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Bis(pyrazolyl)carbazole as a Versatile Ligand for Supporting Lutetium Alkyl and Hydride Complexes

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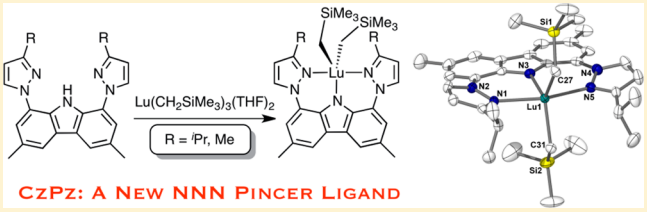
Supporting Information

ABSTRACT: Two derivatives of a new bis(pyrazolyl)-carbazole pincer ligand H(CzPz^{R}), R = ^{i}Pr and Me, and their syntheses are reported. Lutetium dialkyl complexes of the ligand (CzPz^{R})Lu(CH$_2$SiMe$_3$)$_2$, R = ^{i}Pr and Me, have been prepared and found to exhibit high thermal stability in solution. These organolutetium compounds are Lewis base free, and the solid-state structure of (CzPz^{iPr})Lu(CH$_2$SiMe$_3$)$_2$ revealed that the complex is monomeric with a trigonal-bipyramidal geometry. Hydrogenolysis of (CzPz^{iPr})Lu(CH$_2$SiMe$_3$)$_2$ afforded a trimetallic lutetium hydride complex that possesses five bridging hydride ligands. Notably, intramolecular C−H bond activation of the CzPz^{iPr} ligand was found to occur during the formation of this latter hydride complex, with metalation of a pyrazole carbon atom.



INTRODUCTION

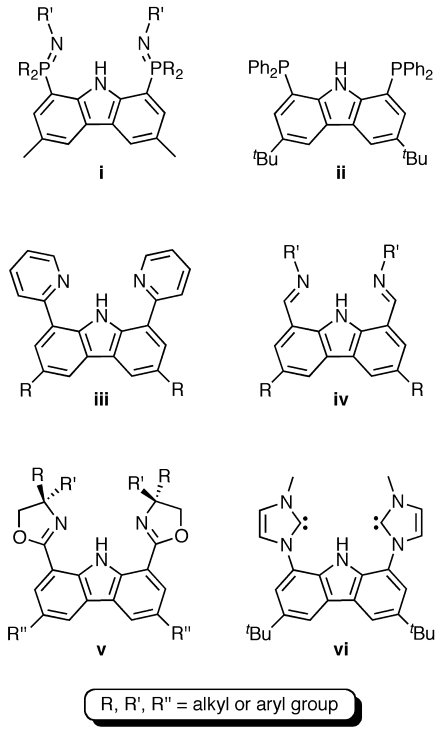
Ancillary ligands containing pyrazole-based donor groups are becoming increasingly popular in organometallic and coordination chemistry of the lanthanides. For example, the versatile family of tris(pyrazolyl)borate (Tp) scorpionate ligands has garnered increased use in rare earth chemistry in recent years,[1] as they offer strong donor properties and a framework that can be easily fine-tuned.[2]

A variety of other pyrazole-containing chelating ligands have also witnessed considerable interest, but predominately with transition metals.[3] A recent example is the di(2-pyrazolyl-aryl)amine pincer ligand, wherein modulation at the 3-position of pyrazole was shown to have a significant inductive effect on rhodium(III) complexes.[4] In this system, the degree of electron density at the metal center was directly correlated to the identity of the pyrazole R group (H < Me < ^{i}Pr).[4c]

Our research group is interested in developing tridentate pincer ligands as rigid scaffolds for stabilizing highly reactive rare earth complexes. We previously incorporated two phosphinimine donor groups onto the 1- and 8-positions of a carbazole framework to generate a pincer ligand (**i**, Chart 1) that proved capable of supporting rare earth ions.[5] While our bis(phosphinimine)carbazole pincers have been useful in generating a variety of well-defined complexes, the organometallic derivatives were often prone to rapid decomposition by cyclometalation of the phosphinimine functionality.[6] Accordingly, we were inclined to replace the phosphinimine donors with groups that were expected to be less susceptible to cyclometalative reactivity.

In addition to our bis(phosphinimine)carbazole pincer (**i**, Chart 1), a variety of other carbazole-based frameworks have previously been reported as supporting ancillary ligands for organometallic and coordination complexes. A selection of these pincer ligands is outlined in Chart 1. Featured ligands include bis(phosphino)carbazole (**ii**),[7] bis(pyridyl)carbazole (**iii**),[8] bis(imino)carbazole (**iv**),[9] bis(oxazolinyl)carbazole (**v**),[10] and bis(3-methylimidazolin-2-yliden-1-yl)carbazole

Chart 1. Selected Carbazole-Based Pincer Ligands



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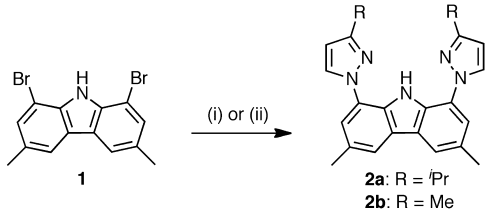
(**vi**).[11] This diverse group of ligands has been shown to stabilize metals with a variety of different coordination modes and steric environments. The donor groups that are bound to the 1- and 8-positions of carbazole are particularly important in this regard. Accordingly, we were interested in expanding this class of carbazole-based pincers by incorporating a new donor group onto these sites.

Because of the ability of pyrazole rings to serve as suitable donors to rare earth metals, it was reasoned that combining the donor properties of pyrazole rings with a rigid carbazole framework would afford a new pincer ligand with remarkable properties. The combined rigidity of the components was anticipated to help mitigate fluxional ligand behavior and allow for greater control of the coordination geometry at the metal center. From an electronic standpoint, the pyrazole and carbazole nitrogen atoms can provide substantial electron donation to the Lewis acidic lanthanide center. Notably, the electronic donating capacity of the ligand can be readily tailored to meet the needs of the metal by modifying the functional group at the 3-position on pyrazole, denoted as R. In addition, the steric properties and solubility of the ancillary ligand can also be easily tuned by modulation of the pyrazole R group.

RESULTS AND DISCUSSION

Ligand Synthesis and Characterization. Two variants of the new proteo ligand, composed of pyrazolyl rings bound to carbazole at the 1- and 8-positions, H(CzPz^{R}), were prepared via an Ullmann-type amination of 1,8-dibromo-3,6-dimethylcarbazole (**1**) with substituted pyrazoles (HPz^{R}, R = ^{i}Pr, Me) in the presence of a copper(I) catalyst (Scheme 1).

