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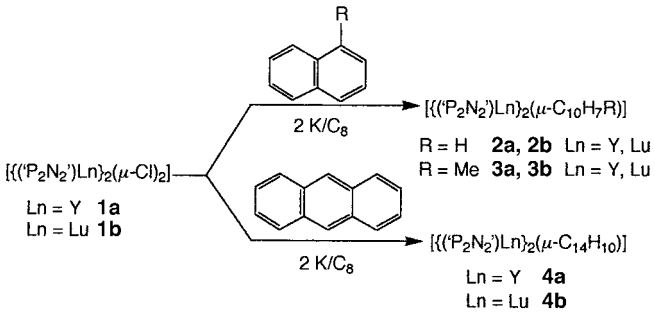
Dinuclear π Complexes of Yttrium and Lutetium with Sandwiched Naphthalene and Anthracene Ligands: Evidence for Rapid Intramolecular Inter-Ring Rearrangements**

Michael D. Fryzuk,* Laleh Jafarpour, Francesca M. Kerton, Jason B. Love, and Steven J. Rettig

The coordination of aromatic hydrocarbons to transition metals is of considerable interest in organometallic chemistry not only from the point of view of bonding but also in organic synthesis.[1] In particular, benzene and substituted benzenes coordinated to $Cr(CO)_3$ have played a central role in this area. Less well developed, but potentially useful, are studies of the coordination of polycyclic arenes such as naphthalene and anthracene to metal atoms.[2–17] These aromatic systems can act as ligands for Group 3 and lanthanide elements, although the intrinsic electropositive nature of the metal ions means the bonding is best described as ionic, with the arene ligands formally carrying considerable negative charge.[4–6, 10, 11, 17, 18] Here we describe some dinuclear yttrium and lutetium complexes of naphthalene and anthracene, for which the solution and solid-state structures can only be correlated by invoking rapid intramolecular inter-ring migration of the metal-complex fragment.

A previous report described the synthesis of $[\{(\text{`}P_2N_2\text{'})Y\}_2(\mu\text{-}Cl)_2]$ (**1a**; `$P_2N_2$' = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$)[19] and its ability to couple aryl units to generate π-bound bis-arene moieties.[20] Given that yttrium could bind to an arene ligand, we examined the formation of yttrium and lutetium complexes with polycyclic aromatic compounds. The reaction of **1a** with potassium graphite (KC_8) in toluene/diethyl ether (75/25) in the presence of naphthalene generated the dark blue π-naphthalene complex $[\{(\text{`}P_2N_2\text{'})Y\}_2(\mu\text{-}C_{10}H_8)]$ (**2a**) in moderate yield (Scheme 1). The ^{1}H NMR spectroscopic data



Scheme 1. Syntheses of polyarene complexes of yttrium and lutetium.

show only two sets of coupled resonances for the $C_{10}H_8$ moiety, which demonstrates that the bridging naphthalene unit is symmetrically bound; in addition, the $^{31}P\{^1H\}$ NMR spectrum shows equivalent phosphane donors on both yttrium(III) centers. A similar reaction with the lutetium complex **1b** (Scheme 1) produced the dark purple dinuclear naphthalene complex **2b**.

The crystal structure[21] of **2a** is shown in Figure 1. Each Y(`P_2N_2') unit binds in an η^4 fashion on the opposite sides of the different rings of the naphthalene unit. The naphthalene moiety is distorted slightly with elongated bond lengths, and the rings have a nonplanar step conformation.

A similar reaction with 1-methylnaphthalene ($MeC_{10}H_7$) gave $[\{(\text{`}P_2N_2\text{'})Ln\}_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-}MeC_{10}H_7)]$ (Ln = Y, **3a**; Ln = Lu, **3b**). The ^{1}H NMR spectrum of **3a** shows signals for the seven inequivalent protons on the naphthalene unit and a singlet for the 1-Me protons. The $^{31}P\{^1H\}$ NMR spectrum shows equivalent phosphane donors (a doublet at $\delta = 21$, $^1J(Y,P) = 60$ Hz). The solid-state molecular structure[21] of **3a** is very similar to that of **2a**; the two yttrium ions are bound to opposite faces of the different rings. However, in this case the methyl group is disordered over all four equivalent positions (centrosymmetric). Nevertheless, since the behavior in solution of the

