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Heterobimetallic Pd(0) Complexes with Pd→Ln (Ln = Sc, Y, Yb, Lu) Dative Bonds: Rare-earth Metal Dominated Frustrated Lewis pair-like Reactivity

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A series of heterobimellic Pd-Ln complexes with $Pd \rightarrow Ln$ (Ln = Sc, Y, Yb, Lu) dative bonds were synthesized via sequential reactions of phosphinoamine Ph_2PNHAd with (Me_3SiCH_2)_3Ln(THF)_2 and (Ph_3P)_4Pd or (COD)Pd(CH_2SiMe_3)_2. These complexes were characterized by NMR spectrosopy, X-Ray diffractions, computational as well as electrochemical studies, which reveled $Pd \rightarrow Ln$ dative interactions that vary according to the ionic radii of Ln^{3+} . Further more, the notable dynamic structural feature of Pd-Ln complexes in solution and their unexpected frustrated Lewis pair-like reactivity toward aryl halides and ketene were also studied.

Introduction

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Transition metal complexes based on metalloligands have drawn increasing attention, which are largely due to the flexible electronic tuning within the LM \rightarrow LA (LM = late metal, LA = Lewis acidic metal) dative interaction.¹ Accordingly, systems based on group 13 LM \rightarrow LA (LA = B, Al, Ga, In) dative bond, were shown to be crucial in a variety of catalytic transformations, including hydrogenation of alkenes,² alkynes and CO_{2} ,^{3,4} hydrosilylation of CO2,5 and more recently, the hydrodechlorination of (hetero)arenes.⁶ chlorinate On the other hand. heterobimetallics of early-late transition metals, such as Zr/Ti-Pt, Zr-Ir, Zr/Ti-Rh, Zr/Ti-Co, Nb/Fe, Cr/Fe-Co, V/Fe-Co, consist of metal-metal bonds varying from dative interaction to multiple bonds, exhibited remarkable cooperative reactivity in the activations of CO₂, H₂, O₂ and related catalysis.⁷⁻¹²

Metalloligands utilizing the Lewis acidic rare-earth metal series are attractive due to the fine Lewis acidity tunable feature of Ln^{3+} (Ln = Sc, Y and lanthanides) by variation of their ionic radii from 0.745 Å (Sc³⁺) to 1.032 Å (La³⁺).^{13,14} However, unlike other transition metals, the highly oxo-, halo- and nitrophilic nature of these large and hard Ln^{3+} ions have posed more challenges to assemble the LM-Ln heterobimetallic complexes containing $LM \rightarrow Ln$ bonds.¹⁵ To date, few examples of

unsupported polar LM-Ln bonds were synthesized via salt metathesis or alkane (or H₂) elimination procedures.¹⁶ Interestingly, recent reports focused on phosphinoamido and phosphine-functionalized amido ligands, which supported not only weak Y/Lu-Pd/Pt interactions in the "ate-type" complexes,^{17a,b} but also stronger Ni \rightarrow Ln dative bonds in the catalytic hydrogenation of styrene and semihydrogenation of alkynes.¹³

We have reported the first $Pd \rightarrow Sc$ dative bond supported by a [Ph₂PCH₂NAd] ligand, where the electronic property of Pd(0) was affected by the Lewis acidic Sc³⁺ center in the reactions with isonitrile, CO and Mel.14a Expansion of the LM→Sc system to all group 10 metals showed versatile structural feature of LM-Sc heterobimetallics with relatively weaker LM→Sc dative bonds. ^{14b} We envisioned that removal of methylene linker in the previous ligand would generate a phosphinoamido [Ph₂PNAd] ligand (L) with a less electron donating phosphine, where the $Pd \rightarrow Ln$ bond and the reactivity of four-membered [P-Pd-Ln-N] hetero-metallacycle could be tuned in a different scenario. Herein we report a series of Pd-Ln complexes with Pd→Ln (Ln



Scheme 1 Syntheses of Complexes 1-10.

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Y, Yb, Lu) dative bonds, which exhibited notable dynamic structural feature, and unexpected frustrated Lewis pair-like reactivity toward aryl halide and ketene dominated by the rare-earth metal center.

Results and discussion

The acid-base reactions of LH with $(Me_3SiCH_2)_3Ln(THF)_2$ (Ln = Y, Yb, Lu) afforded the tris-phosphinoamido complexes 2-4 in ca. 70% yields (Scheme 1). Alternatively, for the smallest scandium, deprotonation of LH with Me_3SiCH_2Li, followed by the reaction with ScCl₃(THF)₃ afforded complex 1 in 60% yield. Compounds 1-4 were characterized by NMR spectroscopy methods and X-Ray diffraction studies (Fig. 1 and Fig. S41, S42). The solid-state structures of 1, 3 and 4 are similar, where the metal center exhibited distorted trigonal prismatic geometries and lies closer to the plane of N atoms than that of the P atoms by ca. 0.5 Å.