Scheme 1. Synthesis of H(CzPz^{R}) Proteo Ligands[a]



[a]Reagents and conditions: (i) 10 HPz^{R}, 5 Cu_2O, 4 TMEDA, 4 NaO^{t}Bu, 150 °C in DMF for 2.5−4.5 days; (ii) 10 HPz^{R}, 1 CuBr, 4 TMEDA, 10 NaO^{t}Bu, 165 °C in toluene for 24 h.

In the synthesis of H(CzPz^{R}), the double amination of 1,8-dibromo-3,6-dimethylcarbazole with substituted pyrazoles appears to occur sequentially, with incomplete reactions resulting in formation of the singly substituted product 1-bromo-3,6-dimethyl-8-pyrazolylcarbazole. We found that use of an excess of base (NaOtBu) and pyrazole in the reaction was required to ensure complete conversion to the desired doubly substituted product **2**. Other reports describing Ullmann-type coupling reactions between halogenated carbazole substrates and substituted pyrazoles have set similar precedents requiring the use of excess reagents.[12] While this may not be the most atom economical approach,[13] the base is an inexpensive and commercially available reagent, and the excess pyrazole can be recovered from the reaction mixture by vacuum distillation.

The ^{1}H NMR spectrum (chloroform-*d*) of H(CzPz^{iPr}), **2a**, exhibits an N*H* signal at δ 11.17, pyrazolyl aromatic protons as two doublets at δ 8.00 and δ 6.35, and the carbazole aromatic protons at δ 7.75 and δ 7.30. It also features diagnostic isopropyl resonances at δ 3.25 (sp, CH) and δ 1.39 (d, CH_3) in addition to the carbazole methyl signal at δ 2.57. Similar signals were observed in the ^{1}H NMR spectrum of H(CzPz^{Me}), **2b**, with the exception of a pyrazolyl methyl resonance at δ 2.59, in place of the pyrazolyl isopropyl signals.

In addition to characterization of **2a** and **2b** by multinuclear NMR spectroscopy, the structures of both proteo ligands were determined by single-crystal X-ray diffraction. Recrystallization of **2a** by slow evaporation from a hexanes solution at ambient temperature generated yellow prisms suitable for an X-ray diffraction experiment. Under these conditions, **2a** crystallized in the rhombohedral space group $R\bar{3}$ and is depicted in Figure 1

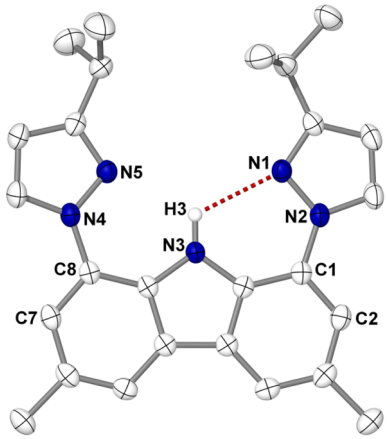


Figure 1. Thermal ellipsoid plot (50% probability) of proteo ligand H(CzPz^{iPr}) (**2a**) with hydrogen atoms (except H3) omitted for clarity.

as a thermal ellipsoid plot. The molecular structure of H(CzPz^{iPr}) reveals that the isopropylpyrazolyl functionalities lay periplanar to the carbazole backbone (C2−C1−N2−N1 and C7−C8−N4−N5 torsion angles of −177.3(1)° and −172.3(1)°, Table 1) with the donor nitrogen atoms aligned

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for Compounds 2a and 2b

	2a	2b
C1−N2	1.418(2)	1.418(2)
C8−N4	1.417(2)	1.419(2)
N2−N1	1.361(1)	1.367(2)
N4−N5	1.364(1)	1.365(2)
N3···N1	2.780(1)	2.753(2)
N3···N5	2.787(1)	2.757(2)
C1−N2−N1	120.8(1)	120.5(1)
C8−N4−N5	120.6(1)	120.5(1)
C2−C1−N2−N1	−177.3(1)	−175.8(1)
C7−C8−N4−N5	−172.3(1)	−171.4(1)

toward the carbazole NH. This orientation is influenced by a hydrogen-bonding interaction that can occur between the carbazole NH and each pyrazolyl nitrogen donor (d(N3···N1) = 2.780(1) Å and d(N3···N5) = 2.787(1) Å). The solid-state structure of the proteo ligand also features a low degree of peripheral steric bulk and a large NNN binding pocket, suitable for chelating rare earth metals. Single crystals of **2b** were obtained from a concentrated benzene solution at ambient temperature. Proteo ligand **2b** crystallized in the orthorhombic

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space group *Pbca*. The solid-state structure of **2b** (depicted in Figure 2) reveals a periplanar arrangement of the methylpyrazolyl rings to the carbazole backbone, similar to that observed in **2a** (C2−C1−N2−N1 and C7−C8−N4−N5 torsion angles of −175.8(1)° and −171.4(1)°, Table 1).

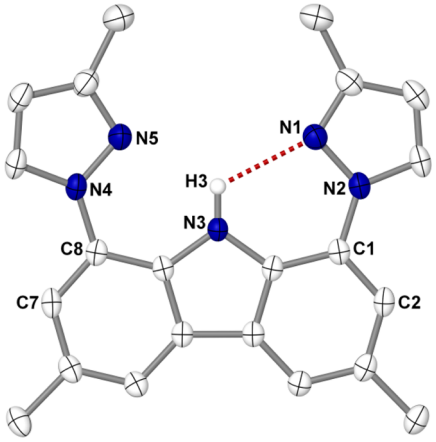
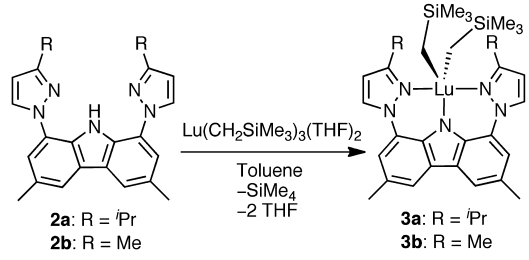


Figure 2. Thermal ellipsoid plot (50% probability) of proteo ligand H(CzPz^{Me}) (**2b**) with hydrogen atoms (except H3) omitted for clarity.