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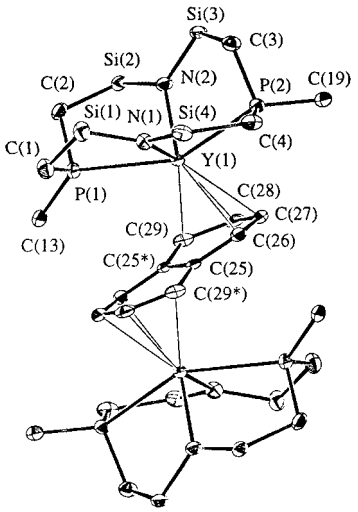
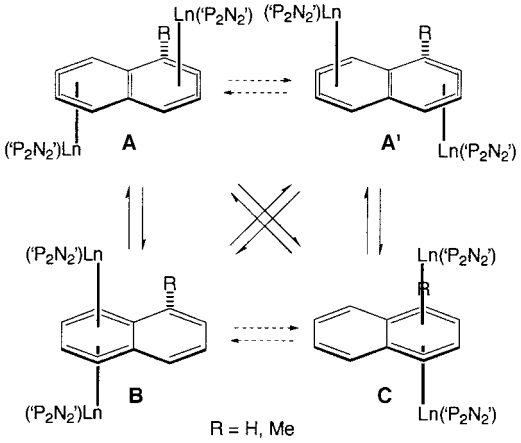


Figure 1. Molecular structure of **2a**. Selected bond lengths [Å] and angles [°]: Y(1)–P(1) 2.8918(7), Y(1)–P(2) 2.8239(7), Y(1)–N(1) 2.308(2), Y(1)–N(2) 2.320(2), Y(1)–C(26) 2.692(2), Y(1)–C(27) 2.684(3), Y(1)–C(28) 2.686(3), Y(1)–C(29) 2.652(3); P(1)-Y(1)-P(2) 150.32(2), N(1)-Y(1)-N(2) 99.03(7), P(1)-Y(1)-C(29) 79.93(6), P(2)-Y(1)-C(28) 99.47(7), N(1)-Y(1)-C(26) 95.57(8), N(2)-Y(1)-C(27) 124.61(7).

1-methylnaphthalene complex **3** is similar to that of **2**, particularly the equivalence of the phosphane donors in the $^{31}P\{^1H\}$ NMR spectrum, a fluxional process must be operative or the signals of the different phosphane donors are incidentally coincident. A reasonable fluxional process is shown in Scheme 2; to interconvert **A** and **A′** directly would require each Ln('P_2N_2') unit to migrate simultaneously from one



Scheme 2. Possible fluxional process occurring in naphthalene complexes: **2a**, **2b**, **3a**, and **3b**.

naphthalene ring to the other. A perhaps more likely alternative is that each Ln('P_2N_2') fragment moves independently, thereby interconverting **A** and **A′** via the intermediates **B** and **C**. Attempts to freeze out this process at low temperatures were unsuccessful; ^1H NMR and $^{31}P\{^1H\}$ NMR spectra at $-90\,^{\circ}C$ showed slight broadening but no evidence for lower symmetry structures, even for the 1-methylnaphthalene complexes **3a** and **3b**.

The reaction of anthracene with **1a** in the presence of KC_8 leads to the formation of a dinuclear complex with π-bound anthracene ($C_{14}H_{10}$) having the formula [{('P_2N_2')Y}$_2$(μ-$C_{14}H_{10}$)] (**4a**). The ^1H NMR spectrum is particularly informative, since one sees three signals for the coordinated anthracene unit that are shifted upfield relative to free anthracene. The highly symmetric nature of the NMR pattern and the fact that the $^{31}P\{^1H\}$ NMR spectrum shows equivalent phosphane donors suggest two possible configurations (Figure 2): a structure in which the Y('P_2N_2') units are bound to opposite faces of the middle ring of anthracene (**E**), or one in which each Y('P_2N_2') moiety is bound to one of the outside rings and on opposite faces (**D**).

