched by addition of 50 mL of 1 M HCl. The layers were separated, and the acidic layer was extracted with a further 2 × 50 mL of DCM. The combined fractions were then washed with 3 × 50 mL of 1 M NaHCO₃ followed by 2 × 50 mL of 3 M NaCl. The organic layer was dried over MgSO₄ and filtered, and the solvent was removed under vacuum. A white product was obtained as an off-white solid.

Yield: 0.506 g (82.4%).[1] ¹H NMR (CDCl₃): δ 7.62 (s, 2H, Ar-H), 7.43 (s, 2H, Ar-H), 2.44 (s, 6H, CH₃), 1.68 (s, 9H, OC(CH₃)₃). ¹³C[¹H] NMR (CDCl₃): δ 151.5 (C=O), 137.0, 133.3, 131.1, 127.5, 119.3, 106.2 (Ar-C), 86.5 (OC(CH₃)₃), 28.1 (OC(CH₃)₃), 20.9 (CH₃). IR (neat): 2978 (w), 2922 (w), 2860 (w), 1749 (m, ν C≡O), 1557 (w), 1478 (m), 1419 (w), 1368 (m), 1309 (m), 1230 (m), 1177 (s), 1064 (m), 836 (s) cm⁻¹. Anal. Calcd (% for C₅₆H₄₃N₃P₂: C, 49.83; H, 4.17; N, 3.16. Found: C, 49.83; H, 4.17; N, 3.16.

1.8-Bis(diphenylphosphino)-3,6-dimethyl-9-BOC-carbazole (2). A pentane solution of BuLi (1.40 mL, 2.38 mmol) was added dropwise to a solution of 1 (0.506 g, 1.12 mmol) in 50 mL of pentane at −78 °C. The resulting pentane layer was washed with ether under vacuum and the residue brought into a glovebox. The product was washed with 5 × 2 mL of pentane to remove excess azide and dried thoroughly under reduced pressure to afford crude HL[P₉] as a pale red solid.

Recrystallization from a hot benzene solution (20 mL) layered with pentane (15 mL) at ambient temperature generated 4a as an analytically pure pale yellow prisms. Yield: 6.03 g (96.4%).[1] ¹H NMR (CDCl₃): δ 11.8 (s, 1H, NH), 8.01 (s, 2H, Ar-H), 7.69 (m, 8H, PPh-H), 7.46 (4H, J = 6.9 Hz, PPh-H), 7.34 (m, 8H, PPh-H), 7.20 (2H, J = 14.5 Hz, Ar-H), 6.85 (4H, ν PPh-H), 6.68 (4H, J = 8.0 Hz, ν PPh-H), 6.58 (2H, J = 14.5 Hz, ν PPh-H), 2.44 (4s, 6H, CH₃). ¹³C[¹H] NMR (CDCl₃): δ 151.0 (d, J = 3.5 Hz, Ar-C), 140.6 (d, J = 2.9 Hz, Ar-C), 132.9 (d, J = 9.8 Hz, Ar-C), 131.7 (d, J = 2.6 Hz, Ar-C), 131.3 (d, J = 10.5 Hz, Ar-C), 130.8 (d, J = 89.5 Hz, Ar-C), 128.7 (d, J = 11.8 Hz, Ar-C), 128.3 (Ar-C), 117.3 (d, J = 17.4 Hz, Ar-C), 112.6 (d, J = 25.5 Hz, Ar-C), 123.8 (d, J = 18.0 Hz, Ar-C), 123.6 (d, J = 8.5 Hz, Ar-C), 117.3 (Ar-C), 111.6 (d, J = 118.8 Hz, Ar-C), 216.6 (CH₃). 3¹¹P[¹H] NMR (CDCl₃): δ 5.4. Anal. Calcd (%) for C₃₈H₂₄P₈N₉: C, 80.52; H, 5.54; N, 5.63. Found: C, 80.60; H, 5.93; N, 5.37.