Lutetium Dialkyl Complexes. Dialkyl lutetium complexes of both proteo ligand derivatives were readily prepared via an alkane elimination reaction with $Lu(CH_2SiMe_3)_3(THF)_2$ (Scheme 2). When this reaction was followed in situ on an NMR tube scale in benzene-d_6, it proceeded rapidly at ambient temperature with the formation of the corresponding metal dialkyl complex, 1 equiv of $SiMe_4$ and 2 equiv of free THF. Upon scale-up of the reaction in toluene solution, the dialkyl products ((CzPz^R)Lu$(CH_2SiMe_3)_2$, R = ^{i}Pr, **3a**; Me, **3b**) were obtained in good yield (66.4% and 73.7%, respectively) after recrystallization. Notably, complexes **3a** and **3b** exhibited high thermal stability at ambient temperature in both the solid state and in solution. This stability was further probed by heating the complexes in benzene-d_6 solution to 75 °C over a period of 12 h, during which no decomposition was observed spectroscopically. As expected, the ^{1}H NMR spectra (benzene-d_6) of complexes **3a** and **3b** revealed diagnostic methylene (δ −0.20, **3a**; −0.30, **3b**) and trimethylsilyl signals (δ −0.26, **3a**; −0.23, **3b**) as sharp singlets, integrating to 4H and 18H, respectively.

Scheme 2. Synthesis of Dialkyl Lutetium Complexes 3a and 3b



High-quality single crystals of **3a** suitable for an X-ray diffraction experiment were grown from a concentrated toluene solution at −35 °C. Dialkyl species **3a** crystallized in the space group $P\bar{1}$ with two crystallographically independent molecules of the complex, in addition to one disordered toluene solvent molecule, in the asymmetric unit. Both crystallographically independent complexes exhibited a similar geometry. A representative thermal ellipsoid plot of one molecule is depicted in Figure 3, and selected metrical parameters of both molecules are listed in Table 2. In the solid state, **3a** is defined by coordination of two $-CH_2SiMe_3$ groups and a CzPz^{iPr} ligand κ^3-bound through three nitrogen atoms. The lutetium center exhibits distorted trigonal-bipyramidal geometry with N1 and N5 in the apical positions, and N3, C27, and C31 occupying the equatorial plane. While the CzPz pincer displays meridional coordination to the metal, the two alkyl groups are arranged so as to exhibit a "folded wing" type of geometry. A similar arrangement has previously been observed in the solid-state structures of dialkyl lanthanide complexes of a carbazole-bis(oxazoline) ligand.[10f] Complex **3a** exhibits Lu−C contacts ranging from 2.343(3) to 2.374(3) Å, which are well within the range expected for typical Lu−CH_2SiMe_3 bonds.[14]

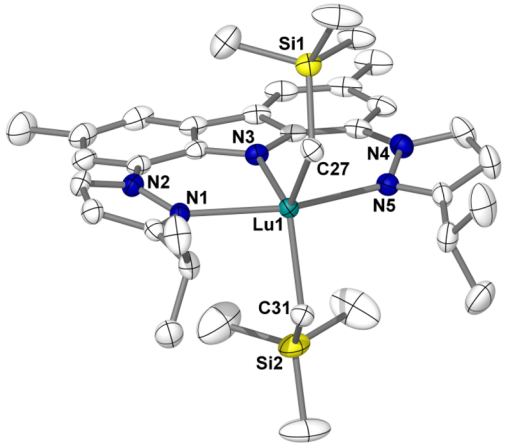


Figure 3. Thermal ellipsoid plot (50% probability) of (CzPz^{iPr})Lu$(CH_2SiMe_3)_2$ (**3a**) with hydrogen atoms omitted for clarity.

Hydrogenolysis and Ligand Metalation. The preparation of rare earth hydride complexes was of interest due to the unique reactivity and the prominent role that such species play in various catalytic and stoichiometric transformations. To this end, hydrogenolysis of (CzPz^{iPr})Lu$(CH_2SiMe_3)_2$ with H_2 (4 atm) at 50 °C in toluene solution (Scheme 3) afforded a trimetallic lutetium hydride complex (**4**). Gratifyingly, the hydride complex selectively crystallized out of solution upon formation. The molecular structure of **4** was determined by single-crystal X-ray diffraction and is depicted in Figure 4, with selected metrical parameters listed in Table 3. Notably, the complex possesses five hydride ligands that bridge three lutetium metal centers. The hydride core exhibits a geometry similar to that of previously documented trimetallic rare earth complexes that possess five bridging hydrides, with three μ_2-H ligands occupying the same plane as the three metal ions and two μ_3-H moieties in apical positions.[15] Interestingly, two of the lutetium atoms (Lu1 and Lu3) are each coordinated by one monoanionic CzPz^{iPr} ligand, while the third metal (Lu2) is bound by a dianionic CzPz^{iPr} ligand that has undergone an intramolecular metalative C−H bond activation process. As a monoanionic ligand, the ancillary framework coordinates to the metal in a similar manner to that observed in complexes **3a** and **3b**, via three nitrogen atoms (two neutral pyrazole nitrogen donors and one anionic carbazolide nitrogen). Conversely, as a dianionic ligand, one pyrazole ring has undergone a C−H bond

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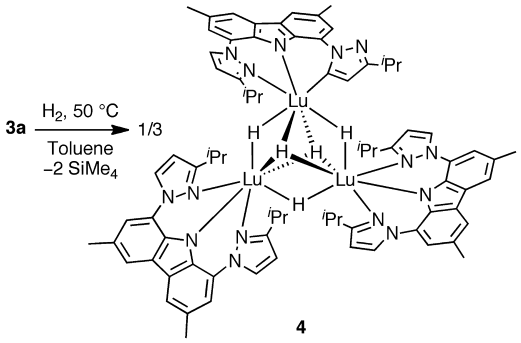
Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for the Crystallographically Independent Molecules of Structure 3a

3a		3a′	
N2−N1	1.376(3)	N2B−N1B	1.371(3)
N4−N5	1.366(3)	N4B−N5B	1.375(3)
Lu1−N1	2.376(3)	Lu2−N1B	2.364(3)
Lu1−N5	2.379(3)	Lu2−N5B	2.361(3)
Lu1−N3	2.231(3)	Lu2−N3B	2.238(2)
Lu1−C27	2.374(3)	Lu2−C27B	2.358(3)
Lu1−C31	2.343(3)	Lu2−C31B	2.351(3)
C27−Si1	1.835(3)	C27B−Si1B	1.823(3)
C31−Si2	1.835(4)	C31B−Si2B	1.832(3)
N1−Lu1−N5	163.5(1)	N1B−Lu2−N5B	163.1(1)
N3−Lu1−C31	117.0(1)	N3B−Lu2−C31B	119.4(1)
N3−Lu1−C27	117.1(1)	N3B−Lu2−C27B	118.3(1)
C31−Lu1−C27	125.8(1)	C31B−Lu2−C27B	122.2(1)
Lu1−C27−Si1	115.1(2)	Lu2−C27B−Si1B	121.1(2)
Lu1−C31−Si2	116.3(2)	Lu2−C31B−Si2B	115.7(2)
C2−C1−N2−N1	155.8(3)	C2B−C1B−N2B−N1B	149.0(3)
C7−C8−N4−N5	−160.3(3)	C7B−C8B−N4B−N5B	−155.0(3)