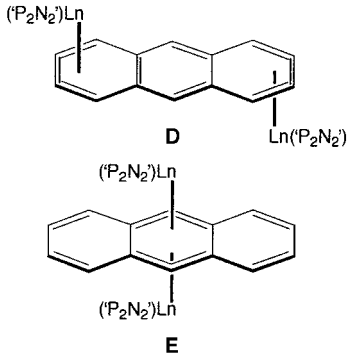


Figure 2. Postulated structures of **4a** on the basis of NMR spectroscopic data.

To our surprise, the solid-state molecular structure[21] (Figure 3) showed that the two yttrium-containing fragments are bound to an outside ring and the middle ring on opposing faces, that is, neither of the proposed symmetric solution

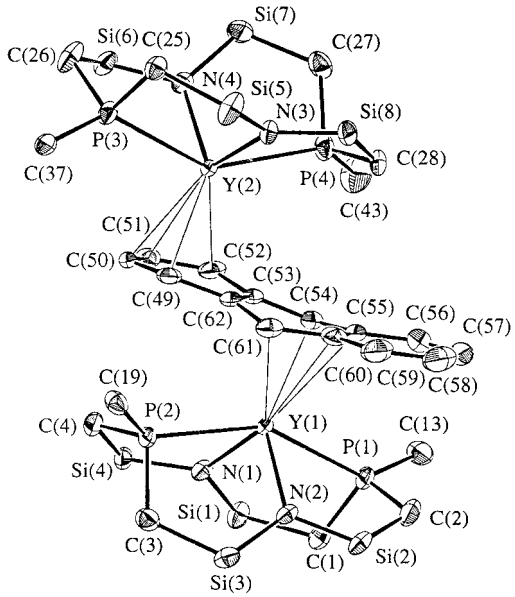


Figure 3. Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: Y(1)–P(1) 2.8469(9), Y(1)–P(2) 2.8335(9), Y(1)–N(1) 2.295(2), Y(1)–N(2) 2.290(2), Y(2)–P(3) 2.9052(9), Y(2)–P(4) 2.8250(9), Y(2)–N(3) 2.284(2), Y(2)–N(4) 2.284(3), Y(1)–C(54) 2.731(3), Y(1)–C(55) 2.832(3), Y(1)–C(60) 2.794(3), Y(1)–C(61) 2.646(3), Y(2)–C(49) 2.721(3), Y(2)–C(50) 2.655(3), Y(2)–C(51) 2.677(3), Y(2)–C(52) 2.724(3); P(1)-Y(1)-P(2) 151.03(3), N(1)-Y(1)-N(2) 96.45(8), P(3)-Y(2)-P(4) 145.40(3), N(3)-Y(2)-N(4) 104.29(9), P(1)-Y(1)-C(54) 81.61(7), P(2)-Y(1)-C(61) 80.30(8), N(1)-Y(1)-C(55) 134.94(9), N(2)-Y(1)-C(60) 104.00(9), P(3)-Y(2)-C(50) 79.62(8), P(4)-Y(2)-C(52) 81.63(8), N(3)-Y(2)-C(49) 100.09(9), N(4)-Y(2)-C(51) 103.81(9).

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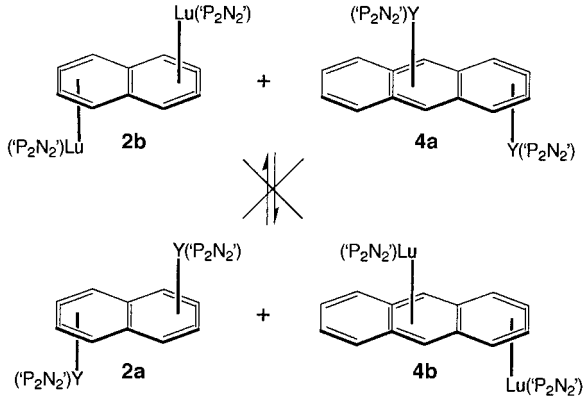
structures **D** or **E** corresponds to the solid-state structure. This solid-state structure is similar to that of a lithium anthracenide complex.[22] Despite the difference in size between yttrium and lithium, the anthracene moiety is distorted to the same extent, as evidenced by C–C bond length variations and deviations from planarity. To rationalize the solution and solid-state data, a fluxional process similar to that shown in Scheme 2 for the naphthalene complexes can be envisioned, wherein the two Ln('P_2N_2') units migrate along the top and the bottom of the anthracene ligand via intermediates such as **E**, the anthracene analogue of **B** (or **C**), and perhaps **D**, although we have no evidence for this particular stereoisomer.