Subsequent reactions of 1-4 with 1 equiv of $(Ph_3P)_4Pd$ in benzene afforded the corresponding heterobimetallic Ln-Pd complexes 5-8 in ca. 60% yields (Scheme 1). Once isolated as solid, these compounds are sparingly soluble in benzene or toluene, and decompose in THF into intractable mixtures. The solid-state structures of 5-8 were determined by X-Ray diffraction studies (Fig. 1 and Fig. S43-S45). All the Ln-Pd complexes are isostructural, however, instead of forming a C_3 symmetric species as that for Sc-Pd complex reported previously,^{14a} in **5-8** one P atom of the phosphinoamide ligand remains ligated on the Ln³⁺ center while an additional PPh₃ ligand binds to the Pd(0) atom besides the other two P atoms of phosphinoamide ligands. The geometries at Pd(0) relative to three coordinated P donors are nearly planar (avg. Σ_{angle} at Pd = 359°), while those at Ln³⁺ relative to the three N donors are less planar (avg. Σ_{angle} at Sc = 353°). The Ln-Pd bond lengths



Figure 1 Representative molecular structures of **1**, **7**, **9** and core bond lengths in **7A**. Co-crystallized solvent molecules and hydrogen atoms were removed for clarity.





increased from 2.6874(18) Å in 5 (Sc) to 2.8096(5) Å in 6 (Y), which follow the order of ionic radii of $Y^{3+} > Yb^{3+} > Lu^{3+} > Sc^{3+}$ (for CN = 6) and are significantly shorter than the sum of the covalent radii of Ln and Pd (3.09 Å and 3.29 Å for Sc/Pd and Y/Pd, respectively).¹⁸ Notably, the observed Ln-Pd bond lengths are significantly shorter than those of 2.9898(6) Å and 2.9712(8) Å in the previously reported Y-Pd and Lu-Pd complexes supported with less bulky phosphinoamido ligand.^{17b} The Pd-P bond lengths with the phosphinoamido ligand are very close for 6-8 (ca. 2.34 and 2.38 Å), but shorter for the 5 (ca. 2.32 and 2.36 Å), consistent with the ionic radii of Ln^{3+} . However, the Pd-P bond lengths with the PPh₃ ligand are nearly identical for 5-8 (ca. 2.367 Å), which might be attributed to steric reasons. For comparison reasons, the palladium complex 9 supported by LH ligand was also synthesized (Scheme 1) and characterized by NMR spectroscopy and X-Ray diffraction studies (Fig. 1).

The solid-state structures of Ln-Pd complexes possess C_1 symmetry (Fig. 1, 7A), as supported by the observation of four peaks in the ratio of 1:1:1:1 in the ³¹P{¹H} CP-MAS NMR spectra of 5 and 6 (Fig. 2). However, the ³¹P{¹H} NMR spectrum of 5 in C_6D_6 at 295K exhibited one broad singlet at δ = 22.31 ppm and a quartet at δ = 19.47 (²J_{PP} = 24.9 Hz) in a ratio of 3:1, which turned at 203K to one sharp doublet at δ = 21.47 (²J_{PP} = 16.4 Hz) ppm and a quartet at δ = 19.70 ppm (²J_{PP} = 16.5 Hz), respectively. For the Y-Pd complex 6, the ³¹P{¹H} NMR spectrum in C₆D₆ at 295K revealed a doublet of doublets at δ = 22.91 ppm $({}^{2}J_{\rm PP}$ = 42.4 Hz, ${}^{1}J_{\rm YP}$ = 16.2 Hz), and a quartet of doublets at δ = 16.90 ppm (${}^{2}J_{PP}$ = 42.4 Hz, ${}^{1}J_{YP}$ = 7.1 Hz) in a ratio of 3:1. At lower temperature, broadening of the former resonance was observed, which showed coalescence at ca. 223K and started to emerge as two broad peaks at ca. δ = 21.9 and 27.3 ppm at 203K. Due to the poor baseline of spectra caused by poor solubility of 6, the relative ratio of these two broad peaks at 203K was not accounted. The ³¹P{¹H} NMR spectroscopy data of 5 and 6 (for 8, see ESI) are consistent with the existence of an apparent C_3 symmetric species in solution at room temperature, due to the rapid exchanges of three phosphine donors in the C_1 symmetric

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Figure 3 localized orbitals representing the dative $Pd \rightarrow Y$ bond in **6** (isovalue = 0.02).

species. The calculated C_3 symmetric structure for **7**, in which all three phosphines of the phosphinoamido ligand coordinate to the palladium, is ca. 4.8 kcal/mol higher in energy than that of the C_1 symmetric structure, thus indicating for **7** the rapid exchange of phosphines in the C_1 symmetric species probably proceeded via the high energetic C_3 symmetric structure.