HL[P₉] (4b). Benzene (75 mL) was added to a flask charged with 3 (2.09 g, 3.71 mmol) to give a light yellow solution. An aliquot of 4-isopropylphenyl azide (1.25 g, 7.72 mmol) was added via syringe at ambient temperature. Upon addition, the solution gradually became a red-orange color with concurrent evolution of nitrogen gas. The solution was stirred under an argon atmosphere for 20 h, following which the solvent was removed under vacuum and the residue brought into a glovebox. The product was purified from benzene (15 mL) layered with pentane (5 mL) at ambient temperature. Pale green crystals of 4b formed over 24 h and were collected by filtration, washed with 2 × 1 mL of pentane, and dried thoroughly under reduced pressure. Yield: 2.17 g (70.4%).[1] ¹H NMR (CDCl₃): δ 11.7 (s, 1H, NH), 8.00 (s, 2H, Ar-H), 7.71 (m, 8H, PPh-H), 7.46 (4H, J = 7.4 Hz, PPh-H), 7.33 (m, 8H, PPh-H), 7.23 (2H, J = 14.6 Hz, Ar-H), 6.74 (4H, J = 8.2 Hz, PPh-H), 6.64 (4H, J = 8.3 Hz, PPh-H), 2.74 (sp, 2H, J = 6.9 Hz, CH(CH₃)₂), 2.45 (4s, 6H, CH₃), 1.17 (d, 12H, J = 6.9 Hz, CH(CH₃)₂). ¹³C[¹H] NMR (CDCl₃): δ 148.3 (Ar-C), 140.5 (d, J = 2.9 Hz, Ar-C), 137.5 (Ar-C), 133.0 (d, J = 9.8 Hz, Ar-C), 131.6 (d, J = 25.5 Hz, Ar-C), 131.3 (d, J = 10.9 Hz, Ar-C), 130.9 (d, J = 87.2 Hz, Ar-C), 128.6 (d, J = 11.7 Hz, Ar-C), 127.9 (d, J = 12.8 Hz, Ar-C), 126.2 (Ar-C), 124.1 (d, J = 2.6 Hz, Ar-C), 123.5 (d, J = 17.6 Hz, Ar-C), 123.5 (d, J = 9.0 Hz, Ar-C), 111.9 (d, J = 120 Hz, Ar-C), 33.2 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 21.6 (CH₃). 3¹¹P[¹H] NMR (CDCl₃): δ 4.57. Anal. Calcd (%) for C₅₆H₄₃N₉P₈: C, 81.04; H, 6.44; N, 5.06. Found: C, 80.21; H, 6.50; N, 4.98.

Luf(P₉)CH₃SiMe₃ (5a). An NMR tube was charged with 4a (0.400 g, 0.0536 mmol) and Luf(CH₃SiMe₃)₂(THF)₂ (0.0312 g, 0.0537 mmol) and sealed with a rubber septum and parafilm. The tube was cooled to −78 °C, and an aliquot of toluene-d₈ (0.5 mL) was added via syringe. The tube was removed from the cold bath, shaken briefly to mix the reagents, and then immediately inserted into a precooled (273.1 K) NMR probe. The dialkyl
complex (5a) was characterized by multinuclear NMR spectroscopy in situ. No decomposition was observed over the course of characterization (2 h). 1H NMR (toluene-d8, 271.3 K): 8.12 (s, 2H, Ar–H), 7.47 (m, 8H PPh–H), 6.93–6.75 (ov, m, 24H, Ar–H), 2.29 (s, 6H, CH3), −0.06 (s, 18H, CH(CH3)2), −0.79 (s, 4H, CH2). 13C{1H} NMR (toluene-d8: 271.3 K): δ 152.5 (d, JCp = 3.6 Hz, Ar–C), 147.4 (d, JCp = 7.4 Hz, Ar–C), 137.1 (Ar–C), 134.1 (d, JCp = 9.4 Hz, Ar–CH), 132.3 (d, JCp = 2.2 Hz, Ar–CH), 130.9 (d, JCp = 11.4 Hz, Ar–CH), 129.4 (d, JCp = 7.9 Hz, Ar–CH), 129.1 (d, JCp = 2.4 Hz, Ar–CH), 128.6 (d, JCp = 11.8 Hz, Ar–CH), 127.3 (d, JCp = 9.3 Hz, Ar–C), 126.0 (d, JCp = 2.2 Hz, Ar–CH), 125.2 (Ar–C), 123.2 (d, JCp = 2.8 Hz, Ar–CH), 108.9 (d, JCp = 111.2 Hz, Ar–C), 40.4 (CH2), 21.3 (CH3), 4.63 (Si(CH3)3). [31P{1H}] NMR (toluene-d8: 271.3 K): δ 29.4.