Scheme 3. Hydrogenolysis of Dialkyl Lutetium Complex 3a



activation, and as a result, the lutetium center is bound via one neutral pyrazole nitrogen donor (N6), the anionic carbazolide nitrogen (N8), and one deprotonated carbon atom (C47). In this case, the pyrazolyl ring is rotated so that the nitrogen donor is facing away from the metal. It is unknown if the C−H bond activation process occurred by metalation of the pyrazolyl carbon in a lutetium hydride complex of generic form $[(CzPz^{iPr})LuH_2]_n$ with loss of H_2[16] or, rather, if metalation occurred prior to hydride formation by extrusion of tetramethylsilane from **3a**. However, it is reasoned that the former scenario is more likely because complex **3a** exhibits relatively high stability in solution at elevated temperatures (vide supra) and, as such, is unlikely that it would undergo metalation with loss of alkane under these experimental conditions (50 °C). The potential for this lutetium complex to undergo intramolecular C−H bond activation with metalation of a pyrazole carbon atom is a testament to the high reactivity of lutetium, as well as the potential for complexes such as **3a**, **3b**, and **4** to participate in applications relevant to the activation and functionalization of small molecules.

In the ^{1}H NMR spectrum (THF-d_8) of **4**, all hydride ligands resonate as one broad signal at δ 10.3, presumably because they are rapidly exchanging on the NMR time scale. Notably, the complex exhibits very low symmetry in solution with all proton and carbon atoms corresponding to the three $CzPz^{iPr}$ ligands

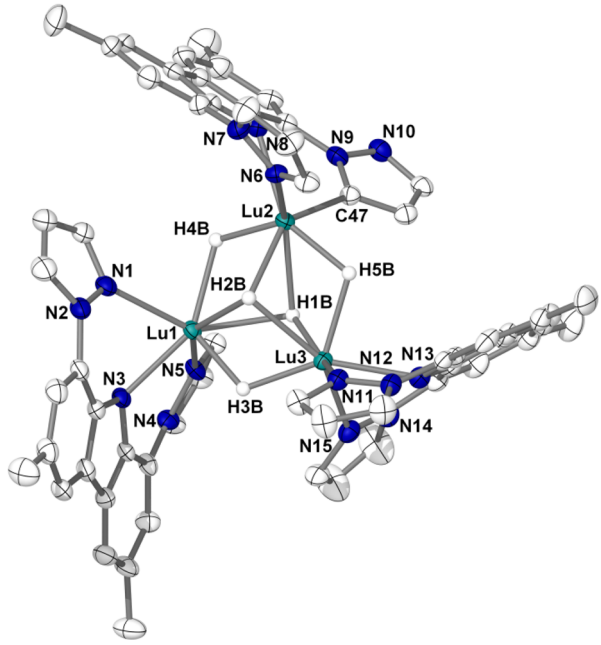


Figure 4. Thermal ellipsoid plot (50% probability) of **4** with isopropyl groups, hydrogen atoms (except hydride ligands), and two toluene solvent molecules omitted for clarity.

resonating as independent signals. Complex **4** is insoluble in typical aromatic and aliphatic solvents; however, it can be dissolved in Lewis basic solvents such as THF. Unfortunately, decomposition toward multiple products, likely Lewis base adducts, is evident within 5 min if left in THF at ambient temperature; this transformation is slower at reduced temperatures. Attempts to prepare the $CzPz^{Me}$ analogue of **4** by hydrogenolysis of **3b** were unfortunately unsuccessful; all attempts resulted in intractable mixtures. This difference in reactivity of **3b** with dihydrogen relative to **3a** is useful in highlighting the influence of ligand R group modification on the chemistry of coordinated metal complexes.

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Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound 4

N1−N2	1.372(5)	N2−C15	1.349(6)
N4−N5	1.386(4)	N4−C21	1.343(5)
N6−N7	1.372(5)	N7−C41	1.342(5)
N9−N10	1.375(4)	N9−C47	1.391(5)
N11−N12	1.383(5)	N12−C67	1.336(5)
N14−N15	1.380(5)	N14−C73	1.338(6)
Lu1−N1	2.422(4)	Lu2−C47	2.363(4)
Lu1−N3	2.254(3)	Lu3−N11	2.396(3)
Lu1−N5	2.385(3)	Lu3−N13	2.242(3)
Lu2−N6	2.485(3)	Lu3−N15	2.420(3)
Lu2−N8	2.268(3)		
N1−Lu1−N3	71.4(1)	N8−Lu2−C47	77.9(1)
N1−Lu1−N5	123.4(1)	N11−Lu3−N13	77.8(1)
N3−Lu1−N5	78.6(1)	N11−Lu3−N15	121.6(1)
N6−Lu2−N8	75.8(1)	N13−Lu3−N15	70.8(1)
N6−Lu2−C47	126.8(1)		
C2−C1−N2−N1	176.0(4)	C33−C34−N9−C47	−159.9(4)
C7−C8−N4−N5	−148.9(4)	C54−C53−N12−N11	148.5(4)
C28−C27−N7−N6	154.8(4)	C59−C60−N14−N15	176.3(4)

CONCLUSIONS

In summary, we have presented the synthesis of two derivatives of a bis(pyrazolyl)carbazole ligand. These ligands were used to prepare monomeric and Lewis base free lutetium dialkyl complexes (**3a** and **3b**) that exhibited remarkably high thermal stability. Hydrogenolysis of **3a** afforded a rare lutetium hydride trimetallic complex (**4**) that formed via a C−H bond activation process. We expect our new class of CzPz ancillary ligands to be useful scaffolds for supporting group 3 and lanthanide metals and anticipate that rich organometallic chemistry can be harvested from further study, including bond-forming catalytic transformations or, potentially, the synthesis of metal−element multiple bonds.

EXPERIMENTAL SECTION

General Synthetic 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. The solvents tetrahydrofuran (THF), pentane, benzene, and toluene were dried and purified using a solvent purification system (MBraun) and distilled under vacuum prior to use from sodium benzophenone ketyl (THF) or "titanocene" indicator (pentane, benzene, and toluene). Deuterated solvents were dried over sodium benzophenone ketyl (benzene-d_6 and THF-d_8) or CaH_2 (chloroform-*d*), degassed via three freeze−pump−thaw cycles, distilled under vacuum, and stored over 4 Å molecular sieves under an argon atmosphere. Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (ultrashield) spectrometer (^{1}H 300.13 MHz, ^{13}C{^{1}H} 75.47 MHz) and referenced relative to $SiMe_4$ through the residual solvent resonance(s) for ^{1}H and ^{13}C{^{1}H}. All NMR spectra were recorded at ambient temperature (295 K) unless specified otherwise. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. The reagents $Lu(CH_2SiMe_3)_3(THF)_2$,[17] 1,8-dibromo-3,6-dimethylcarbazole,[9b] and 3(5)-isopropylpyrazole[18] were prepared according to literature procedures. Purification by chromatography was performed on silica gel (230−400 mesh, used as received and without activation) using a fritted column (3 × 45 cm). All other reagents were obtained from Aldrich Chemicals or Alfa Aesar and used as received.