Computational studies based on density functional theory (ORCA quantum chemistry package version 4.1.1) were performed to further elucidate the Ln-Pd bonding feature in 5-8.19 The calculated Ln-Pd bond lengths (5-8: 2.688, 2.797, 2.781 and 2.763 Å, respectively) are comparable to the experimental values (5-8: 2.6874(18), 2.8096(5), 2.7879(6) and 2.7623(10) Å). Other core parameters of the first coordiantion sphere (see ESI) are also in well agreement with those from X-Ray diffraction studies. The localized orbitals based on Pipek-Mezey algorithm showed that all Ln-Pd bonds in 5-8 were mainly constructed by overlap of the d_z^2 -like atomic orbitals of Pd (from 5-8: 82.6%, overlap of the d_z^2 -like atomic orbitals of Pd (from 5-8: 82.6%, 87.0%, 83.0% and 84.6%, respectively) and Ln (11.3%, 7.3%,11.4% and 11.5%, respectively), indicating a dative Pd→Ln bonding character (Fig. 3). The other four doubly-occupied d orbitals of Pd in 5-8 (d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$) showed no significant interactions with the symmetry allowed d orbitals of Ln³⁺. In accordance, the NBO analysis ²⁰ showed formal d¹⁰ electron configurations for Pd atom and d⁰ electron configuration for Ln atom in these compounds (See ESI). The calculated Mayer bond orders of 0.414 (5), 0.334 (6), 0.368 (7) and 0.359 (8) are close to each other and smaller than that of 0.795 for the Pd \rightarrow Sc dative bond reported previously,^{14a} indicating a weaker $Pd \rightarrow Ln$ dative interaction in the current system.

The electrochemical properties of **5-9** were studied (details see ESI). As shown in Fig. 4, similar redox features were exhibited for the series. The Sc-Pd complex showed a quasi-reversible redox event at -0.55V assigned as Pd-based redox process, which is 0.21V more positive than that of -0.76V observed for **9**. All the other Ln-Pd complexes showed similar redox peaks that are more positive than -0.76 V. It is notable that within the series of **5-8**, the Sc-Pd complex holds the most positive Pd-based redox process, consistent with the strongest



Figure 4 Cyclic voltammograms of complexes **5-8** obtained with 0.1M $[{}^{n}Pr_{4}N][BAr_{4}^{F}]$ in 1,2-difluorobenzene as supporting electrolyte; scan rate: 50 mV/s, vs. Fc/Fc⁺.

Lewis acidity of Sc^{3+} among the rare-earth metals. The second major oxidation peaks were observed from 0.1 to 0.3V for **5-8**, by comparison with the oxidation peaks at -0.31 V and -0.13 V based on Pd for **9**, which indicated other Pd species under the electrochemical condition, we tentatively assigned the second major oxidation peaks for **5-8** were from other Pd species due to the dissociation of PPh₃ or other processes. The last two redox events were all attributed to ligand-based processes according to the observed oxidation peaks at 0.78 V for **LH** and 0.66 V for **9**.

Reactivity of Y-Pd complex **6** toward aryl halides were initially targeted for the studies of Heck-type reaction (Scheme 2). However, the reaction of **6** with 3 equiv of iodobenzene at 60° C for 0.5 h produced phosphinimine **11** as the only observable product in the NMR spectra in C₆D₆. Based on the off-white precipitates and a dark solution formed during the reaction, the fate of yttrium and palladium was most likely to be YI₃ and nanoparticles of [Ph₃PPd]_n, respectively. Chloro- (24h at 120°C for 55% conv.) and bromobenzene (4h at 100°C for 100% conv.) reacted with **6** in similar fashion to form **11**. Even the bulky MesBr reacted with **6** at 100°C for 24h to produce phosphinimine **12** in 50% yield. The observed halides abstraction and formation of phosphinimines highlighted the halophilic property of Ln³⁺ in the heterobimetallic Ln-Pd complexes. On the other hand, the depletion of electron density



Scheme 2 FLP-like reactivity of Ln-Pd complexes.

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Figure 5 Molecular structures of **13** and **14**. Co-crystallized solvent molecules and hydrogen atoms were removed for clarity.

from Pd(0) via the Pd \rightarrow Ln dative bond would also retard the oxidative addition on the Pd(0).

Treatment of 6 with 1 equiv of diphenylketene led to the isolation of a zwitterionic complex 13 caused by a nucleophilic attack of the ketene by the phosphine that initially coordinated with the $Y^{3\ast}$ ion, in reminiscent of the recently reported Y/Pfrustrated Lewis-pair reactivity.²¹ The crystal structure of 13 was determined by X-Ray diffraction studies, which showed the PPh₃ ligand on the palladium remains intact (Fig. 5). In order to probe if the observed Y/P FLP reactivity was forced by the axial PPh₃ ligand on palladium, which blocked the potential Ln/Pd FLPtype reactivity, complex 10 was synthesized via the metalation of 1 with 1 equiv of (COD)Pd(CH₂SiMe₃)₂. The ${}^{31}P{}^{1}H$ NMR spectrum of **10** showed a singlet peak at δ = 19.03 ppm, indicating a C_3 symmetry with only one type of phosphine donor. Interestingly, the reaction of 10 with 1 equiv of diphenylketene afforded a similar zwitterionic complex 14 formed via a Sc/P frustrated Lewis-pair, which was confirmed by an X-Ray diffraction studies (Fig. 5). The observed FLP-type reaction with ketene was largely attributed to the highly oxophilic property of rare-earth metal center, which dominated the reactivity of heterbimetallic Ln-Pd complexes. The coordination of axial PPh₃ showed little effect on the observed reactivity pattern.