Luf6Pip2(CH2SiMe3)2 (5b). An NMR tube was charged with 4b (0.0216 g, 0.0262 mmol) and Lu(CH2SiMe3)3(THF)2 (0.0152 g, 0.0262 mmol) and sealed with a rubber septum and parafilm. The tube was cooled to −78 °C, and an aliquot of toluene-d8 (0.5 mL) was added via syringe. The tube was removed from the cold bath, shaken briefly to mix the reagents, and then immediately inserted into a precooled multinuclear NMR probe. The dialkyl complex (5b) was characterized by multinuclear NMR spectroscopy in situ. No decomposition was observed over the course of characterization (3 h). 1H NMR (toluene-d8: 249.1 K): 8.11 (s, 2H, Ar–H), 7.49 (m, 8H PPh–H), 7.10–7.10 (ov, m, 4H, Ar–H), 6.96–6.79 (ov, m, 18H, Ar–H), 2.63 (2H, CH2), 2.5 (CH2), 1.13 (s, 6H, CH3), 1.04 (s, 18H, CH(CH3)2), −0.01 (s, 18H, Si(CH3)3), −0.72 (s, 4H, CH2). 13C{1H} NMR (toluene-d8: 249.1 K): δ 152.5 (d, JCp = 3.5 Hz, Ar–C), 144.8 (d, JCp = 7.5 Hz, Ar–C), 143.4 (d, JCp = 3.6 Hz, Ar–C), 137.0 (Ar–C), 134.1 (d, JCp = 9.6 Hz, Ar–C), 132.2 (Ar–C), 130.9 (d, JCp = 11.6 Hz, Ar–CH), 129.2 (Ar–CH), 128.5 (d, JCp = 11.7 Hz, Ar–CH), 127.3 (d, JCp = 9.3 Hz, Ar–C), 127.0 (Ar–C), 126.0 (Ar–CH), 125.0 (Ar–C), 108.9 (d, JCp = 110.6 Hz, Ar–C), 40.0 (CH3), 33.9 (CH2), 24.5 (CH3(CH2)), 21.3 (CH3), 4.71 (Si(CH3)3). [31P{1H}] NMR (toluene-d8: 249.1 K): δ 29.4.

Luf6Pip2(THF)2 (7a). In a glovebox, a small Erlenmeyer flask was charged with 4a (0.193 g, 0.252 mmol) and Lu(CH2SiMe3)3(THF)2 (0.147 g, 0.252 mmol). Benzene (5 mL) was added to this solution to yield a clear red solution. The reaction mixture was stirred for 18 h, following which the volatiles were removed to afford a yellow powder. The product was recrystallized from a 9:1 benzene/THF solution (10 mL) layered with pentane (10 mL). The crystals were collected by filtration, washed with pentane (2 mL), and dried under vacuum. Yield: 0.201 g (80.5%). 1H NMR (benzene-d6): 8.08 (s, 2H, Ar–H), 7.97 (m, 4H, PPh–H), 7.71 (m, 2H, PPh–H), 7.56 (d, 2H, JCp = 13.4 Hz, Ar–H), 7.11–6.97 (ov, m, 12H, PPh–H), 6.77 (ov, m, 10H, NPh–H), 4.00 (s, 4H, OCH2CH2), 2.34 (s, 6H, CH3), 1.15 (s, 4H, OCH2CH2). 13C{1H} NMR (benzene-d6): δ 204.6 (dd, JCp = 41.2 Hz, JCp = 1.1 Hz, Lu–Ar–C), 151.5 (d, JCp = 5.7 Hz, Ar–C), 147.5 (d, JCp = 7.3 Hz, Ar–C), 140.0 (d, JCp = 25.6 Hz, Ar–CH), 138.5 (d, JCp = 126.7 Hz, Ar–C), 134.2 (d, JCp = 8.5 Hz, Ar–CH), 132.2 (d, JCp = 1.7 Hz, Ar–CH), 129.6 (d, JCp = 8.7 Hz, Ar–CH), 129.1 (d, JCp = 2.1 Hz, Ar–CH), 128.7 (s, Ar–C), 128.6 (d, JCp = 7.2 Hz, Ar–CH), 128.2 (Ar–CH), 127.8 (d, JCp = 3.7 Hz, Ar–CH), 127.0 (d, JCp = 9.8 Hz, Ar–C), 126.3 (d, JCp = 81.5 Hz, Ar–C), 124.9 (d, JCp = 11.3 Hz, Ar–C), 124.6 (d, JCp = 14.7 Hz, Ar–CH), 124.2 (d, JCp = 2.3 Hz, Ar–CH), 122.6 (d, JCp = 3.2 Hz, Ar–CH), 115.0 (d, JCp = 87.0 Hz, Ar–C), 71.3 (OCH2CH2), 25.3 (OCH2CH2), 21.5 (CH3). [31P{1H}] NMR (benzene-d6): δ 25.5. Anal. Calcd (%) for C60H58Lu6O12: C, 67.10; H, 5.44; N, 3.91. Found: C, 67.07; H, 6.02; N, 3.64.