Synthesis of H(CzPz^{iPr}) (2a). *Method 1.* Under an inert atmosphere, NaO^{t}Bu (0.561 g, 8.83 mmol, 4 equiv) was transferred to a two-neck 100 mL round-bottom flask. The flask was quickly connected to a condenser, and the apparatus was then evacuated and purged with argon three times. Dimethylformamide (8 mL) and 3(5)-isopropylpyrazole (1.61 g, 14.6 mmol, 10 equiv) were added to the flask via syringe, and the solution was stirred for 15 min. While still under argon, TMEDA (0.88 mL, 5.83 mmol, 4 equiv) was added to the flask by syringe, followed by Cu_2O (1.04 g, 7.29 mmol, 5 equiv), and 1,8-dibromo-3,6-dimethylcarbazole (0.516 g, 1.46 mmol, 1 equiv) as solids. The resulting red suspension was then heated to 150 °C in an oil bath for 4.5 days under argon. The solution was cooled to ambient temperature and exposed to air, resulting in a change from deep red to blue-green in appearance. The solution was diluted with 200 mL of diethyl ether, transferred to a separatory funnel, and mixed vigorously with 50 mL of 1 M HCl until the color of the organic layer changed from dark blue-green to yellow. The layers were separated, and the organic layer was then washed a second time with 1 M HCl (50 mL), followed by 1 M NH_4OH (3 × 50 mL) and 3 M NH_4Cl (8 × 50 mL), whereby washings with NH_4Cl were performed until no more color was apparent in the aqueous layer. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation, yielding a dark yellow solid. The product was purified by column chromatography (eluting with benzene) to afford an amorphous yellow solid. Recrystallization of the solid by slowly cooling a hot concentrated benzene solution to ambient temperature afforded analytically pure yellow prisms. Yield: 0.292 g (48.7%).

Method 2. A 100 mL thick-walled reaction vessel equipped with a Teflon Kontes valve was charged with 1,8-dibromo-3,6-dimethylcarbazole (0.506 g, 1.43 mmol, 1 equiv), CuBr (0.205 g, 1.43 mmol, 1 equiv), NaO^{t}Bu (1.38 g, 14.3 mmol, 10 equiv), and 40 mL of toluene in a glovebox. The reagents 3(5)-isopropylpyrazole (1.58 g, 14.3 mmol, 10 equiv), and TMEDA (0.86 mL, 5.72 mmol, 4 equiv) were then added to the solution by syringe. The reaction vessel was sealed under argon and heated to 165 °C in an oil bath for 24 h, whereby the solution changed from cloudy yellow to a darker amber color in appearance. The solution was cooled to ambient temperature, exposed to air, and then transferred to a separatory funnel, where it rapidly took on a dark brown color. The solution was diluted with 200 mL of diethyl ether and mixed vigorously with 50 mL of 1 M HCl until the color of the organic layer changed from dark brown to yellow. The layers were separated, and the organic layer was then washed a second time with 1 M HCl (50 mL), followed by 1 M NH_4OH (50 mL) and 3 M NH_4Cl (50 mL). The solvent was removed by rotary evaporation, affording a crude dark orange solid. The material was purified by column chromatography (eluting with benzene) to afford **2a** as a pure

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yellow solid. Yield: 0.187 g (31.8%). R_f (silica, benzene) 0.35. ^{1}H NMR (chloroform-*d*): δ 11.17 (s, 1H, N*H*), 8.00 (d, $^3J_{HH}$ = 2.0 Hz, 2H, Pz C*H*), 7.75 (s, 2H, Cz C*H*), 7.30 (s, 2H, Cz C*H*), 6.35 (d, $^3J_{HH}$ = 2.0 Hz, 2H, Pz C*H*), 3.26 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.57 (s, 6H, Cz C*H*$_3$), 1.39 (d, $^2J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (chloroform-*d*): δ 160.8 (aromatic *ipso*-*C*), 130.0 (aromatic *ipso*-*C*), 128.5 (aromatic *ipso*-*C*), 127.8 (aromatic *C*H), 125.5 (aromatic *ipso*-*C*), 124.6 (aromatic *ipso*-*C*), 118.0 (aromatic *C*H), 116.1 (aromatic *C*H), 103.5 (aromatic *C*H), 28.2 (*C*H(CH$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$, 21.5 (Cz *C*H$_3$). Anal. Calcd (%) for $C_{26}H_{29}N_5$: C, 75.88; H, 7.10; N, 17.02. Found: C, 75.96; H, 7.10; N, 16.84.

Synthesis of H(CzPz^{Me}) (2b). Under an inert atmosphere, KO^{t}Bu (1.94 g, 17.2 mmol, 4 equiv) was transferred to a 100 mL two-neck round-bottom flask equipped with a refluxing condenser. Dimethylformamide (25 mL) was added via syringe, and the slurry was stirred for 15 min under argon. Aliquots of 3-methylpyrazole (3.55 g, 43.2 mmol, 10 equiv) and TMEDA (2.01 g, 17.2 mmol, 4 equiv) were added to the slurry via syringe, followed by Cu_2O (2.06 g, 21.6 mmol, 5 equiv) and 1,8-dibromo-3,6-dimethylcarbazole (1.53 g, 4.32 mmol, 1 equiv) as solids. The resulting red suspension was then heated to 150 °C in an oil bath for 3 days under argon. The solution was cooled to ambient temperature, exposed to air, and diluted with 80 mL of dichloromethane. A saturated solution of $NH_4Cl_{(aq)}$ was added, and the two layers were mixed by vigorous stirring until the aqueous layer turned blue, after which it was decanted off. This process was repeated until the aqueous layer was no longer colored. The organic layer was then separated, dried over $MgSO_4$, and filtered, and the solvent was removed by rotary evaporation, yielding a crude green powder. The product was purified by column chromatography (eluting with benzene) to afford a pure yellow solid. Yield: 0.136 g (13.5%). R_f (silica, benzene) 0.19. ^{1}H NMR (chloroform-*d*): δ 11.66 (s, 1H, N*H*), 8.03 (d, $^3J_{HH}$ = 2.4 Hz, 2H, Pz C*H*), 7.76 (s, 2H, Cz C*H*), 7.32 (s, 2H, Cz C*H*), 6.34 (d, $^3J_{HH}$ = 2.4 Hz, 2H, Pz C*H*), 2.59 (s, 6H, C*H*$_3$), 2.55 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (chloroform-*d*): δ 150.0 (aromatic *ipso*-*C*), 130.0 (aromatic *ipso*-*C*), 128.5 (aromatic *ipso*-*C*), 127.8 (aromatic *C*H), 125.6 (aromatic *ipso*-*C*), 124.6 (aromatic *ipso*-*C*), 118.1 (aromatic *C*H), 115.2 (aromatic *C*H), 106.9 (aromatic *C*H), 22.9 (*C*H$_3$), 14.4 (*C*H$_3$). Anal. Calcd (%) for $C_{22}H_{21}N_5$: C, 74.34; H, 5.96; N, 19.70. Found: C, 74.30; H, 5.97; N, 19.55