The facile inter-ring migratory behavior displayed by these yttrium and lutetium complexes is not found for the majority of naphthalene and anthracene complexes of the transition metals. For example, activation barriers for inter-ring migrations in $[(\eta^4\text{-}C_{10}H_8)Cr(CO)_3]$ and $[(\eta^4\text{-}C_{14}H_{10})Cr(CO)_3]$ were determined to be in excess of 25 kcal mol^{-1}.[8] In contrast, the only system to the best of our knowledge to exhibit fast inter-ring rearrangements is the Ni^0 complex $[Ni(\eta^2\text{-}C_{10}H_8)(dippe)]$ (dippe = 1,2-bis(diisopropylphosphanyl)ethane),[2] for which a $\Delta G^{\neq}$ of 15 kcal mol^{-1} was estimated. Presumably, the formally d^{10} nickel center does not engage in strong π back-donation to the naphthalene ring, and this facilitates both intra- and inter-ring migration.

Consideration of these dinuclear lanthanide π-complexes as having covalent bonding between the Y or Lu and the polycyclic aromatic hydrocarbon is probably unrealistic. However, if we consider the bonding to be electrostatic in nature, then the motion can be regarded as the migration of the cation $[Ln('P_2N_2')]^+$ over the polycyclic aromatic dianions. This then raises an important question: do these ion pairs dissociate in solution? We devised a crossover experiment to test this (Scheme 3): a mixture of the lutetium naphthalene



Scheme 3. Crossover experiment indicating no ion dissociation in solution.

complex **2b** with the yttrium anthracene complex **4a** was monitored as a function of time. The complementary experiment with **2a** and **4b** was also carried out to ensure that thermodynamic factors were not preventing crossover. No evidence of intermolecular migration of a $[Ln('P_2N_2')]^+$ ion between naphthalene and anthracene was obtained, since only the starting materials were observed by $^{31}P\{^1H\}$ NMR spectroscopy throughout this experiment. In addition, no mixed-metal complexes were detected. The $^{31}P\{^1H\}$ NMR spectroscopic data also demonstrated that no exchange occurs with free naphthalene or anthracene.

The solubility[23] of these complexes in hydrocarbons is a result of the ancillary 'P_2N_2' ligand attached to the lanthanide(III) ion and suggests that these complexes will serve as versatile reducing agents and synthons for other organometallic derivatives of f-block elements.

Experimental Section

General procedure for **2**–**4**: Toluene (30 mL) and diethyl ether (10 mL) were added to a mixture of **1** (0.5 g, 0.38 mmol), C_8K (0.11 g, 0.84 mmol), and polycyclic aromatic compound (0.57 mmol) at room temperature. The reaction mixture, which turned dark blue for **2a**, **3a**, and **4a**, and dark purple for **2b**, **3b**, and **4b**, was stirred for 4 d. The solvent was then evaporated to dryness, the residue extracted with toluene, and the extract filtered through celite and dried in vacuo to yield a dark blue or dark purple semicrystalline material (60 %). Crystals suitable for X-ray analysis were grown by slow evaporation of solutions in toluene.

2a: Elemental analysis calcd (found) for $C_{58}H_{92}N_4P_4Si_8Y_2$: C 50.78 (50.67), H 6.76 (6.79), N 4.08 (4.01); ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): δ = 7.40 (m, 4H, *o*-H), 7.00 (m, 6H, *m*/*p*-H, phenyl), 4.50 (m, 4H, naphthalene), 2.80 (m, 4H, naphthalene), 1.40 (AB m, 4H, ring CH_2), 1.20 (AB m, 4H, ring CH_2), 0.50 (s, 6H, ring $SiMe_2$), 0.25 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 81 MHz, 298 K): δ = −26.00 (d, $J_{Y,P}$ = 87.2 Hz); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): δ = 139.2 (m, *ipso*-C_6H_5P), 133.9 (s, *ipso*-C, naphthalene), 131.1 (t, $J_{C,P}$ = 8 Hz, *o*-C_6H_5P), 129.5 (s, *m*/*p*-C_6H_5P), 128.8 (s, *m*/*p*-C_6H_5P), 116.8 (s, CH, naphthalene), 92.9 (s, CH, naphthalene), 19.0 (s, PCH_2), 7.3 (s, $Si(CH_3)_2$), 7.0 (s, $Si(CH_3)_2$). No Y^{89}-C^{13} coupling was observed in this complex or in **3a** or **4a** as the half-height peak width was approximately 10 Hz for all signals.

2b: Elemental analysis calcd (found) for $C_{58}H_{92}N_4P_4Si_8Lu_2$: C 45.12 (45.18), H 6.01 (6.01), N 3.63 (3.59); ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): δ = 7.20 (m, 4H, *o*-H), 6.90 (m, 6H, *m*/*p*-H, phenyl), 4.50 (m, 4H, naphthalene), 2.80 (m, 4H, naphthalene), 1.30 (AB m, 4H, ring CH_2), 1.10 (AB m, 4H, ring CH_2), 0.20 (s, 6H, ring $SiMe_2$), 0.10 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 81 MHz, 298 K): δ = −18.37; $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): δ = 138.3 (m, *ipso*-C_6H_5P), 134.0 (s, *ipso*-C, naphthalene), 132.4 (t, $J_{C,P}$ = 8 Hz, *o*-C_6H_5P), 129.4 (s, *m*/*p*-C_6H_5P), 128.8 (s, *m*/*p*-C_6H_5P), 115.5 (s, CH, naphthalene), 93.3 (s, CH, naphthalene), 20.1 (s, PCH_2), 6.5 (s, $Si(CH_3)_2$), 6.0 (s, $Si(CH_3)_2$).

3a: Elemental analysis calcd (found) for $C_{59}H_{94}N_4P_4Si_8Y_2$: C 51.14 (51.45), H 6.84 (6.94), N 4.04 (3.89); ^{1}H NMR ([D$_6$]benzene, 500 MHz, 298 K): δ = 7.50 (m, 4H, *o*-H), 7.10 (m, 6H, *m*/*p*-H, phenyl), 4.78 (AB m, 1H, 1-methylnaphthalene), 4.60 (AB m, 3H, 1-methylnaphthalene), 4.53 (AB m, 1H, 1-methylnaphthalene), 3.00 (AB m, 1H, 1-methylnaphthalene), 2.90 (AB m, 1H, 1-methylnaphthalene), 2.60 (AB m, 1H, 1-methylnaphthalene), 2.15 (s, 3H, CH_3, 1-methylnaphthalene), 1.40 (AB m, 4H, ring CH_2), 1.20 (AB m, 4H, ring CH_2), 0.50 (s, 6H, ring $SiMe_2$), 0.25 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 202.5 MHz, 298 K): δ = −25.96 (d, $J_{Y,P}$ = 87.9 Hz); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): δ = 139.2 (s, *ipso*-C, 1-methylnaphthalene), 134.5 (m, *ipso*-C_6H_5P), 131.4 (t, $J_{C,P}$ = 7.2 Hz, *o*-C_6H_5P), 129.2 (s, *m*/*p*-C_6H_5P), 128.8 (s, *m*/*p*-C_6H_5P), 125.6 (s, CH, 1-methylnaphthalene), 117.6 (s, CH, 1-methylnaphthalene), 116.6 (s, CH, 1-methylnaphthalene), 114.7 (s, CH, 1-methylnaphthalene), 112.8 (s, CH, 1-methylnaphthalene), 101.8 (s, CH, 1-methylnaphthalene), 95.6 (s, CH, 1-methylnaphthalene), 31.8 (s, *ipso*-C, 1-methylnaphthalene), 19.0 (s, PCH_2), 14.3 (s, CH_3, 1-methylnaphthalene), 7.4 (s, $Si(CH_3)_2$), 7.2 (s, $Si(CH_3)_2$).