Conclusions

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In summary, a series of heterobimetallic Ln-Pd complexes supported by a bulky phosphinoamido ligand showed notable structural features compared to the previously known systems with P-N ligand. While a relatively weaker Pd \rightarrow Ln dative bond was observed, the current heterobimetallic system exhibited an unexpected reactivity involving the Ln/P frustrated Lewis-pair, indicating a dramatic effect caused by variation of the ancillary phosphinoamido ligand. Further studies toward the reactivity of Ln-Pd complexes within the Pd \rightarrow Ln bond is underway.

Experimental

General. All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. THF, pentane, *n*-hexane, benzene, toluene, C_6D_6 , toluene- d_8 and THF- d_8 were dried over K-Na alloy, followed by vacuum transferred, and stored in the glovebox. CH₂Cl₂ were

dried over CaH₂ and distilled under nitrogen prior to the spectral were recorded or the prior of the spectral were recorded or the prior of the spectral spectral

Synthesis of LH: To a 250 mL Schlenk flask charged with Et₃N (11.12 ml, 80 mmol), AdNH₂ (6.05 g, 40 mmol) and 100 mL of CH₂Cl₂, Ph₂PCl (7.18 mL, 40 mol) was added dropwise by syringe over the course of 30 min at 0°C. The reaction mixture was allowed to stir at room temperature for 24 h, and the volatiles were removed under reduced pressure. The residues were extracted with n-hexane (3×50 mL) and filtered. The n-hexane solution was evaporated under reduced pressure to give a white waxy solid, which was recrystallized in n-hexane to yield LH as a white solid. Yield: 11.5 g (86%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.54-7.51 (m, 4H, ArH), 7.18-7.08 (m, 4H, ArH, overlapped with C_6D_6 residue peak), 7.09 (tt, ${}^3J_{HH}$ = 7.3 Hz, ${}^4J_{HH}$ = 1.5 Hz, 2H, ArH), 1.91 (s, 3H, CH), 1.89 (s, 1H, NH), 1.77 (s, 6H, CH₂), 1.50 (s, 6H, CH₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 144.85 (d, J_{PC} = 12.6 Hz, ArC), 131.49 (d, J_{PC} = 20.2 Hz, ArC), 128.47 (d, J_{PC} = 6.3 Hz, ArC), 128.30 (s, ArC, overlapped with $C_6 D_6$ residue peak), 51.35 (d, $J_{PC} = 17.6$ Hz, NC), 46.26 (d, J_{PC} = 8.8 Hz, CH₂), 36.64 (s, CH), 30.42 (s, CH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 18.26 (s). Anal. Calcd for C₂₂H₂₆NP (335.42 g/mol): C, 78.78; H, 7.81; N, 4.18. Found: C, 78.87; H, 7.86; N, 4.24.

Synthesis of 1: LiCH₂SiMe₃ (62.1 mg, 0.66 mmol) in 2 mL of toluene was slowly added to a solution of LH (200 mg, 0.60 mmol) in 3 mL of toluene at -35°C. The reaction mixture was then stirred at room temperature for 4 h, and added to a slurry of ScCl₃(THF)₃ (73.5 mg, 0.20 mmol) in 5 mL of toluene at room temperature. After stirring for 12 h, the reddish-brown reaction mixture was filtered and 5 mL of *n*-hexane was layered, which was stored at -35°C overnight to afford 1 as colorless crystals. Yield: 126 mg (60%). ¹H NMR (C_6D_6 , 500 MHz, 25°C): δ (ppm) = 7.94 (br s, 12H, ArH), 7.08 (br s, 18H, ArH), 2.11 (s, 18H, CH₂), 1.96 (s, 9H, CH), 1.53 (s, 18H, CH₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 140.80 (s, ArC), 134.15 (d, J_{PC} = 13.9 Hz, ArC), 128.62 (s, ArC), 60.44 (d, J_{PC} = 11.3 Hz, NC), 48.39 (s, AdCH₂), 37.01 (s, AdCH), 31.08 (s, AdCH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 15.57 (s). Anal. Calcd for $C_{66}H_{75}N_3P_3Sc$ (1048.20 g/mol): C, 75.63; H, 7.21; N, 4.01. Found: C, 76.16; H, 7.62; N, 3.50.

Synthesis of 2: $Y(CH_2SIMe_3)_3(THF)_2$ (98.4 mg, 0.20 mmol) in 2 mL of *n*-hexane was slowly added to a solution of LH (200 mg, 0.60 mmol) in 5 mL of *n*-hexane at room temperature. The reaction mixture was then stirred at room temperature for 4 h, during which time white powder precipitated from the solution. The solvent was evaporated under reduced pressure and the

resulted white solid was recrystallized in toluene/*n*-hexane at - 35°C to afford **2** as white crystalline solid. Yield: 142 mg (65%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.87 (t, ³J_{HH} = 7.0 Hz, 12H, Ar*H*), 7.11-7.06 (m, 18H, Ar*H*), 2.11 (s, 18H, C*H*₂), 1.99 (s, 9H, C*H*), 1.60 (d, ²J_{HH} = 11.5 Hz, 9H, C*H*₂), 1.54 (d, ²J_{HH} = 12.0 Hz, 9H, C*H*₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 141.01 (s, ArC), 133.76 (m, ArC), 128.56 (d, J_{PC} = 11.3 Hz, ArC), 59.36 (d, J_{PC} = 15.1 Hz, NC), 49.19 (s, AdCH₂), 37.02 (s, AdCH), 31.08 (s, AdCH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 16.11 (d, ¹J_{YP} = 30.3 Hz). Anal. Calcd for C₆₆H₇₅N₃P₃Y (1092.15 g/mol): C, 72.58; H, 6.92; N, 3.85. Found: C, 72.30; H, 7.13; N, 3.49.