Synthesis of (CzPz^{iPr})Lu(CH$_2$SiMe$_3$)$_2$ (3a). In a glovebox, toluene (15 mL) was added to a 25 mL Erlenmeyer flask charged with **2a** (0.274 g, 0.666 mmol) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.387 g, 0.666 mmol) to give a cloudy yellow solution. The reaction mixture was stirred at ambient temperature for 1.5 h and acquired a clear dark yellow-brown appearance as the reaction progressed. The solution was filtered through a bed of Celite, and the Celite was washed with a further 2 mL of toluene. The clear light yellow filtrate was concentrated to 2 mL under vacuum, heated very gently to redissolve all material, and then slowly cooled, first to ambient temperature over 2 h, then to −35 °C over 18 h to crystallize. Pale yellow crystals of **3a** were collected by filtration, washed with cold pentane (3 × 1 mL), and dried under reduced pressure. Yield: 0.336 g (66.4%). ^{1}H NMR (benzene-d_6): δ 7.87 (d, $^4J_{HH}$ = 1.0 Hz, 2H, Cz C*H*), 7.49 (d, $^3J_{HH}$ = 2.6 Hz, 2H, Pz C*H*), 6.86 (d, $^4J_{HH}$ = 1.0 Hz, 2H, Cz C*H*), 6.05 (d, $^2J_{HH}$ = 2.6 Hz, 2H, Pz C*H*), 4.24 (sp, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 2.41 (s, 6H, Cz C*H*$_3$), 1.38 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), −0.20 (s, 4H, LuC*H*$_2$), −0.26 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 164.8 (aromatic *ipso*-*C*), 137.8 (aromatic *ipso*-*C*), 131.7 (aromatic *C*H), 128.7 (aromatic *ipso*-*C*), 126.7 (aromatic *ipso*-*C*), 125.2 (aromatic *ipso*-*C*), 119.8 (aromatic *C*H), 118.6 (aromatic *C*H), 104.3 (aromatic *C*H), 41.3 (LuCH$_2$), 28.6 (CH(CH$_3$)$_2$), 23.2 (CH(CH$_3$)$_2$), 21.0 (Cz CH$_3$), 3.2 (Si(CH$_3$)$_3$). Anal. Calcd (%) for $C_{34}H_{50}LuN_5Si_2$: C, 53.74; H, 6.63; N, 9.22. Found: C, 53.97; H, 6.29; N, 9.43.

Synthesis of (CzPz^{Me})Lu(CH$_2$SiMe$_3$)$_2$ (3b). In a glovebox, benzene (6 mL) was added to a 25 mL Erlenmeyer flask charged with H(CzPz^{Me}) (0.109 g, 0.307 mmol) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.178 g, 0.307 mmol), resulting in a yellow solution. The reaction mixture was stirred at ambient temperature for 1.5 h, after which it was filtered through a bed of Celite, and the Celite was washed with a further 1 mL of benzene. All volatiles were removed from the filtrate under reduced pressure, leaving **3b** as a yellow solid. Yield: 0.159 g (73.7%). ^{1}H NMR (benzene-d_6): δ 7.86 (d, $^4J_{HH}$ = 0.8 Hz, 2H, aromatic C*H*), 7.41 (d, $^3J_{HH}$ = 2.5 Hz, 2H, aromatic C*H*), 6.86 (d, $^4J_{HH}$ = 0.8 Hz, 2H, aromatic C*H*), 5.82 (d, $^3J_{HH}$ = 2.5 Hz, 2H, aromatic C*H*), 2.75 (s, 6H, C*H*$_3$), 2.41 (s, 6H, C*H*$_3$), −0.23 (s, 18H, Si(C*H*$_3$)$_3$), −0.30 (s, 4H, LuC*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 153.4 (aromatic *ipso*-*C*), 138.0 (aromatic *ipso*-*C*), 131.2 (aromatic *C*H), 129.0 (aromatic *ipso*-*C*), 126.8 (aromatic *ipso*-*C*), 125.4 (aromatic *ipso*-*C*), 119.9 (aromatic *C*H), 118.2 (aromatic *C*H), 108.8 (aromatic *C*H), 42.9 (LuCH$_2$), 21.2 (CH$_3$), 15.2 (CH$_3$), 3.4 (Si(CH$_3$)$_3$). Anal. Calcd (%) for $C_{30}H_{42}LuN_5Si_2$: C, 51.19; H, 6.01; N, 9.95. Found: C, 51.40; H, 5.37; N, 9.94. Repeated attempts to obtain higher quality elemental analysis results for this compound were unsuccessful. These data represent the best values obtained to date. As an indication of compound purity, representative ^{1}H and ^{13}C NMR spectra are provided in the Supporting Information.