3b: Elemental analysis calcd (found) for $C_{59}H_{94}N_4P_4Si_8Lu_2$: C 44.20 (44.50), H 6.23 (6.09), N 3.68 (3.44); ^{1}H NMR ([D$_6$]benzene, 500 MHz, 298 K): δ = 7.20 (m, 4H, *o*-H), 6.90 (m, 6H, *m*/*p*-H, phenyl), 4.78 (AB m, 1H, 1-methylnaphthalene), 4.60 (AB m, 3H, 1-methylnaphthalene), 4.53(AB m, 1H, 1-methylnaphthalene), 3.00 (AB m, 1H, 1-methylnaphthalene), 2.70 (AB m, 2H, 1-methylnaphthalene), 2.25 (s, 3H, CH_3 1-methylnaphthalene), 1.20 (AB m, 4H, ring CH_2), 1.10 (AB m, 4H, ring CH_2), 0.20 (s, 6H, ring $SiMe_2$), 0.1 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene,

202.5 MHz, 298 K): $\delta = -18.28$; $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): $\delta = 139.4$ (t, $J_{C,P} = 7.2$ Hz, *ipso*-C_6H_5P), 131.4 (t, $J_{C,P} = 7.0$ Hz, *o*-C_6H_5P), 129.5 (s, *m*/*p*-C_6H_5P), 129.2 (s, *m*/*p*-C_6H_5P), 125.6 (s, CH, 1-methylnaphthalene), 121.4 (s, CH, 1-methylnaphthalene), 115.7 (s, CH, 1-methylnaphthalene), 113.1 (s, CH, 1-methylnaphthalene), 94.5 (s, CH, 1-methylnaphthalene), 91.0 (s, CH, 1-methylnaphthalene), 88.7 (s, CH, 1-methylnaphthalene), 31.2 (s, *ipso*-C, 1-methylnaphthalene), 19.0 (s, PCH_2), 14.0 (s, CH_3, 1-methylnaphthalene), 7.7 (s, $Si(CH_3)_2$), 7.2 (s, $Si(CH_3)_2$).

4a: Elemental analysis calcd (found) for ($C_{62}H_{94}N_4P_4Si_8Y_2$): C 52.45 (52.29), H 6.53 (6.39), N 3.95 (4.16); ^1H NMR ([D$_6$]benzene, 500 MHz, 298 K): $\delta = 7.50$ (m, 4H, *o*-H), 7.10 (m, 6H, *m*/*p*-H, phenyl), 5.55 (AB m, 4H, anthracene), 4.43 (AB m, 4H, anthracene), 3.00 (s, 2H, anthracene), 1.40 (AB m, 4H, ring CH_2), 1.20 (AB m, 4H, ring CH_2), 0.50 (s, 6H, ring $SiMe_2$), 0.25 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 202.5 MHz, 298 K): $\delta = -27.29$ (d, $J_{Y,P} = 88.05$ Hz); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): $\delta = 140.7$ (s, *ipso*-C, anthracene), 139.2 (m, *ipso*-C_6H_5P), 132.9 (t, $J_{C,P} = 8$ Hz, *o*-C_6H_5P), 130.8 (t, $J_{C,P} = 8$ Hz, *m*-C_6H_5P), 129.5 (s, *p*-C_6H_5P), 119.7 (s, CH, anthracene), 109.0 (s, CH, anthracene), 89.6 (s, CH, anthracene), 19.4 (s, PCH_2), 7.0 (br, $Si(CH_3)_2$).