Synthesis of 3: Yb(CH₂SiMe₃)₃(THF)₂ (115.4 mg, 0.20 mmol) in 2 mL of *n*-hexane was slowly added to a solution of **LH** (200 mg, 0.60 mmol) in 5 mL of *n*-hexane at room temperature. The reaction mixture was then stirred at room temperature for 4 h, during which time yellow powder precipitated from the solution. The solvent was evaporated under reduced pressure and the resulted yellow solid was recrystallized in toluene/*n*-hexane at -35°C to afforded **3** as pale yellow crystals. Yield: 169 mg (72%). Anal. Calcd for C₆₆H₇₅N₃P₃Yb (1176.30 g/mol): C, 67.39; H, 6.43; N, 3.57. Found: C, 66.88; H, 6.69; N, 3.29.

Synthesis of 4: Lu(CH₂SiMe₃)₃(THF)₂ (116.2 mg, 0.20 mmol) in 2 mL of *n*-hexane was slowly added to a solution of LH (200 mg, 0.60 mmol) in 5 mL of *n*-hexane at room temperature. The reaction mixture was then stirred at room temperature for 4 h, during which time white powder precipitated from the solution. The solvent was evaporated under reduced pressure and the resulted white solid was recrystallized in toluene/n-hexane at -35°C to afforded 4 as white block crystals. Yield: 160 mg (68%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.88 (br t, not resolved, 12H, ArH), 7.10-7.06 (m, 18H, ArH), 2.13 (s, 18H, CH₂), 2.00 (s, 9H, CH), 1.60 (d, ²J_{HH} = 11.5 Hz, 9H, CH₂), 1.54 (d, ²J_{HH} = 12.0 Hz, 9H, CH₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 140.66 (s, ArC), 133.98 (m, ArC), 128.60 (s, ArC), 59.57 (d, J_{PC}= 15.1 Hz, NC), 49.14 (s, AdCH₂), 37.02 (s, AdCH), 31.12 (s, AdCH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 27.09 (s). Anal. Calcd for $C_{66}H_{75}N_3P_3Lu$ (1178.21 g/mol): C, 67.28; H, 6.42; N, 3.57. Found: C, 67.02; H, 6.73; N, 3.16.

Synthesis of 5: Complex 1 (52 mg, 0.05 mmol) in 2 mL of C₆H₆ was added to a solution of (PPh₃)₄Pd (58 mg, 0.05 mmol) in 3 mL of C₆H₆ at room temperature. The reaction mixture was then stirred at 60°C for 12 h. After cooling, the brown solution was filtered and 5 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford 5 as yellow crystals. Yield: 28 mg (53%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.66 (s, 12H, ArH), 7.10-7.05 (m, 12H, ArH), 7.00 (t, ³J_{HH} = 7.0 Hz, 12H, ArH), 6.90 (t, ${}^{3}J_{HH}$ = 7.0 Hz, 3H, ArH), 6.67 (t, ${}^{3}J_{HH}$ = 7.5 Hz, 6H, ArH), 2.29 (s, 18H, CH₂), 2.02 (s, 9H, CH), 1.63 (d, ²J_{HH} = 11.5 Hz, 9H, CH₂), 1.54 (d, ²J_{HH} = 12.0 Hz, 9H, CH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 22.31 (br s, 3P), 19.47 (q, ²J_{PP} = 24.9 Hz, 1P). ³¹P{¹H} NMR (CP-MAS, 15kHz, 25°C): δ (ppm) = 28.45 (s, 1P), 23.00 (s, 1P), 18.09 (s, 1P), 10.99 (s, 1P). Anal. Calcd for C₈₄H₉₀N₃P₄PdSc (1416.90 g/mol): C, 71.20; H, 6.40; N, 2.97. Found: C, 71.23; H, 6.59; N, 2.93. Due to its poor solubility in

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common organic solvent, a satisfactory ¹³C{¹H} NMR spactrum was not obtained. DOI: 10.1039/D0DT02708A