Synthesis of (CzPz^{iPr})$_2$(CzPz^{iPr})′Lu$_3$(H)$_5$ (4). A 200 mL thick-walled reaction vessel equipped with a Teflon Kontes valve was charged with **3a** (0.101 g, 0.133 mmol) and 5 mL of toluene. The clear light yellow solution was then degassed by three freeze−pump−thaw cycles. The reaction vessel was chilled in a liquid N_2 bath, filled with 1 atm of H_2, sealed with a Teflon Kontes valve, and then heated to 50 °C for 24 h without stirring. Over the duration of the reaction, the solution darkened slightly, and product **4** selectively crystallized out as fine pale yellow needles. In a glovebox, the crystals were collected by filtration on a fine fritted funnel, washed thoroughly with toluene (10 × 1 mL), followed by pentane (5 × 1 mL), and then dried under vacuum. Yield: 0.0310 g (39.2%). ^{1}H NMR (THF-d_8): δ 10.3 (br s, 5H, Lu*H*), 8.40 (d, $^3J_{HH}$ = 2.5 Hz, 1H, aromatic C*H*), 8.25 (d, $^3J_{HH}$ = 2.6 Hz, 1H, aromatic C*H*), 8.20 (m, 2H, aromatic C*H*), 8.05 (m, 2H, aromatic C*H*), 7.88 (s, 2H, aromatic C*H*), 7.82 (s, 1H, aromatic C*H*), 7.79 (s, 1H, aromatic C*H*), 7.71 (s, 1H, aromatic C*H*), 7.45 (s, 1H, aromatic C*H*), 7.40 (s, 1H, aromatic C*H*), 7.34 (s, 1H, aromatic C*H*), 7.26 (s, 2H, aromatic C*H*), 7.17 (s, 1H, aromatic C*H*), 6.30 (d, $^3J_{HH}$ = 2.5 Hz, 1H, aromatic C*H*), 6.24 (d, $^3J_{HH}$ = 2.6 Hz, 1H, aromatic C*H*), 6.20 (d, $^3J_{HH}$ = 2.6 Hz, 1H, aromatic C*H*), 6.04 (d, $^3J_{HH}$ = 2.6 Hz, 1H, aromatic C*H*), 6.01 (d, $^3J_{HH}$ = 2.4 Hz, 1H, aromatic C*H*), 5.10 (s, 1H, aromatic C*H*), 3.29−2.75 (ov m, 6H, C*H*(CH$_3$)$_2$), 2.57 (s, 3H, Cz C*H*$_3$), 2.55 (s, 6H, Cz C*H*$_3$), 2.51 (s, 6H, Cz C*H*$_3$), 2.48 (s, 3H, Cz C*H*$_3$), 1.18 (m, 6H, CH(C*H*$_3$)$_2$), 0.77 (m, 9H, CH(C*H*$_3$)(CH$_3$)), 0.71 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH(C*H*$_3$)(CH$_3$)), 0.67 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH(C*H*$_3$)(CH$_3$)), 0.62 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.44 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH(C*H*$_3$)(CH$_3$)), 0.30 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH(C*H*$_3$)(CH$_3$)), 0.21 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH(C*H*$_3$)(CH$_3$)). ^{13}C{^{1}H} NMR (THF-d_8, 263 K): δ 194.8 (LuC), 165.0 (aromatic *ipso*-*C*), 164.2 (aromatic *ipso*-*C*), 161.1 (aromatic *ipso*-*C*), 157.3 (aromatic *ipso*-*C*), 157.0 (aromatic *ipso*-*C*), 142.9 (aromatic *ipso*-*C*), 141.63 (aromatic *ipso*-*C*), 141.57 (aromatic *ipso*-C) 141.0 (aromatic *ipso*-*C*), 139.9 (aromatic *ipso*-*C*), 135.0 (aromatic *ipso*-*C*), 133.7 (aromatic *C*H), 133.3 (aromatic *C*H), 133.0 (aromatic *C*H), 132.0 (aromatic *C*H), 130.1 (aromatic *ipso*-*C*), 129.9 (aromatic *ipso*-*C*), 129.6 (aromatic *ipso*-C), 129.5 (aromatic *ipso*-C), 129.3 (aromatic *ipso*-*C*), 129.1 (aromatic *ipso*-*C*), 128.6 (aromatic *C*H), 128.1 (aromatic *ipso*-*C*), 127.7 (aromatic *ipso*-*C*), 127.4 (aromatic *ipso*-*C*), 127.2 (aromatic *ipso*-*C*), 127.2 (aromatic *ipso*-*C*), 126.31 (aromatic *ipso*-*C*), 126.29 (aromatic *ipso*-*C*) 126.2 (aromatic *ipso*-*C*), 125.9 (aromatic *ipso*-*C*), 125.8 (aromatic *ipso*-*C*), 125.6 (aromatic *ipso*-*C*), 125.1 (aromatic *ipso*-*C*), 123.1 (aromatic *ipso*-*C*), 119.8 (aromatic *C*H), 119.7 (aromatic *C*H), 119.5 (aromatic *C*H), 118.34 (aromatic *C*H), 118.27 (aromatic *C*H), 117.3 (aromatic *C*H), 116.7 (aromatic *C*H), 116.2 (aromatic *C*H), 115.7 (aromatic *C*H), 114.8 (aromatic *C*H), 113.8 (aromatic *C*H), 113.5 (aromatic *C*H), 107.0 (aromatic *C*H), 106.2 (aromatic *C*H), 106.0 (aromatic *C*H), 104.6 (aromatic *C*H), 104.0 (aromatic *C*H), 101.2 (aromatic *C*H), 33.1 (alkyl *C*), 30.9 (alkyl *C*), 29.3 (alkyl *C*), 29.0 (alkyl *C*), 28.7 (alkyl *C*), 28.5 (alkyl *C*), 28.4 (alkyl *C*), 28.1 (alkyl *C*), 28.0 (alkyl *C*), 26.0 (alkyl *C*), 25.8 (alkyl *C*), 24.6 (alkyl *C*), 24.5 (alkyl *C*), 24.4 (alkyl *C*), 23.8 (alkyl *C*), 23.7 (alkyl *C*), 23.6 (alkyl *C*), 23.0 (alkyl *C*), 22.5 (alkyl *C*), 22.2 (alkyl *C*), 21.70 (alkyl *C*), 21.66 (alkyl *C*), 21.60 (alkyl *C*), 21.5 (alkyl *C*). Anal. Calcd (%) for

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$C_{78}H_{88}Lu_3N_{15}$: C, 53.21; H, 5.04; N, 11.93. Found: C, 53.47; H, 4.71; N, 11.53.