NMR Kinetics. All rate constants were determined by monitoring the 31P{1H} NMR resonance(s) over the course of the reaction (to at least 3 half-lives) at a given temperature. In a typical experiment, proteo ligand 4a (0.0400 g, 0.0537 mmol) and Lu(CH2SiMe3)3(THF)2 (0.0312 g, 0.0537 mmol) were added to a Wilmad NMR tube, which was then sealed with a rubber septum (Sigma-Aldrich) and parafilm. The tube was cooled to −78 °C and 0.5 mL of toluene-d8 was injected via syringe. The tube was removed from the cold bath and shaken briefly, generating Luf6Pip2(CH2SiMe3)2 (5a), in situ. The tube was then immediately inserted into the NMR probe, which was pre-equilibrated to the appropriate temperature. The sample was allowed to equilibrate at the set temperature over the course of shimming the tube in the magnet. 31P{1H} NMR spectra (16 scans) were recorded at preset time intervals until the reaction had progressed to at least 3 half-lives. The extent of reaction at each time interval was determined by integration of the peak intensity of the starting material relative to that of the intermediate and product. An appropriately long delay between scans was utilized to ensure that integration was quantitative and not affected by the T1 relaxation times of the reacting species. A summary of the observed rate constants and half-lives is listed in Table 1.

X-ray crystallography. Suitable crystals of 4a, 4b, 6b, or 7b were selected, coated in dry Paratone oil, and mounted on a glass fiber. Data were collected at 173 K using a Bruker SMART APEX II instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a CCD area detector and a KRYO-FLEX liquid nitrogen vapor cooling device. Unit cell parameters were determined and refined on all observed reflections using APEX2 software.27 Data reduction and correction for Lorentz polarization were performed using the SAINT-Plus software.28 Absorption corrections were applied using SADABS.29 The structure was solved by Patterson (4a) or direct (4b, 6b, and 7b) methods and refined by the least-squares method on F2 using the

(27) APEX2, version 2.1.4; Data Collection and Refinement Program; Bruker AXS: Madison, WI, 2006.
(28) SAINT-Plus, version 7.22a; Data Reduction and Correction Program; Bruker AXS: Madison, WI, 2004.
SHELXTL program package. Details of the data collection and refinement are given in Table 2 and the Supporting Information.

Acknowledgment. P.G.H. acknowledges financial support from the Natural Sciences and Engineering Research Council of Canada for a Discovery Grant, the Canada Foundation for Innovation for a Leaders Opportunity Grant, and the University of Lethbridge for a start-up fund. The authors also wish to thank Dr. Adrien Côté (Xerox Canada) for expert assistance with X-ray crystallography and Mr. Craig Wheaton of this department for performing elemental analyses.

Supporting Information Available: X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.