Synthesis of 6: Complex 2 (55 mg, 0.05 mmol) in 2 mL of C₆H₆ was added to a solution of (PPh₃)₄Pd (58 mg, 0.05 mmol) in 3 mL of C₆H₆ at room temperature. The reaction mixture was then allowed to stir at room temperature for 12 h. The resulted brown solution was filtered and 5 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford 6 as yellow crystals. Yield: 46 mg (63%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.77 (br s, 12H, ArH), 7.12-7.07 (m, 18H, ArH), 7.01 (t, ³J_{HH} = 7.5 Hz, 6H, ArH), 6.87 (t, ³J_{HH} = 7.5 Hz, 3H, ArH), 6.69 (t, ³J_{HH} = 7.5 Hz, 6H, ArH), 2.17 (s, 18H, CH₂), 1.94 (s, 9H, CH), 1.59 (d, ²J_{HH} = 11.8 Hz, 9H, CH₂), 1.50 (d, ²J_{HH} = 11.5 Hz, 9H, CH_2). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 22.91 (dd, ${}^{2}J_{PP}$ = 42.4 Hz, ${}^{1}J_{YP}$ = 16.2 Hz, 3P), 16.90 (qd, ${}^{2}J_{PP}$ = 42.4 Hz, ${}^{1}J_{YP}$ = 7.1 Hz, 1P). ³¹P{¹H} NMR (CP-MAS, 15kHz, 25°C): δ (ppm) = 27.51 (s, 1P), 21.34 (s, 1P), 16.21 (s, 1P), 12.45 (s, 1P). Anal. Calcd for C₈₄H₉₀N₃P₄PdY (1460.85 g/mol): C, 69.06; H, 6.21; N, 2.88. Found: C, 69.08; H, 6.23; N, 2.97. Due to its poor solubility in common organic solvent, a satisfactory ¹³C{¹H} NMR spectrum was not obtained.

Synthesis of 7: Complex **4** (59 mg, 0.05 mmol) in 2 mL of C_6H_6 was added to a solution of (PPh₃)₄Pd (58 mg, 0.05 mmol) in 3 mL of C_6H_6 at room temperature. The reaction mixture was then allowed to stir at room temperature for 12 h. The resulted brown solution was filtered and 5 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford **7** as red crystals. Yield: 50 mg (65%). Anal. Calcd for $C_{84}H_{90}N_3P_4PdYb$ (1545.00 g/mol): C, 65.30; H, 5.87; N, 2.72. Found: C, 65.47; H, 6.01; N, 2.60.

Synthesis of 8: Complex 5 (59 mg, 0.05 mmol) in 2 mL of C₆H₆ was added to a solution of (PPh₃)₄Pd (58 mg, 0.05 mmol) in 3 mL of C_6H_6 at room temperature. The reaction mixture was then allowed to stir at room temperature for 12 h. The resulted brown solution was filtered and 5 mL of n-hexane was layered, which was stored at room temperature overnight to afford 8 as yellow crystals. Yield: 47 mg (61%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.77 (br s, ArH), 7.12-7.00 (m, 24H, ArH), 6.88 (td, ${}^{3}J_{HH}$ = 7.5 Hz, ${}^{4}J_{HH}$ = 1.2 Hz, 3H, ArH), 6.68 (td, ${}^{3}J_{HH}$ = 7.8 Hz, ⁴J_{HH} = 1.3 Hz, 6H, ArH), 2.22 (s, 18H, CH₂), 1.98 (s, 9H, CH), 1.61 (d, ${}^{2}J_{HH} = 11.5$ Hz, 9H, CH₂), 1.52 (d, ${}^{2}J_{HH} = 12.5$ Hz, 9H, CH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 31.88 (d, ²J_{PP} = 46.5 Hz, 3P), 18.48 (q, ${}^{2}J_{PP}$ = 41.1 Hz, 1P). Anal. Calcd for C₈₄H₉₀N₃P₄PdLu (1546.92 g/mol): C, 65.22; H, 5.86; N, 2.72. Found: C, 65.25; H, 5.92; N, 2.75. Due to its poor solubility in common organic solvent, a satisfactory ¹³C{¹H} NMR spectrum was not obtained.

Synthesis of 9: Method A: LH (50 mg, 0.15 mmol) in 2 mL of THF was added to a suspension of (COD)PdCl₂ (14 mg, 0.05 mmol) in 3 mL of THF. After stirring at room temperature for 3 h, magnesium power (3.65 mg, 0.15 mmol) was added and the slurry was stirred for another 12 h, during which time a dark green solution was formed. The solution was filtered and 5 mL of *n*-hexane was layered at room temperature to afford yellow crystals, which was washed with *n*-hexane and dried under

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vacuum. Yield: 18 mg (32%). Method **B**: LH (50 mg, 0.15 mmol) in 2 mL of toluene was added to a solution of (COD)Pd(CH₂SiMe₃)₂ (20 mg, 0.05 mmol) in 2 mL of toluene. After stirring at room temperature for 2 h, during which time a red solution was formed. The solution was filtered and 6 mL of *n*-hexane was layered at -35°C to afford yellow crystals. Yield: 22 mg (40%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.78 (br s, 12H, Ar*H*), 7.17-7.14 (m, 12H, Ar*H*, overlapped with C₆D₆ residue peak), 7.08 (tt, ³J_{HH} = 7.3 Hz, ³J_{HH} = 1.5 Hz, 6H, Ar*H*), 1.98-1.90 (m, 28H, N*H* and AdC*H*), 1.49 (s, 18H, AdC*H*₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 145.01 (s, Ar*C*), 132.14 (s, Ar*C*), 52.06 (s, N*C*), 46.42 (s, AdCH₂), 36.71 (s, AdCH), 30.57 (s, AdCH₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 39.47 (br s). Anal. Calcd for C₆₆H₇₈N₃P₃Pd (1112.69 g/mol): C, 71.24; H, 7.07; N, 3.78. Found: C, 70.62; H, 7.42; N, 3.43.