General Crystallographic Details for 2a, 2b, 3a, and 4. Recrystallization of compounds **2a** and **2b** from concentrated benzene solutions at ambient temperature, **3a** from a concentrated mixture of toluene and THF at −35 °C, and **4** from a toluene solution at 50 °C afforded single crystals suitable for X-ray diffraction. Crystals were coated in dry Paratone oil under an argon atmosphere and mounted onto a glass fiber. Data were collected at −100 °C using a Bruker SMART APEX II diffractometer (Mo Kα radiation, λ = 0.71073 Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapor cooling device. A data collection strategy using ω and φ scans at 0.5° steps yielded full hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using APEX2 software.[19] Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software.[20] Absorption corrections were applied using SADABS.[21] The structures were solved by direct (**2a**, **2b**, and **4**) or Patterson (**3a**) methods and refined by the least-squares method on F^2 using the SHELXTL software suite.[22] In the refinement of **3a**, one toluene solvent molecule (C1S, 65%/C1R, 35%) was disordered over two positions. Some geometrical constraints were applied, and both components were modeled anisotropically. In the refinement of **4**, one toluene solvent molecule (C8S, 75%/C8R, 25%) was disordered over two positions. Some geometrical restraints and constraints were applied, and the major component was modeled anisotropically, while the minor component was held isotropic. All other non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms, except for all hydride ligands in **4**, which were located on the difference map and refined freely. Details of the data collection and refinement are given in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic details in CIF format, bond lengths and angles for **2a**, **2b**, **3a**, and **4** in PDF format, and NMR spectra of **3b** in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Cheng, J.; Saliu, K.; Kiel, G. Y.; Ferguson, M. J.; McDonald, R.; Takats, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 4910. (b) Ferrence, G. M.; McDonald, R.; Takats, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2233. (c) Long, D. P.; Bianconi, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 12453. (d) Lopes, I.; Lin, G. Y.; Domingos, A.; McDonald, R.; Marques, N.; Takats, J. *J. Am. Chem. Soc.* **1999**, *121*, 8110. (e) Cheng, J.; Saliu, K.; Ferguson, M. J.; McDonald, R.; Takats, J. *J. Organomet. Chem.* **2010**, *695*, 2696.

(2) (a) Trofimenko, S. *J. Chem. Educ.* **2005**, *82*, 1715. (b) Trofimenko, S. *Polyhedron* **2004**, *23*, 197.

(3) Mukherjee, R. *Coord. Chem. Rev.* **2000**, *203*, 151.

(4) (a) Wanniarachchi, S.; Liddle, B. J.; Toussaint, J.; Lindeman, S. V.; Bennett, B.; Gardinier, J. R. *Dalton Trans.* **2010**, *39*, 3167. (b) Wanniarachchi, S.; Liddle, B. J.; Toussaint, J.; Lindeman, S. V.; Bennett, B.; Gardinier, J. R. *Dalton Trans.* **2011**, *40*, 8776. (c) Wanniarachchi, S.; Liddle, B. J.; Lindeman, S. V.; Gardinier, J. R. *J. Organomet. Chem.* **2011**, *696*, 3623.

(5) (a) Johnson, K. R. D.; Hayes, P. G. *Organometallics* **2009**, *28*, 6352. (b) Johnson, K. R. D.; Hayes, P. G. *Organometallics* **2013**, *32*, 4046. (c) Johnson, K. R. D.; Hayes, P. G. *Dalton Trans.* **2014**, *43*, 2448.

(6) Johnson, K. R. D.; Hayes, P. G. *Chem. Soc. Rev.* **2013**, *42*, 1947.

(7) Wang, L.; Cui, D.; Hou, Z.; Li, W.; Li, Y. *Organometallics* **2011**, *30*, 760.

(8) Mudadu, M. S.; Singh, A. N.; Thummel, R. P. *J. Org. Chem.* **2008**, *73*, 6513.

(9) (a) Gibson, V. C.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 2718. (b) Britovsek, G. J. P.; Gibson, V. C.; Hoarau, O. D.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2003**, *42*, 3454. (c) Hollas, A. M.; Gu, W.; Bhuvanesh, N.; Ozerov, O. V. *Inorg. Chem.* **2011**, *50*, 3673.

(10) (a) Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140. (b) Suzuki, T.; Kinoshita, A.; Kawada, H.; Nakada, M. *Synlett* **2003**, *2003*, 570. (c) Inoue, M.; Nakada, M. *Org. Lett.* **2004**, *6*, 2977. (d) Inoue, M.; Nakada, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 252. (e) Inoue, M.; Nakada, M. *Heterocycles* **2007**, *72*, 133. (f) Zou, J.; Berg, D. J.; Stuart, D.; McDonald, R.; Twamley, B. *Organometallics* **2011**, *30*, 4958. (g) Zou, J.; Berg, D. J.; Oliver, A.; Twamley, B. *Organometallics* **2013**, *32*, 6532. (h) Durán-Galván, M.; Worlikar, S. A.; Connell, B. T. *Tetrahedron* **2010**, *66*, 7707. (i) Durán-Galván, M.; Connell, B. T. *Eur. J. Org. Chem.* **2010**, 2445. (j) Durán-Galván, M.; Hemmer, J. R.; Connell, B. T. *Tetrahedron Lett.* **2010**, *51*, 5080.

(11) Moser, M.; Wucher, B.; Kunz, D.; Rominger, F. *Organometallics* **2007**, *26*, 1024.

(12) (a) Pieters, R. J.; Rebek, J., Jr. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 330. (b) Zhou, H.-P.; Wang, P.; Hu, Z.-J.; Li, L.; Chen, J.-J.; Cui, Y.; Tian, Y.-P.; Wu, J.-Y.; Yang, J.-X.; Tao, X.-T.; Jiang, M.-H. *Eur. J. Inorg. Chem.* **2007**, 1854.

(13) Antilla, J. C.; Baskin, J. M.; Barder, T. E.; Buchwald, S. L. *J. Org. Chem.* **2004**, *69*, 5578.

(14) Johnson, K. R. D.; Hannon, M. A.; Ritch, J. S.; Hayes, P. G. *Dalton Trans.* **2012**, *41*, 7873.

(15) (a) Nishiura, M.; Baldamus, J.; Shima, T.; Mori, K.; Hou, Z. *Chem.—Eur. J.* **2011**, *17*, 5033. (b) Cheng, J.; Shima, T.; Hou, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 1857. (c) Lyubov, D. M.; Döring, C.; Ketkov, S. Y.; Kempe, R.; Trifonov, A. A. *Chem.—Eur. J.* **2011**, *17*, 3824. (d) Lyubov, D. M.; Döring, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Kempe, R.; Trifonov, A. A. *Organometallics* **2008**, *27*, 2905. (e) Avent, A. G.; Cloke, F. G. N.; Elvidge, B. R.; Hitchcock, P. B. *Dalton Trans.* **2004**, 1083. (f) Konkol, M.; Okuda, J. *Coord. Chem. Rev.* **2008**, *252*, 1577.

(16) Fegler, W.; Venugopal, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 7976.

(17) (a) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690. (b) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, *22*, 1212. (c) Masuda, J. D.; Jantunen, K. C.; Ozerov, O. V.; Noonan, K. J. T.; Gates, D. P.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 2408. (d) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422.

(18) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.

(19) *APEX2*, 2010.7-0; Bruker AXS: Madison, WI, 2010.

(20) *SAINT-Plus*, 7.68A; Bruker AXS: Madison, WI, 2009.

(21) Sheldrick, G. M. *SADABS*, 2008/1; Bruker AXS: Madison, WI, 2008.

(22) Sheldrick, G. M. *SHELXTL*, 6.19; Bruker AXS: Madison, WI, 2003.