4b: Elemental analysis calcd (found) for ($C_{62}H_{94}N_4P_4Si_8Lu_2$): C 46.72 (46.59), H 5.94 (6.04), N 3.51 (3.45); ^1H NMR ([D$_6$]benzene, 500 MHz, 298 K): $\delta = 7.20$ (m, 4H, *o*-H), 6.90 (m, 6H, *m*/*p*-H, phenyl), 5.65 (AB m, 4H, anthracene), 4.60 (AB m, 4H, anthracene), 3.25 (s, 2H, anthracene), 1.20 (AB m, 4H, ring CH_2), 1.10 (AB m, 4H, ring CH_2), 0.20 (s, 6H, ring $SiMe_2$), 0.10 (s, 6H, ring $SiMe_2$); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 202.5 MHz, 298 K): $\delta = -19.04$; $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 75.45 MHz, 298 K): $\delta = 140.2$ (s, *ipso*-C, anthracene), 139.7 (t, $J_{C,P} = 7.0$ Hz, *ipso*-C_6H_5P), 131.3 (t, $J_{C,P} = 8$ Hz, *o*-C_6H_5P), 129.3 (t, $J_{C,P} = 7.5$ Hz, *m*-C_6H_5P), 128.8 (s, *p*-C_6H_5P), 119.5 (s, CH, anthracene), 110.9 (s, CH, anthracene), 89.5 (s, CH, anthracene), 17.8 (s, PCH_2), 7.8 (s, $Si(CH_3)_2$), 7.2 (s, $Si(CH_3)_2$).

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[21] X-ray structure analyses: Data for **2a**–**4a** were collected at 180 K on a Rigaku/ADSC CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were fixed in idealized positions with C–H distances of 0.98 Å and $B_H = 1.2\,B_{\text{bonded atom}}$. Unmodified statistical weights ($w = 1/\sigma^2(F_o^2)$) were employed for all structures. Crystal data: **2a**: $C_{58}H_{92}N_4P_4Si_8Y_2$, $M_r = 1371.78$, crystal dimensions $0.35 \times 0.40 \times 0.50$ mm, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.5439(8)$, $b = 15.206(2)$, $c = 20.2735(5)$ Å, $\beta = 104.0445(7)^\circ$, $Z = 2$, $V = 3452.3(4)$ Å^3, $\rho_{calcd} = 1.320$ g cm^{-3}, $\mu = 19.4$ cm^{-1}, $2\theta_{max} = 60.1^\circ$, 32111 reflections measured, 8309 of which were unique ($R_{int} = 0.038$), 5837 with $I \geq 3\sigma(I)$. Lp and empirical absorption correction (multiscan: three-dimensional analysis of symmetry-equivalent data including corrections for crystal decay and scaling; correction factors: 0.697–1.000). The structure was solved by the Patterson method and was refined by full-matrix least-squares methods on F^2 for all data: $R_w(F^2) = 0.075$, $R(F, I \geq 3\sigma(I)) = 0.040$, GOF = 2.16, $\Delta/\sigma_{max} = 0.0008$, data-to-parameter ratio 24.2, residual electron density $+0.94/-1.28$ e Å^{-3} (both near Y). **4a**: $C_{62}H_{94}N_4P_4Si_8Y_2$ $M_r = 1421.84$, crystal dimensions $0.30 \times 0.35 \times 0.45$ mm, triclinic, space group $P\bar{1}$, $a = 11.4774(7)$, $b = 15.2221(10)$, $c = 23.705(3)$ Å, $\alpha = 99.534(4)$, $\beta = 101.126(2)$, $\gamma = 111.7038(10)^\circ$, $Z = 2$, $V = 3645.8(5)$ Å^3, $\rho_{calcd} = 1.295$ g cm^{-3}, $\mu = 18.4$ cm^{-1}, $2\theta_{max} = 60.1^\circ$, 34293 reflections measured, of which 16404 were unique ($R_{int} = 0.041$), 8778 with $I \geq 3\sigma(I)$. Lp and empirical absorption correction (multiscan: three-dimensional analysis of symmetry-equivalent data including corrections for crystal decay and scaling; correction factors: 0.679–1.000). The structure was solved by the Patterson method and was refined by full-matrix least-squares methods on F^2 for all data: $R_w(F^2) = 0.065$, $R(F, I \geq 3\sigma(I)) = 0.035$, GOF = 1.13, $\Delta/\sigma_{max} = 0.09$, data-to-parameter ratio 21.8, residual electron density $+1.02/-1.29$ e Å^{-3} (both near Y). The C(43–48) phenyl group was modeled as twofold disordered (53:47). Atoms C(43) and C(48) could not be resolved successfully, and the disorder was only partially resolved. As a result the geometry and thermal parameters of this moiety are anomalous. This model does, however, account for the electron density in the region. The partially occupied atom C(46) was refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101973 (**2a**), -101974 (**3a**), and -101975 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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