Synthesis of 10: Complex 1 (50 mg, 0.048 mmol) in 2 mL of toluene was added to a solution of (COD)Pd(CH₂SiMe₃)₂ (19 mg, 0.048 mmol) in 2 mL of toluene at room temperature. The reaction mixture was then stirred at room temperature for 24 h. The resulted red solution was filtered and 6 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford 10 as red crystalline solid. Yield: 20 mg (36%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.72 (s, 12H, ArH), 7.13 (t, ³J_{HH} = 7.5 Hz, 6H, ArH), 7.07 (t, ³J_{HH} = 7.4 Hz, 12H, ArH), 2.13 (s, 18H, CH₂), 1.99 (s, 9H, CH), 1.60 (d, ²J_{HH} = 12.1 Hz, 9H, CH₂), 1.52 (d, $^{2}J_{HH}$ = 12.0 Hz, 9H, CH₂). $^{31}P{^{1}H}$ NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 19.03 (s, 1P). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 143.83 (s, ArC), 134.87 (s, ArC), 128.92 (s, ArC), 127.86 (s, ArC), 59.25 (s, NC), 49.67 (s, AdCH₂), 37.32 (s, AdCH), 31.34 (s, AdCH₂). Anal. Calcd for C₆₆H₇₅N₃P₃PdSc (1154.62 g/mol): C, 68.66; H, 6.55; N, 3.64. Found: C, 69.39; H, 6.85; N, 3.16.

Synthesis of 11: PhI (11.5 μ L, 0.1 mmol) in 1 mL of C₆H₆ was added to a suspension of 6 (50 mg, 0.034 mmol) in 3 mL of C_6H_6 at room temperature. The reaction mixture was stirred at 60°C for 0.5 h, during which time a dark red solution was gradually formed. The solution was evaporated under vacuum and the residue was extracted into 2 mL of n-hexane, which was filtered and stored at -35°C overnight to afford 11 as colorless crystals. Yield: 18 mg (43%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 7.93-7.89 (m, 6H, ArH), 7.08-7.05 (m, 9H, ArH), 2.05 (s, 9H, CH and CH_2), 1.67 (d, ${}^2J_{HH}$ = 11.5 Hz, 3H, CH_2), 1.61 (d, ${}^2J_{HH}$ = 11.5 Hz, 3H, CH₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 137.88 (s, ArC), 137.11 (s, ArC), 133.29 (d, J_{PC} = 9.6 Hz, ArC), 130.80 (s, ArC), 52.69 (s, AdCH₂), 50.41 (d, J_{PC} = 10.0 Hz, NC), 37.62 (s, AdCH₂), 31.51 (s, AdCH). $^{31}P\{^{1}H\}$ NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = -15.67 (s, 1P). Anal. Calcd for C₂₈H₃₀NP (411.52 g/mol): C, 81.72; H, 7.35; N, 3.40. Found: C, 81.15; H, 7.52; N, 3.39.

Synthesis of 12: 2,4,6-trimethybromombenzene (15.8 μ L, 0.1 mmol) in 1 mL of C₆H₆ was added to a suspension of **6** (50 mg, 0.034 mmol) in 3 mL of C₆H₆ at room temperature. The reaction mixture was stirred at 100°C for 24 h, during which time a dark red solution was gradually formed. The solution was evaporated under vacuum and the residue was extracted into 2 mL of *n*-hexane, which was filtered and stored at -35°C overnight to

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afford **12** as colorless crystals. Yield: 23 mg (50%). ¹HeNMR($G_{6D}G_{9}$ 500 MHz, 25°C): δ (ppm) = 8.06 (dd, ³J_{HH} \cong 7.0°H2, ³J_H \cong 7.2°H2, 4H, ArH), 7.05 (td, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 2.5 Hz, 4H, ArH), 6.98 (td, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.5 Hz, 2H, ArH), 6.67 (d, J_{PH} = 3 Hz, 2H, ArH), 2.18 (s, 6H, CH₃), 2.11 (s, 6H, CH₂), 2.09 (s, 3H, CH₃), 2.05 (s, 3H, CH), 1.72 (d, ²J_{HH} = 11.3 Hz, 3H, CH₂), 1.65 (d, ²J_{HH} = 12.0 Hz, 3H, CH₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz, 25°C): δ (ppm) = 143.37 (d, J_{PC} = 9.2 Hz, ArC), 142.52 (s, ArC), 140.36 (d, J_{PC} = 9.1 Hz, ArC), 132.42 (s, ArC), 131.89 (s, ArC), 131.50 (d, J_{PC} = 9.1 Hz, ArC), 131.11 (d, J_{PC} = 9.1 Hz, ArC), 129.84 (d, J_{PC} = 2.1 Hz, ArC), 52.27 (s, AdCH₂), 50.38 (d, J_{PC} = 5.9 Hz, CH₃), 21.26 (s, CH₃). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = -24.06 (s, 1P). Anal. Calcd for C₃₁H₃₆NP (453.60 g/mol): C, 82.08; H, 8.00; N, 3.09. Found: C, 81.90; H, 8.66; N, 2.91.

Synthesis of 13: Diphenylketene (6 µL, 0.034 mmol) in 1 mL of toluene was added to a suspension of 6 (50 mg, 0.034 mmol) in 3 mL of toluene at room temperature. The reaction mixture was stirred at room temperature for 2 h, during which time a clear reddish brown solution was gradually formed. The solution was filtered and 4 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford 13 as yellow crystals. Yield: 22 mg (39%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 8.24 (d, ²J_{HH} = 8.8 Hz, 2H, ArH), 7.92 (br s, 10H, ArH), 6.96-6.91 (m, 6H, ArH), 6.85 (t, ³J_{HH} = 8.2 Hz, 2H, ArH), 6.78-6.65 (m, 14H, ArH), 6.46 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 2H, ArH), 2.50 (d, ${}^{2}J_{HH}$ = 12.5 Hz, 6H, CH_2), 2.39 (d, ${}^2J_{HH}$ = 12.4 Hz, 6H, CH_2), 2.20 (s, 6H, CH_2), 1.96 (s, 6H, CH₂), 1.63 (d, ²J_{HH} = 10.8 Hz, 6H, CH₂), 1.56 (s, 3H, CH), 1.46 (d, ${}^{2}J_{HH}$ = 12.3 Hz, 6H, CH₂), 1.41 (d, ${}^{2}J_{HH}$ = 10.5 Hz, 3H, CH), 1.12 (d, ²J_{HH} = 11.4 Hz, 3H, CH). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 30.33 (d, ${}^{2}J_{PP}$ = 60.2 Hz, 2P), 27.53 (d, J_{YP} = 10.6 Hz, 1P), 16.18 (t, not well resolved, ${}^{2}J_{PP}$ = 62.2 Hz, 1P). Anal. Calcd for C₉₈H₁₀₀N₃OP₄PdY (1653.49 g/mol): C, 71.12; H, 6.09; N, 2.54. Found: 70.94; H, 6.34; N, 2.36. Due to its poor solubility in common organic solvent, a satisfactory ¹³C{¹H} NMR spectrum was not obtained. Although satisfactory elemental analyses were obtained, bulk sample of 13 contains small amount of impurities, which could not be removed by fractional recrystallization.

Synthesis of 14: Diphenylketene (7.6 µL, 0.043 mmol) in 1 mL of toluene was added to a suspension of 10 (50 mg, 0.043 mmol) in 3 mL of toluene at room temperature. The reaction mixture was stirred at room temperature for 2 h, during which time a clear reddish brown solution was gradually formed. The solution was filtered and 4 mL of *n*-hexane was layered, which was stored at room temperature overnight to afford 14 as yellow crystals. Yield: 24 mg (41%). ¹H NMR (C₆D₆, 500 MHz, 25°C): δ (ppm) = 8.10 (s, 6H, ArH), 8.02 (s, 3H, ArH), 7.93 (s, 3H, Ar*H*), 7.26 (t, ³J_{HH} = 6.8 Hz, 8H, Ar*H*), 7.16 (s, 7H, Ar*H*), 7.14-7.11 (m, 7H, ArH), 6.97 (t, ³J_{HH} = 7.1 Hz, 1H, ArH), 6.85 (t, ³J_{HH} = 7.4 Hz, 1H, ArH), 6.66 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 2H, ArH), 6.38 (d, ${}^{3}J_{HH}$ = 7.4 Hz, 2H, ArH), 2.59 (d, ${}^{2}J_{HH}$ = 11.5 Hz, 6H, CH₂), 2.54 (d, ${}^{2}J_{HH}$ = 11.7 Hz, 6H, CH₂), 2.13 (s, 6H, CH₃), 2.04 (s, 6H, CH₃), 1.61 (d, ²J_{HH} = 11.6 Hz, 6H, CH₂), 1.48 (d, ²J_{HH} = 12.5 Hz, 9H, CH₂), 1.24 (s, 6H, CH). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 25°C): δ (ppm) = 33.06 (s, 1P), 30.00 (s, 2P). Anal. Calcd for C₈₀H₈₅N₃OP₃PdSc (1348.85 g/mol):

C, 71.24; H, 6.35; N, 3.12. Found: C, 70.40; H, 6.54; N, 2.93. Due to its poor solubility in common organic solvent, a satisfactory ${}^{13}C{}^{1}H$ NMR spectrum was not obtained. Although satisfactory elemental analyses were obtained, bulk sample of **14** contains small amount of impurities, which could not be removed by fractional recrystallization.

X-ray crystallography

Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.^{23a} All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.^{23b} The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.^{23c} Crystal parameters and refinement results are given in the ESI.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Textual for the table of contents entry:

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A series of Pd-Ln complexes with $Pd \rightarrow Ln$ (Ln = Sc, Y, Yb, Lu) dative bonds showed notable dynamic structural feature and unexpected frustrated Lewis pair-like reactivity.

Graphical abstract for the table of contents entry:

