**Supporting Information**

# Rare-Earth/Iridium Heterobimetallic Complexes with Bridging Imido and Silylmethyl Ligands: Synthesis, Structure and Reactivity

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## Contents

**STable 1** Summary of crystallographic data

| | **2a** | **3'** | **4** | **5** | **6'** |
|---|---|---|---|---|---|
| formula | $C_{28}H_{49}IrLuNSi$ | $C_{35}H_{60}IrN_2ScSi_2$ | $C_{45}H_{62}IrLuN_3Si$ | $C_{42}H_{59}IrLuN_3Si$ | $C_{36}H_{54}IrLuN_2OSi$ |
| formula weight | 794.94 | 802.19 | 1040.24 | 1001.18 | 926.07 |
| crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic | Triclinic |
| space group | *P*2(1)/*n* | *P*-1 | *C*2/*c* | *P*2(1)/*n* | *P*-1 |
| a, Å | 9.3823(11) | 9.6879(10) | 46.05(3) | 12.688(7) | 9.431(2) |
| b, Å | 20.167(2) | 10.9527(11) | 9.620(6) | 15.745(9) | 10.568(3) |
| c, Å | 16.4339(19) | 18.836(2) | 19.635(13) | 20.071(11) | 18.813(5) |
| α, deg | | 73.1590(10) | | | 85.387(4) |
| β, deg | 99.864(2) | 85.811(2) | 90.619(11) | 95.867(9) | 79.968(3) |
| γ, deg | | 78.9610(10) | | | 74.367(3) |
| *V*, Å$^3$ | 3063.5(6) | 1877.2(3) | 8698(10) | 3989(4) | 1776.9(8) |
| Z | 4 | 2 | 8 | 4 | 2 |
| $D_{calcd}$, g/cm$^3$ | 1.724 | 1.419 | 1.589 | 1.667 | 1.731 |
| temp, K | 163(2) | 173(2) | 173(2) | 173(3) | 173(2) |
| μ, mm$^{-1}$(MoKα) | 7.597 | 3.810 | 5.374 | 5.856 | 6.565 |
| $2\theta_{max}$ | 50 | 54 | 52 | 55 | 53 |
| reflections collected | 16244 | 11447 | 24115 | 24414 | 10513 |
| independent reflections ($R_{int}$) | 5395 (0.0783) | 7820 (0.0858) | 8632 (0.1608) | 8868 (0.0938) | 7120 (0.0788) |
| $R1$ ($I > 2\sigma(I)$) | 0.0631 | 0.0733 | 0.0524 | 0.0424 | 0.0715 |
| $wR2$ ($I > 2\sigma(I)$) | 0.1233 | 0.2075 | 0.0809 | 0.0698 | 0.1669 |
| parameters | 162 | 391 | 391 | 451 | 340 |
| GOF | 0.913 | 1.142 | 0.885 | 0.963 | 0.924 |

**1. X-ray crystallographic data**

**Figure S1.** ORTEP drawing of [($C_5Me_5$)Ir($\mu$-N$^t$Bu)($\mu$-$CH_2SiMe_2CH_2$-)Lu($C_5Me_5$)] (**2a**)

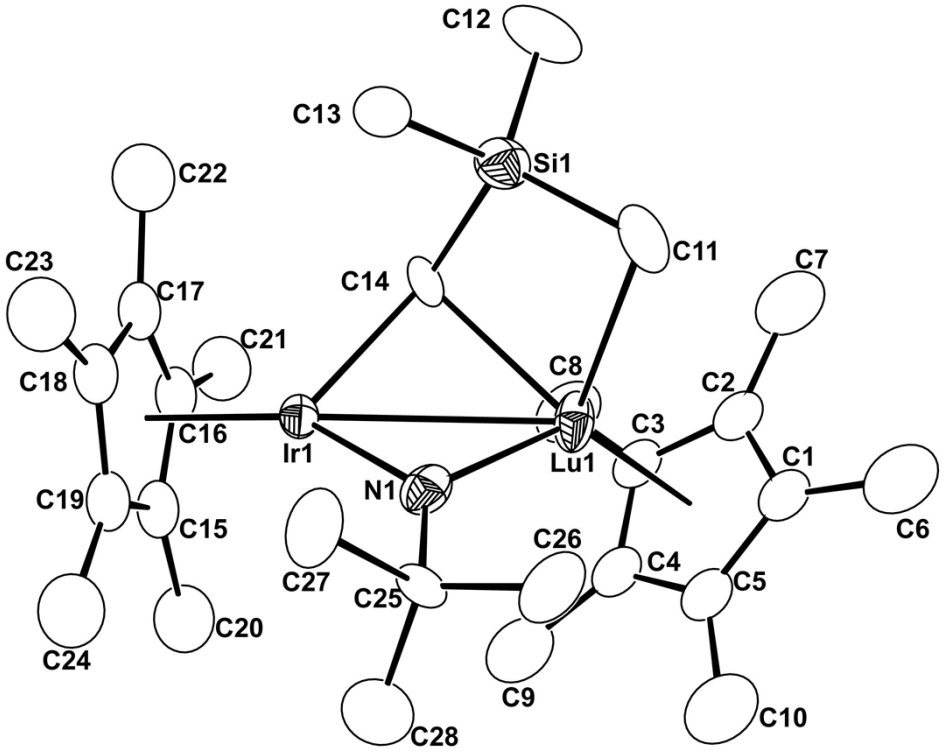

**Table S1.** Crystal data and structure refinement for **2a**.

| | | |
|---|---|---|
| Identification code | 1157yng | |
| Empirical formula | C28 H49 Ir Lu N Si | |
| Formula weight | 794.94 | |
| Temperature | 163(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 9.3823(11) Å | α= 90°. |
| | b = 20.167(2) Å | β= 99.864(2)°. |
| | c = 16.4339(19) Å | γ = 90°. |
| Volume | 3063.5(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.724 $Mg/m^3$ | |
| Absorption coefficient | 7.597 $mm^{-1}$ | |
| F(000) | 1544 | |
| Crystal size | 0.10 x 0.05 x 0.01 $mm^3$ | |
| Theta range for data collection | 1.61 to 25.08°. | |
| Index ranges | -11<=h<=11, -18<=k<=24, -19<=l<=19 | |
| Reflections collected | 16244 | |
| Independent reflections | 5395 [R(int) = 0.0783] | |
| Completeness to theta = 25.08° | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9279 and 0.5171 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5395 / 0 / 162 | |
| Goodness-of-fit on $F^2$ | 0.913 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0631, wR2 = 0.1233 | |
| R indices (all data) | R1 = 0.1231, wR2 = 0.1379 | |
| Largest diff. peak and hole | 3.258 and -2.680 $e.Å^{-3}$ | |

**Table S2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 2510(1) | 1394(1) | 8421(1) | 36(1) |
| Lu(1) | 2564(1) | 2773(1) | 9136(1) | 53(1) |
| N(1) | 4014(14) | 2029(6) | 8836(8) | 49(4) |
| Si(1) | 1632(6) | 1864(3) | 10356(3) | 59(1) |
| C(1) | 2343(8) | 4088(3) | 9109(5) | 61(2) |
| C(2) | 895(8) | 3864(4) | 9031(5) | 61(2) |
| C(3) | 540(9) | 3529(4) | 8265(5) | 61(2) |
| C(4) | 1769(8) | 3546(4) | 7870(5) | 61(2) |
| C(5) | 2884(8) | 3892(3) | 8392(5) | 61(2) |
| C(6) | 3165(12) | 4469(6) | 9829(7) | 109(4) |
| C(7) | -94(13) | 3964(6) | 9652(7) | 109(4) |
| C(8) | -893(13) | 3210(6) | 7929(7) | 109(4) |
| C(9) | 1873(13) | 3249(6) | 7041(7) | 109(4) |
| C(10) | 4380(12) | 4027(6) | 8215(7) | 109(4) |
| C(11) | 2740(20) | 2602(9) | 10591(11) | 75(6) |
| C(12) | -80(20) | 1926(12) | 10787(12) | 100(8) |
| C(13) | 2580(20) | 1073(8) | 10673(10) | 74(6) |
| C(14) | 1009(19) | 1847(8) | 9151(10) | 55(5) |
| C(15) | 1980(8) | 955(3) | 7155(5) | 57(2) |
| C(16) | 794(8) | 863(3) | 7568(5) | 57(2) |
| C(17) | 1245(8) | 445(3) | 8253(5) | 57(2) |
| C(18) | 2710(8) | 279(3) | 8263(5) | 57(2) |
| C(19) | 3164(8) | 594(4) | 7584(5) | 57(2) |
| C(20) | 1982(11) | 1365(5) | 6392(7) | 92(3) |
| C(21) | -687(11) | 1157(5) | 7322(7) | 92(3) |
| C(22) | 328(11) | 217(5) | 8864(7) | 92(3) |
| C(23) | 3624(11) | -157(5) | 8886(7) | 92(3) |
| C(24) | 4646(11) | 553(6) | 7359(7) | 92(3) |
| C(25) | 5616(15) | 2040(7) | 8826(9) | 36(4) |
| C(26) | 6250(20) | 2552(9) | 9396(13) | 81(7) |
| C(27) | 6241(16) | 1341(8) | 9206(12) | 68(6) |
| C(28) | 5790(20) | 2128(10) | 7931(13) | 89(7) |

**Table S3.** Bond lengths [Å] and angles [°] for **2a**.

| | |
|---|---|
| Ir(1)-N(1) | 1.940(13) |
| Ir(1)-C(14) | 2.200(16) |
| Ir(1)-C(16) | 2.221(7) |
| Ir(1)-C(15) | 2.237(7) |
| Ir(1)-C(17) | 2.244(7) |
| Ir(1)-C(19) | 2.271(7) |
| Ir(1)-C(18) | 2.275(7) |
| Ir(1)-Lu(1) | 3.0158(9) |
| Lu(1)-N(1) | 2.138(13) |
| Lu(1)-C(14) | 2.373(17) |
| Lu(1)-C(11) | 2.395(18) |
| Lu(1)-C(4) | 2.605(7) |
| Lu(1)-C(5) | 2.609(7) |
| Lu(1)-C(3) | 2.655(7) |
| Lu(1)-C(1) | 2.661(7) |
| Lu(1)-C(2) | 2.689(7) |
| Lu(1)-Si(1) | 2.956(5) |
| N(1)-C(25) | 1.507(18) |
| Si(1)-C(11) | 1.818(18) |
| Si(1)-C(13) | 1.856(17) |
| Si(1)-C(12) | 1.867(18) |
| Si(1)-C(14) | 1.966(17) |
| C(1)-C(2) | 1.417(5) |
| C(1)-C(5) | 1.417(5) |
| C(1)-C(6) | 1.507(5) |
| C(2)-C(3) | 1.417(5) |
| C(2)-C(7) | 1.507(5) |
| C(3)-C(4) | 1.417(5) |
| C(3)-C(8) | 1.507(5) |
| C(4)-C(5) | 1.417(5) |
| C(4)-C(9) | 1.507(5) |
| C(5)-C(10) | 1.507(5) |
| C(15)-C(16) | 1.412(4) |
| C(15)-C(19) | 1.412(4) |
| C(15)-C(20) | 1.501(5) |
| C(16)-C(17) | 1.412(4) |
| C(16)-C(21) | 1.501(5) |
| C(17)-C(18) | 1.412(4) |
| C(17)-C(22) | 1.501(5) |
| C(18)-C(19) | 1.412(4) |
| C(18)-C(23) | 1.501(5) |
| C(19)-C(24) | 1.501(5) |
| C(25)-C(26) | 1.45(2) |
| C(25)-C(28) | 1.52(2) |
| C(25)-C(27) | 1.61(2) |
| | |
| N(1)-Ir(1)-C(14) | 91.7(6) |
| N(1)-Ir(1)-C(16) | 160.9(4) |
| C(14)-Ir(1)-C(16) | 94.7(5) |
| N(1)-Ir(1)-C(15) | 128.3(4) |
| C(14)-Ir(1)-C(15) | 127.6(5) |
| C(16)-Ir(1)-C(15) | 36.93(13) |
| N(1)-Ir(1)-C(17) | 160.7(4) |
| C(14)-Ir(1)-C(17) | 92.6(5) |
| C(16)-Ir(1)-C(17) | 36.87(13) |
| C(15)-Ir(1)-C(17) | 61.3(2) |
| N(1)-Ir(1)-C(19) | 115.2(4) |
| C(14)-Ir(1)-C(19) | 152.9(5) |
| C(16)-Ir(1)-C(19) | 61.1(2) |
| C(15)-Ir(1)-C(19) | 36.50(13) |
| C(17)-Ir(1)-C(19) | 60.8(2) |
| N(1)-Ir(1)-C(18) | 128.6(4) |
| C(14)-Ir(1)-C(18) | 123.0(5) |
| C(16)-Ir(1)-C(18) | 61.1(2) |
| C(15)-Ir(1)-C(18) | 60.8(2) |
| C(17)-Ir(1)-C(18) | 36.40(13) |
| C(19)-Ir(1)-C(18) | 36.19(13) |
| N(1)-Ir(1)-Lu(1) | 44.9(4) |
| C(14)-Ir(1)-Lu(1) | 51.3(4) |
| C(16)-Ir(1)-Lu(1) | 130.72(19) |
| C(15)-Ir(1)-Lu(1) | 135.49(19) |
| C(17)-Ir(1)-Lu(1) | 143.84(19) |
| C(19)-Ir(1)-Lu(1) | 154.49(19) |
| C(18)-Ir(1)-Lu(1) | 163.66(19) |
| N(1)-Lu(1)-C(14) | 82.4(5) |
| N(1)-Lu(1)-C(11) | 101.1(6) |
| C(14)-Lu(1)-C(11) | 79.2(6) |
| N(1)-Lu(1)-C(4) | 110.0(4) |
| C(14)-Lu(1)-C(4) | 112.8(5) |
| C(11)-Lu(1)-C(4) | 147.7(5) |
| N(1)-Lu(1)-C(5) | 111.7(4) |
| C(14)-Lu(1)-C(5) | 143.7(5) |
| C(11)-Lu(1)-C(5) | 126.8(5) |
| C(4)-Lu(1)-C(5) | 31.54(12) |
| N(1)-Lu(1)-C(3) | 134.7(4) |
| C(14)-Lu(1)-C(3) | 94.2(5) |
| C(11)-Lu(1)-C(3) | 122.8(5) |
| C(4)-Lu(1)-C(3) | 31.24(11) |
| C(5)-Lu(1)-C(3) | 51.64(18) |
| N(1)-Lu(1)-C(1) | 138.3(4) |
| C(14)-Lu(1)-C(1) | 137.6(4) |
| C(11)-Lu(1)-C(1) | 98.7(5) |
| C(4)-Lu(1)-C(1) | 51.62(18) |
| C(5)-Lu(1)-C(1) | 31.18(12) |
| C(3)-Lu(1)-C(1) | 51.11(18) |
| N(1)-Lu(1)-C(2) | 161.0(4) |
| C(14)-Lu(1)-C(2) | 107.0(4) |
| C(11)-Lu(1)-C(2) | 96.9(5) |
| C(4)-Lu(1)-C(2) | 51.31(18) |
| C(5)-Lu(1)-C(2) | 51.27(18) |
| C(3)-Lu(1)-C(2) | 30.75(11) |
| C(1)-Lu(1)-C(2) | 30.72(11) |
| N(1)-Lu(1)-Si(1) | 89.7(3) |
| C(14)-Lu(1)-Si(1) | 41.5(4) |
| C(11)-Lu(1)-Si(1) | 37.9(4) |
| C(4)-Lu(1)-Si(1) | 146.6(2) |
| C(5)-Lu(1)-Si(1) | 157.7(2) |
| C(3)-Lu(1)-Si(1) | 117.0(2) |
| C(1)-Lu(1)-Si(1) | 126.7(2) |
| C(2)-Lu(1)-Si(1) | 108.3(2) |
| N(1)-Lu(1)-Ir(1) | 39.8(3) |
| C(14)-Lu(1)-Ir(1) | 46.3(4) |
| C(11)-Lu(1)-Ir(1) | 104.5(4) |
| C(4)-Lu(1)-Ir(1) | 104.94(18) |
| C(5)-Lu(1)-Ir(1) | 127.66(19) |
| C(3)-Lu(1)-Ir(1) | 110.91(18) |
| C(1)-Lu(1)-Ir(1) | 156.49(18) |
| C(2)-Lu(1)-Ir(1) | 139.36(17) |

| | |
|---|---|
| Si(1)-Lu(1)-Ir(1) | 72.88(11) |
| C(25)-N(1)-Ir(1) | 132.2(10) |
| C(25)-N(1)-Lu(1) | 131.9(9) |
| Ir(1)-N(1)-Lu(1) | 95.2(5) |
| C(11)-Si(1)-C(13) | 114.6(9) |
| C(11)-Si(1)-C(12) | 111.2(10) |
| C(13)-Si(1)-C(12) | 110.5(10) |
| C(11)-Si(1)-C(14) | 106.9(8) |
| C(13)-Si(1)-C(14) | 108.2(7) |
| C(12)-Si(1)-C(14) | 104.9(8) |
| C(11)-Si(1)-Lu(1) | 54.0(6) |
| C(13)-Si(1)-Lu(1) | 122.8(6) |
| C(12)-Si(1)-Lu(1) | 126.2(8) |
| C(14)-Si(1)-Lu(1) | 53.1(5) |
| C(2)-C(1)-C(5) | 108.0 |
| C(2)-C(1)-C(6) | 126.0 |
| C(5)-C(1)-C(6) | 126.0 |
| C(2)-C(1)-Lu(1) | 75.7(2) |
| C(5)-C(1)-Lu(1) | 72.4(3) |
| C(6)-C(1)-Lu(1) | 117.8(2) |
| C(1)-C(2)-C(3) | 108.0 |
| C(1)-C(2)-C(7) | 126.0 |
| C(3)-C(2)-C(7) | 126.0 |
| C(1)-C(2)-Lu(1) | 73.5(2) |
| C(3)-C(2)-Lu(1) | 73.3(2) |
| C(7)-C(2)-Lu(1) | 119.0(2) |
| C(2)-C(3)-C(4) | 108.0 |
| C(2)-C(3)-C(8) | 126.0 |
| C(4)-C(3)-C(8) | 126.0 |
| C(2)-C(3)-Lu(1) | 76.0(3) |
| C(4)-C(3)-Lu(1) | 72.4(3) |
| C(8)-C(3)-Lu(1) | 117.6(2) |
| C(5)-C(4)-C(3) | 108.0 |
| C(5)-C(4)-C(9) | 126.0 |
| C(3)-C(4)-C(9) | 126.0 |
| C(5)-C(4)-Lu(1) | 74.4(2) |
| C(3)-C(4)-Lu(1) | 76.3(3) |
| C(9)-C(4)-Lu(1) | 115.5(3) |
| C(4)-C(5)-C(1) | 108.0 |
| C(4)-C(5)-C(10) | 126.0 |
| C(1)-C(5)-C(10) | 126.0 |
| C(4)-C(5)-Lu(1) | 74.1(2) |
| C(1)-C(5)-Lu(1) | 76.4(3) |
| C(10)-C(5)-Lu(1) | 115.6(2) |
| Si(1)-C(11)-Lu(1) | 88.0(7) |
| Si(1)-C(14)-Ir(1) | 116.7(8) |
| Si(1)-C(14)-Lu(1) | 85.4(6) |
| Ir(1)-C(14)-Lu(1) | 82.4(6) |
| C(16)-C(15)-C(19) | 108.0 |
| C(16)-C(15)-C(20) | 126.0 |
| C(19)-C(15)-C(20) | 126.0 |
| C(16)-C(15)-Ir(1) | 70.9(2) |
| C(19)-C(15)-Ir(1) | 73.0(2) |
| C(20)-C(15)-Ir(1) | 121.8(2) |
| C(17)-C(16)-C(15) | 108.0 |
| C(17)-C(16)-C(21) | 126.0 |
| C(15)-C(16)-C(21) | 126.0 |
| C(17)-C(16)-Ir(1) | 72.5(2) |
| C(15)-C(16)-Ir(1) | 72.2(2) |
| C(21)-C(16)-Ir(1) | 121.1(2) |
| C(16)-C(17)-C(18) | 108.0 |
| C(16)-C(17)-C(22) | 126.0 |
| C(18)-C(17)-C(22) | 126.0 |
| C(16)-C(17)-Ir(1) | 70.7(2) |
| C(18)-C(17)-Ir(1) | 73.0(2) |
| C(22)-C(17)-Ir(1) | 122.0(2) |
| C(17)-C(18)-C(19) | 108.0 |
| C(17)-C(18)-C(23) | 126.0 |
| C(19)-C(18)-C(23) | 126.0 |
| C(17)-C(18)-Ir(1) | 70.6(2) |
| C(19)-C(18)-Ir(1) | 71.7(2) |
| C(23)-C(18)-Ir(1) | 123.3(2) |
| C(15)-C(19)-C(18) | 108.0 |
| C(15)-C(19)-C(24) | 126.0 |
| C(18)-C(19)-C(24) | 126.0 |
| C(15)-C(19)-Ir(1) | 70.5(2) |
| C(18)-C(19)-Ir(1) | 72.1(2) |
| C(24)-C(19)-Ir(1) | 123.1(2) |
| C(26)-C(25)-N(1) | 107.6(13) |
| C(26)-C(25)-C(28) | 116.2(15) |
| N(1)-C(25)-C(28) | 106.7(13) |
| C(26)-C(25)-C(27) | 106.9(13) |
| N(1)-C(25)-C(27) | 106.3(12) |
| C(28)-C(25)-C(27) | 112.6(14) |

Symmetry transformations used to generate equivalent atoms:

**Table S4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 47(1) | 32(1) | 27(1) | 1(1) | 1(1) | 3(1) |
| Lu(1) | 77(1) | 31(1) | 44(1) | -1(1) | -13(1) | 6(1) |
| N(1) | 58(9) | 42(8) | 47(9) | 12(7) | 3(7) | -2(7) |
| Si(1) | 64(4) | 69(4) | 42(3) | -1(3) | 4(3) | -8(3) |
| C(1) | 83(6) | 41(5) | 55(6) | 17(4) | 5(5) | -6(4) |
| C(2) | 83(6) | 41(5) | 55(6) | 17(4) | 5(5) | -6(4) |
| C(3) | 83(6) | 41(5) | 55(6) | 17(4) | 5(5) | -6(4) |
| C(4) | 83(6) | 41(5) | 55(6) | 17(4) | 5(5) | -6(4) |
| C(5) | 83(6) | 41(5) | 55(6) | 17(4) | 5(5) | -6(4) |
| C(6) | 124(9) | 79(7) | 123(10) | 28(7) | 24(7) | -2(6) |
| C(7) | 124(9) | 79(7) | 123(10) | 28(7) | 24(7) | -2(6) |
| C(8) | 124(9) | 79(7) | 123(10) | 28(7) | 24(7) | -2(6) |
| C(9) | 124(9) | 79(7) | 123(10) | 28(7) | 24(7) | -2(6) |
| C(10) | 124(9) | 79(7) | 123(10) | 28(7) | 24(7) | -2(6) |
| C(11) | 104(16) | 77(14) | 39(12) | -23(10) | -1(11) | 6(12) |
| C(12) | 82(16) | 170(20) | 52(14) | -19(15) | 24(12) | -14(15) |
| C(13) | 141(18) | 58(11) | 20(11) | 13(8) | 9(11) | -2(12) |
| C(14) | 89(14) | 42(10) | 39(11) | -15(8) | 21(10) | 8(9) |
| C(15) | 69(6) | 45(5) | 55(6) | -13(4) | 3(5) | 0(4) |
| C(16) | 69(6) | 45(5) | 55(6) | -13(4) | 3(5) | 0(4) |
| C(17) | 69(6) | 45(5) | 55(6) | -13(4) | 3(5) | 0(4) |
| C(18) | 69(6) | 45(5) | 55(6) | -13(4) | 3(5) | 0(4) |
| C(19) | 69(6) | 45(5) | 55(6) | -13(4) | 3(5) | 0(4) |
| C(20) | 108(8) | 88(7) | 73(7) | -4(6) | 1(6) | 1(6) |
| C(21) | 108(8) | 88(7) | 73(7) | -4(6) | 1(6) | 1(6) |
| C(22) | 108(8) | 88(7) | 73(7) | -4(6) | 1(6) | 1(6) |
| C(23) | 108(8) | 88(7) | 73(7) | -4(6) | 1(6) | 1(6) |
| C(24) | 108(8) | 88(7) | 73(7) | -4(6) | 1(6) | 1(6) |
| C(25) | 31(9) | 51(10) | 27(9) | 0(7) | 7(7) | 12(7) |
| C(26) | 76(14) | 72(13) | 86(17) | 1(12) | -8(12) | -36(11) |
| C(27) | 39(10) | 51(11) | 107(17) | -7(11) | -10(10) | 5(9) |
| C(28) | 69(14) | 113(19) | 86(18) | -16(14) | 16(13) | -13(12) |

**Table S5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **2a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(6A) | 2485 | 4645 | 10166 | 163 |
| H(6B) | 3689 | 4836 | 9624 | 163 |
| H(6C) | 3855 | 4173 | 10166 | 163 |
| H(7A) | 486 | 4046 | 10198 | 163 |
| H(7B) | -685 | 3565 | 9674 | 163 |
| H(7C) | -726 | 4345 | 9489 | 163 |
| H(8A) | -741 | 2841 | 7565 | 163 |
| H(8B) | -1535 | 3539 | 7616 | 163 |
| H(8C) | -1334 | 3043 | 8388 | 163 |
| H(9A) | 941 | 3297 | 6671 | 163 |
| H(9B) | 2119 | 2778 | 7108 | 163 |
| H(9C) | 2625 | 3480 | 6803 | 163 |
| H(10A) | 4793 | 3616 | 8038 | 163 |
| H(10B) | 4995 | 4194 | 8716 | 163 |
| H(10C) | 4326 | 4360 | 7776 | 163 |
| H(11A) | 3733 | 2511 | 10882 | 90 |
| H(11B) | 2274 | 2955 | 10874 | 90 |
| H(12A) | 112 | 1807 | 11375 | 150 |
| H(12B) | -800 | 1621 | 10490 | 150 |
| H(12C) | -448 | 2381 | 10725 | 150 |
| H(13A) | 3604 | 1116 | 10638 | 111 |
| H(13B) | 2147 | 716 | 10307 | 111 |
| H(13C) | 2475 | 969 | 11243 | 111 |
| H(20A) | 1984 | 1071 | 5917 | 137 |
| H(20B) | 2847 | 1646 | 6467 | 137 |
| H(20C) | 1115 | 1645 | 6295 | 137 |
| H(21A) | -612 | 1579 | 7037 | 137 |
| H(21B) | -1117 | 1234 | 7817 | 137 |
| H(21C) | -1298 | 851 | 6953 | 137 |
| H(22A) | -319 | 577 | 8968 | 137 |
| H(22B) | 952 | 92 | 9382 | 137 |
| H(22C) | -249 | -167 | 8640 | 137 |
| H(23A) | 3427 | -55 | 9439 | 137 |
| H(23B) | 4649 | -77 | 8869 | 137 |
| H(23C) | 3392 | -623 | 8756 | 137 |
| H(24A) | 5290 | 869 | 7693 | 137 |
| H(24B) | 4588 | 659 | 6772 | 137 |
| H(24C) | 5027 | 103 | 7464 | 137 |
| H(26A) | 5945 | 2988 | 9170 | 121 |
| H(26B) | 7308 | 2520 | 9476 | 121 |
| H(26C) | 5928 | 2492 | 9928 | 121 |
| H(27A) | 7199 | 1264 | 9063 | 102 |
| H(27B) | 5585 | 983 | 8978 | 102 |
| H(27C) | 6317 | 1350 | 9808 | 102 |
| H(28A) | 5328 | 2542 | 7716 | 134 |
| H(28B) | 5341 | 1754 | 7603 | 134 |
| H(28C) | 6825 | 2144 | 7896 | 134 |

**Figure S2.** ORTEP drawing of [($C_5Me_5$)Ir($\mu$-N$^t$Bu)($\mu$-CHSiMe$_3$)Sc($C_5H_5N$)($C_5Me_4SiMe_3$)] (**3'**).

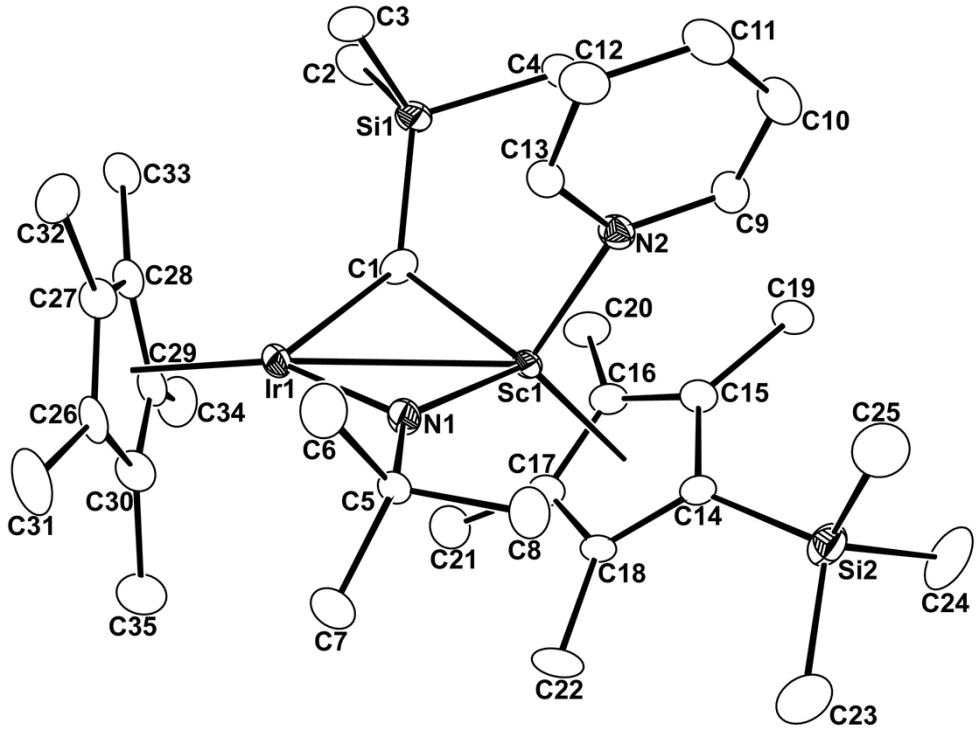

**Table S6.** Crystal data and structure refinement for **3'**.

| | | |
|---|---|---|
| Identification code | 15166ts | |
| Empirical formula | C35 H60 Ir N2 Sc Si2 | |
| Formula weight | 802.19 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.6879(10) Å | α= 73.1590(10)°. |
| | b = 10.9527(11) Å | β= 85.811(2)°. |
| | c = 18.836(2) Å | γ = 78.9610(10)°. |
| Volume | 1877.2(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.419 $Mg/m^3$ | |
| Absorption coefficient | 3.810 $mm^{-1}$ | |
| F(000) | 820 | |
| Crystal size | 0.40 x 0.40 x 0.40 $mm^3$ | |
| Theta range for data collection | 1.97 to 27.00°. | |
| Index ranges | -12<=h<=12, -7<=k<=13, -24<=l<=24 | |
| Reflections collected | 11447 | |
| Independent reflections | 7820 [R(int) = 0.0858] | |
| Completeness to theta = 27.00° | 95.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.3110 and 0.3110 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7820 / 0 / 391 | |
| Goodness-of-fit on $F^2$ | 1.142 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0733, wR2 = 0.2075 | |
| R indices (all data) | R1 = 0.0784, wR2 = 0.2178 | |
| Largest diff. peak and hole | 4.787 and -3.732 $e.Å^{-3}$ | |

**Table S7.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3'**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 7098(1) | 6942(1) | 6609(1) | 26(1) |
| Sc(1) | 8432(2) | 4634(2) | 7744(1) | 23(1) |
| N(1) | 7458(8) | 5080(7) | 6752(4) | 29(2) |
| N(2) | 6719(7) | 3460(7) | 8376(4) | 28(2) |
| Si(1) | 6354(3) | 6847(3) | 8516(1) | 32(1) |
| Si(2) | 10870(3) | 1045(3) | 8156(2) | 41(1) |
| C(1) | 7581(10) | 6573(9) | 7770(6) | 33(2) |
| C(2) | 6533(14) | 8316(13) | 8833(6) | 51(3) |
| C(3) | 4445(11) | 6973(11) | 8340(7) | 45(2) |
| C(4) | 6698(13) | 5520(12) | 9415(6) | 47(3) |
| C(5) | 7137(9) | 4402(8) | 6214(4) | 26(2) |
| C(6) | 5554(12) | 4703(11) | 6066(6) | 45(3) |
| C(7) | 7977(14) | 4764(12) | 5508(6) | 49(3) |
| C(8) | 7553(14) | 2923(10) | 6578(6) | 46(3) |
| C(9) | 6873(10) | 2493(11) | 9017(6) | 41(2) |
| C(10) | 5799(14) | 1933(13) | 9383(6) | 53(3) |
| C(11) | 4455(12) | 2331(13) | 9085(6) | 46(3) |
| C(12) | 4285(11) | 3333(12) | 8438(6) | 45(2) |
| C(13) | 5431(10) | 3858(10) | 8104(5) | 33(2) |
| C(14) | 10633(9) | 2833(9) | 8047(5) | 30(2) |
| C(15) | 10453(8) | 3422(9) | 8656(5) | 30(2) |
| C(16) | 10651(9) | 4686(9) | 8401(5) | 30(2) |
| C(17) | 10965(9) | 4945(10) | 7628(5) | 32(2) |
| C(18) | 10968(9) | 3824(10) | 7413(5) | 30(2) |
| C(19) | 10253(11) | 2709(12) | 9467(5) | 41(2) |
| C(20) | 10697(11) | 5603(12) | 8863(6) | 44(2) |
| C(21) | 11382(12) | 6191(12) | 7134(7) | 47(3) |
| C(22) | 11396(12) | 3719(14) | 6640(6) | 48(3) |
| C(23) | 11460(16) | 622(14) | 7257(8) | 63(3) |
| C(24) | 12280(17) | 142(14) | 8842(10) | 76(5) |
| C(25) | 9249(16) | 292(15) | 8463(10) | 69(4) |
| C(26) | 6307(13) | 8125(10) | 5457(5) | 43(2) |
| C(27) | 5475(9) | 8539(9) | 6024(5) | 30(2) |
| C(28) | 6234(11) | 9050(9) | 6437(5) | 33(2) |
| C(29) | 7662(12) | 8875(10) | 6161(6) | 42(2) |
| C(30) | 7714(10) | 8283(10) | 5580(6) | 37(2) |
| C(31) | 5780(20) | 7843(14) | 4797(7) | 69(4) |
| C(32) | 3857(10) | 8547(11) | 6109(7) | 47(3) |
| C(33) | 5668(14) | 9778(11) | 6985(6) | 47(3) |
| C(34) | 8823(13) | 9355(12) | 6406(8) | 52(3) |
| C(35) | 8972(14) | 8037(13) | 5099(8) | 57(3) |

**Table S8.** Bond lengths [Å] and angles [°] for **3'**.

| | |
|---|---|
| Ir(1)-N(1) | 1.943(8) |
| Ir(1)-C(1) | 2.175(10) |
| Ir(1)-C(30) | 2.188(9) |
| Ir(1)-C(27) | 2.197(9) |
| Ir(1)-C(29) | 2.198(11) |
| Ir(1)-C(28) | 2.237(9) |
| Ir(1)-C(26) | 2.281(9) |
| Ir(1)-Sc(1) | 2.9416(15) |
| Sc(1)-N(1) | 2.042(7) |
| Sc(1)-C(1) | 2.139(9) |
| Sc(1)-N(2) | 2.338(7) |
| Sc(1)-C(17) | 2.527(9) |
| Sc(1)-C(18) | 2.545(9) |
| Sc(1)-C(16) | 2.575(8) |
| Sc(1)-C(14) | 2.584(9) |
| Sc(1)-C(15) | 2.593(8) |
| N(1)-C(5) | 1.499(10) |
| N(2)-C(13) | 1.329(11) |
| N(2)-C(9) | 1.351(12) |
| Si(1)-C(1) | 1.828(10) |
| Si(1)-C(3) | 1.874(11) |
| Si(1)-C(4) | 1.887(11) |
| Si(1)-C(2) | 1.912(11) |
| Si(2)-C(24) | 1.874(13) |
| Si(2)-C(14) | 1.880(10) |
| Si(2)-C(25) | 1.888(14) |
| Si(2)-C(23) | 1.903(14) |
| C(5)-C(7) | 1.500(14) |
| C(5)-C(6) | 1.534(14) |
| C(5)-C(8) | 1.550(13) |
| C(9)-C(10) | 1.352(16) |
| C(10)-C(11) | 1.396(17) |
| C(11)-C(12) | 1.379(16) |
| C(12)-C(13) | 1.375(14) |
| C(14)-C(18) | 1.428(14) |
| C(14)-C(15) | 1.455(12) |
| C(15)-C(16) | 1.374(14) |
| C(15)-C(19) | 1.517(13) |
| C(16)-C(17) | 1.422(13) |
| C(16)-C(20) | 1.516(13) |
| C(17)-C(18) | 1.399(14) |
| C(17)-C(21) | 1.520(15) |
| C(18)-C(22) | 1.515(12) |
| C(26)-C(27) | 1.418(15) |
| C(26)-C(30) | 1.449(16) |
| C(26)-C(31) | 1.508(15) |
| C(27)-C(28) | 1.399(13) |
| C(27)-C(32) | 1.562(12) |
| C(28)-C(29) | 1.439(16) |
| C(28)-C(33) | 1.492(14) |
| C(29)-C(30) | 1.418(16) |
| C(29)-C(34) | 1.483(16) |
| C(30)-C(35) | 1.493(15) |
| | |
| N(1)-Ir(1)-C(1) | 88.5(3) |
| N(1)-Ir(1)-C(30) | 121.5(4) |
| C(1)-Ir(1)-C(30) | 133.6(4) |
| N(1)-Ir(1)-C(27) | 133.8(3) |
| C(1)-Ir(1)-C(27) | 123.3(4) |
| C(30)-Ir(1)-C(27) | 62.2(4) |
| N(1)-Ir(1)-C(29) | 152.1(4) |
| C(1)-Ir(1)-C(29) | 99.6(4) |
| C(30)-Ir(1)-C(29) | 37.7(4) |
| C(27)-Ir(1)-C(29) | 62.0(3) |
| N(1)-Ir(1)-C(28) | 168.6(4) |
| C(1)-Ir(1)-C(28) | 94.7(4) |
| C(30)-Ir(1)-C(28) | 63.1(4) |
| C(27)-Ir(1)-C(28) | 36.8(3) |
| C(29)-Ir(1)-C(28) | 37.9(4) |
| N(1)-Ir(1)-C(26) | 113.9(3) |
| C(1)-Ir(1)-C(26) | 157.1(4) |
| C(30)-Ir(1)-C(26) | 37.8(4) |
| C(27)-Ir(1)-C(26) | 36.8(4) |
| C(29)-Ir(1)-C(26) | 62.8(4) |
| C(28)-Ir(1)-C(26) | 62.4(4) |
| N(1)-Ir(1)-Sc(1) | 43.7(2) |
| C(1)-Ir(1)-Sc(1) | 46.5(2) |
| C(30)-Ir(1)-Sc(1) | 137.8(3) |
| C(27)-Ir(1)-Sc(1) | 160.0(2) |
| C(29)-Ir(1)-Sc(1) | 131.2(3) |
| C(28)-Ir(1)-Sc(1) | 141.2(3) |
| C(26)-Ir(1)-Sc(1) | 156.3(3) |
| N(1)-Sc(1)-C(1) | 87.0(3) |
| N(1)-Sc(1)-N(2) | 92.4(3) |
| C(1)-Sc(1)-N(2) | 103.2(3) |
| N(1)-Sc(1)-C(17) | 114.1(3) |
| C(1)-Sc(1)-C(17) | 95.0(4) |
| N(2)-Sc(1)-C(17) | 148.6(3) |
| N(1)-Sc(1)-C(18) | 102.2(3) |
| C(1)-Sc(1)-C(18) | 125.4(4) |
| N(2)-Sc(1)-C(18) | 129.5(3) |
| C(17)-Sc(1)-C(18) | 32.0(3) |
| N(1)-Sc(1)-C(16) | 145.9(3) |
| C(1)-Sc(1)-C(16) | 90.3(3) |
| N(2)-Sc(1)-C(16) | 121.2(3) |
| C(17)-Sc(1)-C(16) | 32.3(3) |
| C(18)-Sc(1)-C(16) | 53.3(3) |
| N(1)-Sc(1)-C(14) | 120.4(3) |
| C(1)-Sc(1)-C(14) | 143.5(3) |
| N(2)-Sc(1)-C(14) | 99.5(3) |
| C(17)-Sc(1)-C(14) | 53.4(3) |
| C(18)-Sc(1)-C(14) | 32.3(3) |
| C(16)-Sc(1)-C(14) | 53.3(3) |
| N(1)-Sc(1)-C(15) | 152.7(3) |
| C(1)-Sc(1)-C(15) | 115.7(3) |
| N(2)-Sc(1)-C(15) | 96.5(3) |
| C(17)-Sc(1)-C(15) | 52.3(3) |
| C(18)-Sc(1)-C(15) | 52.9(3) |
| C(16)-Sc(1)-C(15) | 30.8(3) |
| C(14)-Sc(1)-C(15) | 32.7(3) |
| N(1)-Sc(1)-Ir(1) | 41.2(2) |
| C(1)-Sc(1)-Ir(1) | 47.5(3) |
| N(2)-Sc(1)-Ir(1) | 109.73(19) |
| C(17)-Sc(1)-Ir(1) | 101.4(2) |
| C(18)-Sc(1)-Ir(1) | 112.9(2) |
| C(16)-Sc(1)-Ir(1) | 120.4(2) |
| C(14)-Sc(1)-Ir(1) | 144.5(2) |
| C(15)-Sc(1)-Ir(1) | 151.0(2) |

| | |
|---|---|
| C(5)-N(1)-Ir(1) | 126.0(6) |
| C(5)-N(1)-Sc(1) | 138.7(6) |
| Ir(1)-N(1)-Sc(1) | 95.1(3) |
| C(13)-N(2)-C(9) | 116.7(8) |
| C(13)-N(2)-Sc(1) | 116.0(6) |
| C(9)-N(2)-Sc(1) | 127.0(6) |
| C(1)-Si(1)-C(3) | 116.0(5) |
| C(1)-Si(1)-C(4) | 112.8(5) |
| C(3)-Si(1)-C(4) | 104.5(6) |
| C(1)-Si(1)-C(2) | 114.2(5) |
| C(3)-Si(1)-C(2) | 107.5(6) |
| C(4)-Si(1)-C(2) | 100.2(6) |
| C(24)-Si(2)-C(14) | 110.1(6) |
| C(24)-Si(2)-C(25) | 107.5(8) |
| C(14)-Si(2)-C(25) | 115.6(6) |
| C(24)-Si(2)-C(23) | 106.0(7) |
| C(14)-Si(2)-C(23) | 112.5(6) |
| C(25)-Si(2)-C(23) | 104.5(7) |
| Si(1)-C(1)-Sc(1) | 119.7(6) |
| Si(1)-C(1)-Ir(1) | 127.1(5) |
| Sc(1)-C(1)-Ir(1) | 86.0(3) |
| N(1)-C(5)-C(7) | 110.9(8) |
| N(1)-C(5)-C(6) | 110.2(7) |
| C(7)-C(5)-C(6) | 111.4(9) |
| N(1)-C(5)-C(8) | 107.7(7) |
| C(7)-C(5)-C(8) | 108.7(8) |
| C(6)-C(5)-C(8) | 107.9(9) |
| N(2)-C(9)-C(10) | 123.6(9) |
| C(9)-C(10)-C(11) | 119.5(10) |
| C(12)-C(11)-C(10) | 117.2(11) |
| C(13)-C(12)-C(11) | 119.6(10) |
| N(2)-C(13)-C(12) | 123.4(9) |
| C(18)-C(14)-C(15) | 105.2(8) |
| C(18)-C(14)-Si(2) | 127.7(7) |
| C(15)-C(14)-Si(2) | 125.0(7) |
| C(18)-C(14)-Sc(1) | 72.3(5) |
| C(15)-C(14)-Sc(1) | 74.0(5) |
| Si(2)-C(14)-Sc(1) | 131.0(4) |
| C(16)-C(15)-C(14) | 109.8(8) |
| C(16)-C(15)-C(19) | 124.6(9) |
| C(14)-C(15)-C(19) | 125.2(9) |
| C(16)-C(15)-Sc(1) | 73.9(5) |
| C(14)-C(15)-Sc(1) | 73.3(5) |
| C(19)-C(15)-Sc(1) | 125.0(6) |
| C(15)-C(16)-C(17) | 107.5(8) |
| C(15)-C(16)-C(20) | 126.8(9) |
| C(17)-C(16)-C(20) | 125.3(9) |
| C(15)-C(16)-Sc(1) | 75.3(5) |
| C(17)-C(16)-Sc(1) | 71.9(5) |
| C(20)-C(16)-Sc(1) | 123.6(6) |
| C(18)-C(17)-C(16) | 109.0(9) |
| C(18)-C(17)-C(21) | 125.4(9) |
| C(16)-C(17)-C(21) | 125.3(9) |
| C(18)-C(17)-Sc(1) | 74.7(5) |
| C(16)-C(17)-Sc(1) | 75.7(5) |
| C(21)-C(17)-Sc(1) | 120.9(6) |
| C(17)-C(18)-C(14) | 108.5(8) |
| C(17)-C(18)-C(22) | 123.0(10) |
| C(14)-C(18)-C(22) | 128.3(9) |
| C(17)-C(18)-Sc(1) | 73.3(5) |
| C(14)-C(18)-Sc(1) | 75.4(5) |
| C(22)-C(18)-Sc(1) | 121.6(6) |
| C(27)-C(26)-C(30) | 104.3(9) |
| C(27)-C(26)-C(31) | 126.8(12) |
| C(30)-C(26)-C(31) | 127.9(12) |
| C(27)-C(26)-Ir(1) | 68.4(5) |
| C(30)-C(26)-Ir(1) | 67.6(5) |
| C(31)-C(26)-Ir(1) | 136.2(8) |
| C(28)-C(27)-C(26) | 112.4(9) |
| C(28)-C(27)-C(32) | 124.7(10) |
| C(26)-C(27)-C(32) | 122.6(9) |
| C(28)-C(27)-Ir(1) | 73.2(5) |
| C(26)-C(27)-Ir(1) | 74.8(6) |
| C(32)-C(27)-Ir(1) | 124.9(6) |
| C(27)-C(28)-C(29) | 105.8(9) |
| C(27)-C(28)-C(33) | 127.5(10) |
| C(29)-C(28)-C(33) | 126.3(10) |
| C(27)-C(28)-Ir(1) | 70.1(5) |
| C(29)-C(28)-Ir(1) | 69.6(6) |
| C(33)-C(28)-Ir(1) | 130.4(7) |
| C(30)-C(29)-C(28) | 108.2(9) |
| C(30)-C(29)-C(34) | 127.0(11) |
| C(28)-C(29)-C(34) | 124.5(11) |
| C(30)-C(29)-Ir(1) | 70.7(6) |
| C(28)-C(29)-Ir(1) | 72.5(6) |
| C(34)-C(29)-Ir(1) | 126.8(7) |
| C(29)-C(30)-C(26) | 109.0(9) |
| C(29)-C(30)-C(35) | 125.4(10) |
| C(26)-C(30)-C(35) | 125.1(11) |
| C(29)-C(30)-Ir(1) | 71.5(6) |
| C(26)-C(30)-Ir(1) | 74.6(5) |
| C(35)-C(30)-Ir(1) | 126.7(8) |

Symmetry transformations used to generate equivalent atoms:

**Table S9.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 33(1) | 28(1) | 16(1) | -4(1) | -4(1) | -1(1) |
| Sc(1) | 25(1) | 29(1) | 12(1) | -5(1) | -3(1) | 1(1) |
| N(1) | 39(4) | 29(4) | 18(3) | -9(3) | -6(3) | 1(3) |
| N(2) | 25(3) | 35(4) | 23(4) | -6(3) | -1(3) | -5(3) |
| Si(1) | 36(1) | 39(1) | 20(1) | -13(1) | 2(1) | -1(1) |
| Si(2) | 36(1) | 36(1) | 46(2) | -12(1) | -7(1) | 6(1) |
| C(1) | 38(5) | 33(5) | 32(5) | -20(4) | -5(4) | 3(4) |
| C(2) | 72(8) | 61(7) | 30(6) | -28(5) | 6(5) | -19(6) |
| C(3) | 39(5) | 49(6) | 44(6) | -18(5) | 9(5) | 1(4) |
| C(4) | 54(6) | 53(6) | 26(5) | -8(5) | 9(4) | 1(5) |
| C(5) | 37(4) | 29(4) | 12(4) | -10(3) | -4(3) | 2(3) |
| C(6) | 54(6) | 48(6) | 38(6) | -18(5) | -19(5) | -5(5) |
| C(7) | 76(8) | 47(6) | 22(5) | -14(4) | 2(5) | 0(5) |
| C(8) | 71(7) | 31(5) | 36(6) | -10(4) | -8(5) | -3(5) |
| C(9) | 26(4) | 48(6) | 35(5) | 4(4) | -4(4) | 1(4) |
| C(10) | 55(7) | 61(7) | 28(5) | 3(5) | -1(5) | -2(5) |
| C(11) | 42(6) | 64(7) | 30(5) | -7(5) | 1(4) | -15(5) |
| C(12) | 32(5) | 64(7) | 36(6) | -11(5) | 0(4) | -6(5) |
| C(13) | 29(4) | 39(5) | 25(5) | -4(4) | -1(3) | -1(4) |
| C(14) | 26(4) | 40(5) | 23(4) | -12(4) | -3(3) | 6(3) |
| C(15) | 20(4) | 45(5) | 24(4) | -11(4) | -6(3) | -3(3) |
| C(16) | 20(4) | 42(5) | 31(5) | -15(4) | -1(3) | -6(3) |
| C(17) | 22(4) | 47(5) | 26(5) | -9(4) | -1(3) | -1(3) |
| C(18) | 25(4) | 45(5) | 17(4) | -12(4) | -3(3) | 6(3) |
| C(19) | 35(5) | 64(7) | 18(4) | -10(4) | -8(4) | 8(4) |
| C(20) | 39(5) | 64(7) | 38(6) | -31(5) | -5(4) | -6(5) |
| C(21) | 39(5) | 53(6) | 47(7) | -7(5) | -3(5) | -11(5) |
| C(22) | 44(6) | 77(8) | 26(5) | -27(5) | 7(4) | -5(5) |
| C(23) | 69(8) | 58(8) | 68(9) | -36(7) | -6(7) | 4(6) |
| C(24) | 79(10) | 54(8) | 89(12) | -27(8) | -42(9) | 31(7) |
| C(25) | 66(8) | 58(8) | 85(11) | -22(8) | 15(8) | -18(7) |
| C(26) | 73(7) | 31(5) | 17(4) | -2(4) | -13(4) | 5(5) |
| C(27) | 23(4) | 34(4) | 34(5) | -5(4) | -3(3) | -14(3) |
| C(28) | 51(6) | 23(4) | 23(5) | -5(3) | -4(4) | -2(4) |
| C(29) | 50(6) | 42(5) | 23(5) | 3(4) | -5(4) | 4(4) |
| C(30) | 38(5) | 33(5) | 39(5) | -1(4) | 8(4) | -19(4) |
| C(31) | 123(13) | 54(7) | 28(6) | -9(5) | -34(7) | 0(8) |
| C(32) | 24(4) | 48(6) | 62(8) | -4(5) | -7(5) | -6(4) |
| C(33) | 69(7) | 45(6) | 23(5) | -12(4) | -4(5) | 5(5) |
| C(34) | 51(6) | 42(6) | 61(8) | -3(5) | -8(6) | -16(5) |
| C(35) | 58(7) | 52(7) | 55(8) | -9(6) | 23(6) | -16(6) |

**Table S10.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **3'**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 7505 | 8233 | 8978 | 76 |
| H(2B) | 5898 | 8359 | 9259 | 76 |
| H(2C) | 6287 | 9108 | 8426 | 76 |
| H(3A) | 4245 | 7451 | 7820 | 67 |
| H(3B) | 3869 | 7433 | 8665 | 67 |
| H(3C) | 4223 | 6102 | 8442 | 67 |
| H(4A) | 6231 | 4803 | 9411 | 70 |
| H(4B) | 6329 | 5861 | 9831 | 70 |
| H(4C) | 7713 | 5206 | 9469 | 70 |
| H(6A) | 5042 | 4361 | 6527 | 68 |
| H(6B) | 5365 | 4298 | 5692 | 68 |
| H(6C) | 5245 | 5644 | 5886 | 68 |
| H(7A) | 7773 | 5706 | 5290 | 73 |
| H(7B) | 7725 | 4335 | 5158 | 73 |
| H(7C) | 8982 | 4487 | 5614 | 73 |
| H(8A) | 8554 | 2710 | 6696 | 70 |
| H(8B) | 7371 | 2453 | 6234 | 70 |
| H(8C) | 6995 | 2671 | 7035 | 70 |
| H(9) | 7785 | 2191 | 9222 | 49 |
| H(10) | 5959 | 1272 | 9839 | 63 |
| H(11) | 3690 | 1928 | 9318 | 55 |
| H(12) | 3383 | 3659 | 8225 | 54 |
| H(13) | 5295 | 4540 | 7655 | 40 |
| H(19A) | 11063 | 2716 | 9748 | 62 |
| H(19B) | 10173 | 1811 | 9512 | 62 |
| H(19C) | 9394 | 3139 | 9665 | 62 |
| H(20A) | 10276 | 5271 | 9354 | 65 |
| H(20B) | 10169 | 6462 | 8616 | 65 |
| H(20C) | 11677 | 5668 | 8918 | 65 |
| H(21A) | 12410 | 6089 | 7099 | 71 |
| H(21B) | 11003 | 6907 | 7347 | 71 |
| H(21C) | 11002 | 6381 | 6638 | 71 |
| H(22A) | 11093 | 4558 | 6277 | 72 |
| H(22B) | 10951 | 3060 | 6535 | 72 |
| H(22C) | 12421 | 3471 | 6609 | 72 |
| H(23A) | 10671 | 895 | 6915 | 94 |
| H(23B) | 11778 | -317 | 7363 | 94 |
| H(23C) | 12235 | 1070 | 7029 | 94 |
| H(24A) | 13158 | 466 | 8677 | 115 |
| H(24B) | 12423 | -785 | 8880 | 115 |
| H(24C) | 11995 | 273 | 9329 | 115 |
| H(25A) | 9022 | 267 | 8982 | 104 |
| H(25B) | 9427 | -593 | 8415 | 104 |
| H(25C) | 8458 | 810 | 8151 | 104 |
| H(31A) | 5015 | 7353 | 4955 | 104 |
| H(31B) | 6555 | 7331 | 4583 | 104 |
| H(31C) | 5444 | 8660 | 4424 | 104 |
| H(32A) | 3591 | 8320 | 6636 | 71 |
| H(32B) | 3618 | 7914 | 5884 | 71 |
| H(32C) | 3349 | 9413 | 5859 | 71 |
| H(33A) | 5318 | 10687 | 6721 | 71 |
| H(33B) | 6417 | 9732 | 7319 | 71 |
| H(33C) | 4897 | 9393 | 7274 | 71 |
| H(34A) | 9718 | 9002 | 6201 | 78 |
| H(34B) | 8855 | 9076 | 6949 | 78 |

| | | | | |
|---|---|---|---|---|
| H(34C) | 8664 | 10304 | 6231 | 78 |
| H(35A) | 9121 | 8857 | 4745 | 86 |
| H(35B) | 8819 | 7436 | 4828 | 86 |
| H(35C) | 9803 | 7658 | 5409 | 86 |
| H(1) | 8310(140) | 7000(130) | 7790(70) | 50 |

**Figure S3.** ORTEP drawing of [($C_5Me_5$)Ir($\mu$-N$^t$Bu)($\mu$-$CH_2SiMe_2NC(Ph)=CH_2$)Lu(NCPh)($C_5Me_5$)] (**4**)

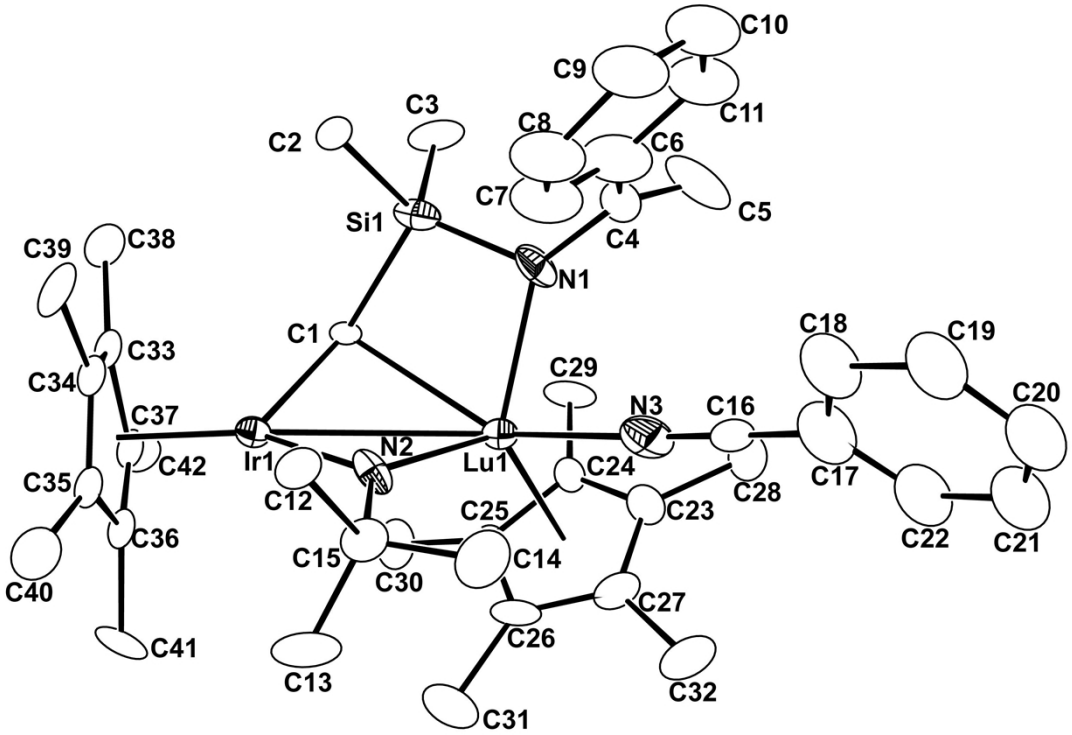

**Table S11.** Crystal data and structure refinement for **4**.

| | | |
|---|---|---|
| Identification code | 16073ts | |
| Empirical formula | C45 H62 Ir Lu N3 Si | |
| Formula weight | 1040.24 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 46.05(3) Å | $\alpha$= 90°. |
| | b = 9.620(6) Å | $\beta$= 90.619(11)°. |
| | c = 19.635(13) Å | $\gamma$ = 90°. |
| Volume | 8698(10) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.589 $Mg/m^3$ | |
| Absorption coefficient | 5.374 $mm^{-1}$ | |
| F(000) | 4120 | |
| Crystal size | 0.40 x 0.10 x 0.10 $mm^3$ | |
| Theta range for data collection | 1.77 to 26.24°. | |
| Index ranges | -56<=h<=56, -11<=k<=7, -24<=l<=23 | |
| Reflections collected | 24115 | |
| Independent reflections | 8632 [R(int) = 0.1608] | |
| Completeness to theta = 26.24° | 98.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.6156 and 0.2224 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8632 / 0 / 391 | |
| Goodness-of-fit on $F^2$ | 0.885 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0524, wR2 = 0.0809 | |
| R indices (all data) | R1 = 0.1749, wR2 = 0.1112 | |
| Largest diff. peak and hole | 1.687 and -1.230 $e.Å^{-3}$ | |

**Table S12.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 1814(1) | 2051(1) | 3638(1) | 31(1) |
| Lu(1) | 1357(1) | 2203(1) | 2439(1) | 33(1) |
| N(1) | 958(2) | 1694(13) | 2984(7) | 48(4) |
| N(2) | 1621(2) | 3462(12) | 3139(7) | 38(4) |
| N(3) | 1042(3) | 3974(14) | 2093(8) | 57(5) |
| Si(1) | 1103(1) | 627(5) | 3626(3) | 47(1) |
| C(1) | 1493(3) | 488(15) | 3381(7) | 27(4) |
| C(2) | 1078(3) | 1311(15) | 4520(7) | 38(4) |
| C(3) | 938(3) | -1141(16) | 3624(8) | 59(6) |
| C(4) | 665(4) | 2080(20) | 2955(9) | 63(6) |
| C(5) | 486(4) | 1420(20) | 2535(12) | 106(9) |
| C(6) | 576(5) | 3350(20) | 3421(12) | 85(3) |
| C(7) | 765(5) | 4150(20) | 3715(11) | 85(3) |
| C(8) | 671(4) | 5270(20) | 4098(11) | 85(3) |
| C(9) | 382(4) | 5510(20) | 4142(12) | 85(3) |
| C(10) | 189(5) | 4730(20) | 3860(12) | 85(3) |
| C(11) | 277(4) | 3631(19) | 3432(11) | 85(3) |
| C(12) | 1655(3) | 5475(15) | 3888(7) | 41(4) |
| C(13) | 2015(3) | 5201(16) | 2977(9) | 61(6) |
| C(14) | 1509(4) | 5791(15) | 2711(9) | 59(5) |
| C(15) | 1707(4) | 4969(18) | 3166(8) | 45(5) |
| C(16) | 867(4) | 4789(19) | 1884(9) | 51(5) |
| C(17) | 676(5) | 5910(20) | 1731(14) | 96(4) |
| C(18) | 541(4) | 6640(20) | 2213(14) | 96(4) |
| C(19) | 355(4) | 7710(20) | 2018(13) | 96(4) |
| C(20) | 308(4) | 7970(20) | 1317(13) | 96(4) |
| C(21) | 442(4) | 7260(20) | 890(13) | 96(4) |
| C(22) | 617(4) | 6140(20) | 1035(14) | 96(4) |
| C(23) | 1248(3) | 1507(18) | 1161(9) | 46(5) |
| C(24) | 1368(3) | 345(16) | 1454(8) | 35(4) |
| C(25) | 1663(3) | 664(16) | 1614(7) | 33(4) |
| C(26) | 1715(3) | 2050(20) | 1404(8) | 51(5) |
| C(27) | 1455(4) | 2567(15) | 1120(8) | 42(4) |
| C(28) | 945(3) | 1586(16) | 896(8) | 51(5) |
| C(29) | 1227(3) | -1013(15) | 1587(8) | 50(5) |
| C(30) | 1897(3) | -323(18) | 1873(8) | 63(6) |
| C(31) | 2012(3) | 2740(20) | 1421(9) | 93(8) |
| C(32) | 1416(4) | 3905(17) | 752(8) | 64(6) |
| C(33) | 1966(3) | 663(17) | 4512(8) | 34(2) |
| C(34) | 1982(3) | 2112(18) | 4682(7) | 34(2) |
| C(35) | 2188(3) | 2764(17) | 4290(7) | 34(2) |
| C(36) | 2273(3) | 1820(16) | 3780(7) | 34(2) |
| C(37) | 2151(3) | 528(17) | 3906(7) | 34(2) |
| C(38) | 1797(3) | -442(16) | 4861(8) | 52(5) |
| C(39) | 1837(3) | 2708(17) | 5304(7) | 52(5) |
| C(40) | 2334(4) | 4131(17) | 4456(9) | 63(6) |
| C(41) | 2514(3) | 2046(18) | 3268(8) | 57(5) |
| C(42) | 2212(3) | -825(16) | 3605(8) | 50(5) |
| C(45) | 260(4) | 9420(20) | 4883(13) | 78(7) |
| C(46) | 99(4) | 8906(19) | 5408(11) | 72(6) |
| C(47) | 174(4) | 10529(19) | 4474(10) | 56(5) |

**Table S13.** Bond lengths [Å] and angles [°] for **4**.

| | |
|---|---|
| Ir(1)-N(2) | 1.890(12) |
| Ir(1)-C(36) | 2.142(13) |
| Ir(1)-C(1) | 2.163(14) |
| Ir(1)-C(34) | 2.186(13) |
| Ir(1)-C(37) | 2.195(15) |
| Ir(1)-C(35) | 2.243(14) |
| Ir(1)-C(33) | 2.279(15) |
| Ir(1)-Lu(1) | 3.1429(18) |
| Lu(1)-N(2) | 2.190(12) |
| Lu(1)-N(1) | 2.191(11) |
| Lu(1)-N(3) | 2.336(15) |
| Lu(1)-C(1) | 2.552(14) |
| Lu(1)-C(25) | 2.617(14) |
| Lu(1)-C(26) | 2.633(13) |
| Lu(1)-C(24) | 2.634(15) |
| Lu(1)-C(23) | 2.642(17) |
| Lu(1)-C(27) | 2.657(15) |
| Lu(1)-Si(1) | 3.025(5) |
| N(1)-C(4) | 1.401(19) |
| N(1)-Si(1) | 1.752(14) |
| N(2)-C(15) | 1.505(18) |
| N(3)-C(16) | 1.19(2) |
| Si(1)-C(3) | 1.863(15) |
| Si(1)-C(1) | 1.870(13) |
| Si(1)-C(2) | 1.880(14) |
| C(4)-C(5) | 1.32(2) |
| C(4)-C(6) | 1.58(3) |
| C(6)-C(7) | 1.29(3) |
| C(6)-C(11) | 1.40(2) |
| C(7)-C(8) | 1.39(2) |
| C(8)-C(9) | 1.36(2) |
| C(9)-C(10) | 1.28(3) |
| C(10)-C(11) | 1.41(2) |
| C(12)-C(15) | 1.522(19) |
| C(13)-C(15) | 1.488(19) |
| C(14)-C(15) | 1.50(2) |
| C(16)-C(17) | 1.42(3) |
| C(17)-C(18) | 1.34(3) |
| C(17)-C(22) | 1.41(3) |
| C(18)-C(19) | 1.39(2) |
| C(19)-C(20) | 1.41(3) |
| C(20)-C(21) | 1.25(3) |
| C(21)-C(22) | 1.37(2) |
| C(23)-C(24) | 1.37(2) |
| C(23)-C(27) | 1.399(19) |
| C(23)-C(28) | 1.484(19) |
| C(24)-C(25) | 1.424(19) |
| C(24)-C(29) | 1.483(18) |
| C(25)-C(26) | 1.42(2) |
| C(25)-C(30) | 1.52(2) |
| C(26)-C(27) | 1.41(2) |
| C(26)-C(31) | 1.52(2) |
| C(27)-C(32) | 1.49(2) |
| C(33)-C(34) | 1.44(2) |
| C(33)-C(37) | 1.477(19) |
| C(33)-C(38) | 1.487(19) |
| C(34)-C(35) | 1.379(17) |
| C(34)-C(39) | 1.510(17) |
| C(35)-C(36) | 1.411(18) |
| C(35)-C(40) | 1.51(2) |
| C(36)-C(37) | 1.388(19) |
| C(36)-C(41) | 1.519(17) |
| C(37)-C(42) | 1.458(19) |
| C(45)-C(46) | 1.37(2) |
| C(45)-C(47) | 1.39(3) |
| C(46)-C(47)#1 | 1.39(2) |
| C(47)-C(46)#1 | 1.39(2) |
| | |
| N(2)-Ir(1)-C(36) | 126.9(5) |
| N(2)-Ir(1)-C(1) | 93.6(5) |
| C(36)-Ir(1)-C(1) | 129.0(5) |
| N(2)-Ir(1)-C(34) | 128.8(6) |
| C(36)-Ir(1)-C(34) | 62.7(5) |
| C(1)-Ir(1)-C(34) | 118.1(6) |
| N(2)-Ir(1)-C(37) | 158.7(5) |
| C(36)-Ir(1)-C(37) | 37.3(5) |
| C(1)-Ir(1)-C(37) | 94.1(5) |
| C(34)-Ir(1)-C(37) | 63.2(5) |
| N(2)-Ir(1)-C(35) | 115.5(6) |
| C(36)-Ir(1)-C(35) | 37.4(5) |
| C(1)-Ir(1)-C(35) | 149.7(6) |
| C(34)-Ir(1)-C(35) | 36.3(4) |
| C(37)-Ir(1)-C(35) | 62.0(6) |
| N(2)-Ir(1)-C(33) | 161.7(5) |
| C(36)-Ir(1)-C(33) | 63.0(5) |
| C(1)-Ir(1)-C(33) | 88.3(6) |
| C(34)-Ir(1)-C(33) | 37.4(5) |
| C(37)-Ir(1)-C(33) | 38.5(5) |
| C(35)-Ir(1)-C(33) | 61.4(6) |
| N(2)-Ir(1)-Lu(1) | 43.2(4) |
| C(36)-Ir(1)-Lu(1) | 139.0(4) |
| C(1)-Ir(1)-Lu(1) | 53.7(4) |
| C(34)-Ir(1)-Lu(1) | 158.3(3) |
| C(37)-Ir(1)-Lu(1) | 132.6(4) |
| C(35)-Ir(1)-Lu(1) | 156.5(4) |
| C(33)-Ir(1)-Lu(1) | 142.0(4) |
| N(2)-Lu(1)-N(1) | 106.2(5) |
| N(2)-Lu(1)-N(3) | 96.8(5) |
| N(1)-Lu(1)-N(3) | 77.4(5) |
| N(2)-Lu(1)-C(1) | 76.8(5) |
| N(1)-Lu(1)-C(1) | 72.7(4) |
| N(3)-Lu(1)-C(1) | 146.1(5) |
| N(2)-Lu(1)-C(25) | 113.8(4) |
| N(1)-Lu(1)-C(25) | 129.5(5) |
| N(3)-Lu(1)-C(25) | 124.7(5) |
| C(1)-Lu(1)-C(25) | 87.3(4) |
| N(2)-Lu(1)-C(26) | 99.7(5) |
| N(1)-Lu(1)-C(26) | 154.0(5) |
| N(3)-Lu(1)-C(26) | 102.0(6) |
| C(1)-Lu(1)-C(26) | 111.9(5) |
| C(25)-Lu(1)-C(26) | 31.3(5) |
| N(2)-Lu(1)-C(24) | 145.2(4) |
| N(1)-Lu(1)-C(24) | 103.3(5) |
| N(3)-Lu(1)-C(24) | 107.3(5) |
| C(1)-Lu(1)-C(24) | 95.0(5) |
| C(25)-Lu(1)-C(24) | 31.5(4) |
| C(26)-Lu(1)-C(24) | 51.6(5) |
| N(2)-Lu(1)-C(23) | 146.7(5) |

| | | | |
|---|---|---|---|
| N(1)-Lu(1)-C(23) | 104.8(5) | C(9)-C(8)-C(7) | 119(2) |
| N(3)-Lu(1)-C(23) | 78.3(5) | C(10)-C(9)-C(8) | 123(2) |
| C(1)-Lu(1)-C(23) | 124.6(5) | C(9)-C(10)-C(11) | 120(2) |
| C(25)-Lu(1)-C(23) | 50.7(5) | C(6)-C(11)-C(10) | 116(2) |
| C(26)-Lu(1)-C(23) | 50.7(5) | C(13)-C(15)-C(14) | 110.5(15) |
| C(24)-Lu(1)-C(23) | 30.1(4) | C(13)-C(15)-N(2) | 112.9(13) |
| N(2)-Lu(1)-C(27) | 116.1(5) | C(14)-C(15)-N(2) | 109.2(13) |
| N(1)-Lu(1)-C(27) | 131.1(5) | C(13)-C(15)-C(12) | 110.2(14) |
| N(3)-Lu(1)-C(27) | 74.4(5) | C(14)-C(15)-C(12) | 106.5(14) |
| C(1)-Lu(1)-C(27) | 138.5(4) | N(2)-C(15)-C(12) | 107.2(13) |
| C(25)-Lu(1)-C(27) | 51.2(5) | N(3)-C(16)-C(17) | 170(2) |
| C(26)-Lu(1)-C(27) | 30.8(5) | C(18)-C(17)-C(22) | 121(2) |
| C(24)-Lu(1)-C(27) | 50.9(5) | C(18)-C(17)-C(16) | 123(3) |
| C(23)-Lu(1)-C(27) | 30.6(4) | C(22)-C(17)-C(16) | 116(2) |
| N(2)-Lu(1)-Si(1) | 90.6(4) | C(17)-C(18)-C(19) | 119(3) |
| N(1)-Lu(1)-Si(1) | 34.8(3) | C(18)-C(19)-C(20) | 119(2) |
| N(3)-Lu(1)-Si(1) | 110.2(4) | C(21)-C(20)-C(19) | 119(2) |
| C(1)-Lu(1)-Si(1) | 38.0(3) | C(20)-C(21)-C(22) | 126(3) |
| C(25)-Lu(1)-Si(1) | 114.1(3) | C(21)-C(22)-C(17) | 116(2) |
| C(26)-Lu(1)-Si(1) | 144.8(5) | C(24)-C(23)-C(27) | 110.2(15) |
| C(24)-Lu(1)-Si(1) | 103.7(4) | C(24)-C(23)-C(28) | 124.2(16) |
| C(23)-Lu(1)-Si(1) | 122.2(4) | C(27)-C(23)-C(28) | 125.5(16) |
| C(27)-Lu(1)-Si(1) | 152.6(3) | C(24)-C(23)-Lu(1) | 74.6(10) |
| N(2)-Lu(1)-Ir(1) | 36.2(3) | C(27)-C(23)-Lu(1) | 75.3(9) |
| N(1)-Lu(1)-Ir(1) | 100.5(4) | C(28)-C(23)-Lu(1) | 119.2(10) |
| N(3)-Lu(1)-Ir(1) | 131.4(4) | C(23)-C(24)-C(25) | 107.3(14) |
| C(1)-Lu(1)-Ir(1) | 43.1(3) | C(23)-C(24)-C(29) | 128.0(15) |
| C(25)-Lu(1)-Ir(1) | 94.4(3) | C(25)-C(24)-C(29) | 124.7(15) |
| C(26)-Lu(1)-Ir(1) | 99.0(4) | C(23)-C(24)-Lu(1) | 75.3(10) |
| C(24)-Lu(1)-Ir(1) | 120.0(3) | C(25)-C(24)-Lu(1) | 73.6(9) |
| C(23)-Lu(1)-Ir(1) | 145.0(3) | C(29)-C(24)-Lu(1) | 117.2(10) |
| C(27)-Lu(1)-Ir(1) | 128.1(4) | C(26)-C(25)-C(24) | 107.6(14) |
| Si(1)-Lu(1)-Ir(1) | 70.22(11) | C(26)-C(25)-C(30) | 124.3(15) |
| C(4)-N(1)-Si(1) | 123.0(11) | C(24)-C(25)-C(30) | 127.7(15) |
| C(4)-N(1)-Lu(1) | 137.2(11) | C(26)-C(25)-Lu(1) | 75.0(8) |
| Si(1)-N(1)-Lu(1) | 99.6(5) | C(24)-C(25)-Lu(1) | 74.9(8) |
| C(15)-N(2)-Ir(1) | 123.5(10) | C(30)-C(25)-Lu(1) | 122.0(10) |
| C(15)-N(2)-Lu(1) | 134.4(10) | C(27)-C(26)-C(25) | 107.6(14) |
| Ir(1)-N(2)-Lu(1) | 100.5(5) | C(27)-C(26)-C(31) | 128.0(18) |
| C(16)-N(3)-Lu(1) | 174.1(16) | C(25)-C(26)-C(31) | 124.0(18) |
| N(1)-Si(1)-C(3) | 112.5(7) | C(27)-C(26)-Lu(1) | 75.5(8) |
| N(1)-Si(1)-C(1) | 102.5(6) | C(25)-C(26)-Lu(1) | 73.7(8) |
| C(3)-Si(1)-C(1) | 109.0(7) | C(31)-C(26)-Lu(1) | 122.0(11) |
| N(1)-Si(1)-C(2) | 116.1(7) | C(23)-C(27)-C(26) | 107.4(14) |
| C(3)-Si(1)-C(2) | 107.0(7) | C(23)-C(27)-C(32) | 125.5(17) |
| C(1)-Si(1)-C(2) | 109.5(7) | C(26)-C(27)-C(32) | 126.6(16) |
| N(1)-Si(1)-Lu(1) | 45.6(4) | C(23)-C(27)-Lu(1) | 74.1(9) |
| C(3)-Si(1)-Lu(1) | 128.1(5) | C(26)-C(27)-Lu(1) | 73.7(9) |
| C(1)-Si(1)-Lu(1) | 57.2(5) | C(32)-C(27)-Lu(1) | 124.5(10) |
| C(2)-Si(1)-Lu(1) | 124.9(5) | C(34)-C(33)-C(37) | 104.1(13) |
| Si(1)-C(1)-Ir(1) | 123.1(7) | C(34)-C(33)-C(38) | 127.9(14) |
| Si(1)-C(1)-Lu(1) | 84.8(5) | C(37)-C(33)-C(38) | 128.0(14) |
| Ir(1)-C(1)-Lu(1) | 83.2(5) | C(34)-C(33)-Ir(1) | 67.8(8) |
| C(5)-C(4)-N(1) | 119(2) | C(37)-C(33)-Ir(1) | 67.7(8) |
| C(5)-C(4)-C(6) | 124.8(19) | C(38)-C(33)-Ir(1) | 127.5(11) |
| N(1)-C(4)-C(6) | 115.9(16) | C(35)-C(34)-C(33) | 110.3(13) |
| C(7)-C(6)-C(11) | 122(2) | C(35)-C(34)-C(39) | 126.3(15) |
| C(7)-C(6)-C(4) | 122.7(19) | C(33)-C(34)-C(39) | 122.3(14) |
| C(11)-C(6)-C(4) | 115(2) | C(35)-C(34)-Ir(1) | 74.1(8) |
| C(6)-C(7)-C(8) | 120(2) | C(33)-C(34)-Ir(1) | 74.8(8) |

| | |
|---|---|
| C(39)-C(34)-Ir(1) | 127.9(9) |
| C(34)-C(35)-C(36) | 107.6(14) |
| C(34)-C(35)-C(40) | 125.6(14) |
| C(36)-C(35)-C(40) | 125.9(13) |
| C(34)-C(35)-Ir(1) | 69.6(8) |
| C(36)-C(35)-Ir(1) | 67.4(8) |
| C(40)-C(35)-Ir(1) | 136.6(11) |
| C(37)-C(36)-C(35) | 109.5(13) |
| C(37)-C(36)-C(41) | 123.1(14) |
| C(35)-C(36)-C(41) | 126.0(14) |
| C(37)-C(36)-Ir(1) | 73.4(9) |
| C(35)-C(36)-Ir(1) | 75.2(8) |
| C(41)-C(36)-Ir(1) | 128.6(10) |
| C(36)-C(37)-C(42) | 130.3(14) |
| C(36)-C(37)-C(33) | 107.7(14) |
| C(42)-C(37)-C(33) | 121.3(14) |
| C(36)-C(37)-Ir(1) | 69.3(9) |
| C(42)-C(37)-Ir(1) | 129.5(11) |
| C(33)-C(37)-Ir(1) | 73.8(8) |
| C(46)-C(45)-C(47) | 123.8(19) |
| C(45)-C(46)-C(47)#1 | 118.9(19) |
| C(46)#1-C(47)-C(45) | 117.2(18) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1

**Table S14.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 27(1) | 33(1) | 32(1) | -1(1) | 5(1) | 1(1) |
| Lu(1) | 31(1) | 35(1) | 32(1) | 1(1) | 6(1) | -1(1) |
| N(1) | 23(7) | 44(10) | 78(11) | 0(8) | 2(7) | 10(6) |
| N(2) | 21(7) | 42(8) | 51(9) | -27(7) | 1(6) | 9(6) |
| N(3) | 52(10) | 37(10) | 83(13) | 1(9) | 6(9) | -19(8) |
| Si(1) | 38(3) | 51(3) | 51(3) | -4(3) | 17(2) | -9(2) |
| C(1) | 20(8) | 40(10) | 21(9) | -1(7) | 10(7) | 1(7) |
| C(2) | 39(9) | 47(11) | 29(10) | 10(8) | 2(7) | -3(8) |
| C(3) | 80(13) | 59(12) | 40(12) | -14(9) | 33(10) | -19(11) |
| C(4) | 43(11) | 82(15) | 64(13) | 22(13) | -14(9) | -33(12) |
| C(5) | 34(12) | 140(20) | 140(20) | -35(18) | 20(14) | -4(13) |
| C(6) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(7) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(8) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(9) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(10) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(11) | 82(7) | 59(7) | 113(8) | 10(5) | 39(7) | 6(5) |
| C(12) | 54(11) | 33(10) | 35(11) | 0(8) | 5(9) | -2(8) |
| C(13) | 88(15) | 28(10) | 70(15) | -9(9) | 39(12) | -25(10) |
| C(14) | 96(16) | 16(9) | 64(14) | -6(9) | -9(12) | -6(10) |
| C(15) | 55(12) | 52(12) | 30(11) | -16(9) | 10(9) | 0(10) |
| C(16) | 43(12) | 57(14) | 54(13) | 25(11) | 5(10) | -14(10) |
| C(17) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(18) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(19) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(20) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(21) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(22) | 62(6) | 70(7) | 155(11) | 30(8) | -5(7) | 7(5) |
| C(23) | 39(10) | 52(12) | 48(12) | -8(9) | -2(9) | -3(9) |
| C(24) | 30(9) | 41(11) | 34(10) | -4(8) | -3(7) | 1(8) |
| C(25) | 33(9) | 50(11) | 15(9) | -6(8) | 4(7) | -3(8) |
| C(26) | 50(10) | 66(12) | 39(11) | -11(11) | 24(8) | -27(11) |
| C(27) | 70(12) | 30(11) | 25(9) | -11(7) | 12(8) | -5(9) |
| C(28) | 58(11) | 59(13) | 37(11) | -17(9) | -9(9) | 3(9) |
| C(29) | 51(11) | 42(11) | 58(13) | -18(9) | 28(9) | -26(9) |
| C(30) | 50(11) | 97(16) | 41(12) | -17(11) | 6(9) | 44(11) |
| C(31) | 56(11) | 150(20) | 68(15) | -23(15) | 12(10) | -43(15) |
| C(32) | 104(16) | 55(13) | 34(12) | -3(10) | 12(11) | -16(12) |
| C(33) | 36(4) | 46(5) | 21(4) | -2(4) | -7(3) | 9(4) |
| C(34) | 36(4) | 46(5) | 21(4) | -2(4) | -7(3) | 9(4) |
| C(35) | 36(4) | 46(5) | 21(4) | -2(4) | -7(3) | 9(4) |
| C(36) | 36(4) | 46(5) | 21(4) | -2(4) | -7(3) | 9(4) |
| C(37) | 36(4) | 46(5) | 21(4) | -2(4) | -7(3) | 9(4) |
| C(38) | 64(12) | 49(12) | 44(12) | 11(9) | -5(9) | -3(10) |
| C(39) | 81(12) | 55(12) | 20(9) | -1(9) | -11(8) | 16(11) |
| C(40) | 71(14) | 67(15) | 50(13) | -3(10) | 2(11) | 7(11) |
| C(41) | 30(9) | 73(13) | 69(13) | -24(12) | 21(8) | -29(10) |
| C(42) | 49(11) | 62(13) | 40(11) | 12(9) | 7(9) | 11(9) |
| C(45) | 57(14) | 63(16) | 110(20) | -27(14) | 9(14) | -3(12) |
| C(46) | 64(14) | 61(15) | 90(18) | 24(13) | 1(13) | -1(12) |
| C(47) | 52(13) | 46(13) | 69(15) | -3(11) | 0(11) | 0(10) |

**Table S15.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **4**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 1169 | 2230 | 4546 | 58 |
| H(2B) | 1178 | 673 | 4833 | 58 |
| H(2C) | 873 | 1387 | 4647 | 58 |
| H(3A) | 728 | -1065 | 3689 | 89 |
| H(3B) | 1024 | -1693 | 3995 | 89 |
| H(3C) | 976 | -1597 | 3188 | 89 |
| H(5A) | 557 | 685 | 2258 | 127 |
| H(5B) | 287 | 1671 | 2511 | 127 |
| H(7) | 967 | 3967 | 3670 | 102 |
| H(8) | 807 | 5861 | 4324 | 102 |
| H(9) | 318 | 6293 | 4395 | 102 |
| H(10) | -11 | 4890 | 3939 | 102 |
| H(11) | 142 | 3112 | 3166 | 102 |
| H(12A) | 1699 | 6469 | 3919 | 61 |
| H(12B) | 1780 | 4960 | 4206 | 61 |
| H(12C) | 1451 | 5323 | 4006 | 61 |
| H(13A) | 2045 | 4904 | 2505 | 92 |
| H(13B) | 2142 | 4661 | 3281 | 92 |
| H(13C) | 2062 | 6191 | 3021 | 92 |
| H(14A) | 1541 | 6786 | 2787 | 88 |
| H(14B) | 1306 | 5562 | 2814 | 88 |
| H(14C) | 1548 | 5564 | 2235 | 88 |
| H(18) | 572 | 6427 | 2681 | 115 |
| H(19) | 260 | 8255 | 2351 | 115 |
| H(20) | 177 | 8677 | 1173 | 115 |
| H(21) | 420 | 7513 | 425 | 115 |
| H(22) | 693 | 5557 | 689 | 115 |
| H(28A) | 872 | 646 | 807 | 77 |
| H(28B) | 941 | 2124 | 472 | 77 |
| H(28C) | 822 | 2041 | 1234 | 77 |
| H(29A) | 1017 | -878 | 1632 | 75 |
| H(29B) | 1306 | -1411 | 2009 | 75 |
| H(29C) | 1265 | -1646 | 1207 | 75 |
| H(30A) | 2016 | -633 | 1491 | 94 |
| H(30B) | 1806 | -1130 | 2088 | 94 |
| H(30C) | 2021 | 158 | 2207 | 94 |
| H(31A) | 2074 | 2879 | 1895 | 139 |
| H(31B) | 2000 | 3644 | 1190 | 139 |
| H(31C) | 2152 | 2147 | 1188 | 139 |
| H(32A) | 1504 | 4659 | 1020 | 96 |
| H(32B) | 1208 | 4090 | 687 | 96 |
| H(32C) | 1510 | 3850 | 308 | 96 |
| H(38A) | 1925 | -941 | 5180 | 78 |
| H(38B) | 1720 | -1095 | 4521 | 78 |
| H(38C) | 1637 | -20 | 5110 | 78 |
| H(39A) | 1967 | 2610 | 5700 | 79 |
| H(39B) | 1656 | 2206 | 5388 | 79 |
| H(39C) | 1795 | 3694 | 5228 | 79 |
| H(40A) | 2465 | 4007 | 4848 | 94 |
| H(40B) | 2187 | 4827 | 4566 | 94 |
| H(40C) | 2446 | 4444 | 4063 | 94 |
| H(41A) | 2697 | 1677 | 3452 | 86 |
| H(41B) | 2535 | 3043 | 3178 | 86 |
| H(41C) | 2464 | 1564 | 2842 | 86 |
| H(42A) | 2183 | -773 | 3110 | 76 |

| | | | | |
|---|---|---|---|---|
| H(42B) | 2079 | -1520 | 3794 | 76 |
| H(42C) | 2413 | -1090 | 3708 | 76 |
| H(45) | 442 | 8993 | 4793 | 93 |
| H(46) | 172 | 8176 | 5687 | 86 |
| H(47) | 296 | 10886 | 4128 | 67 |

**Figure S4.** ORTEP drawing of [($C_5Me_5$)Ir($\mu$-N$^t$Bu)($\mu$-$CH_2SiMe_2NC(Ph)CHC(Ph)NH$-)Lu($C_5Me_5$)] (**5**).

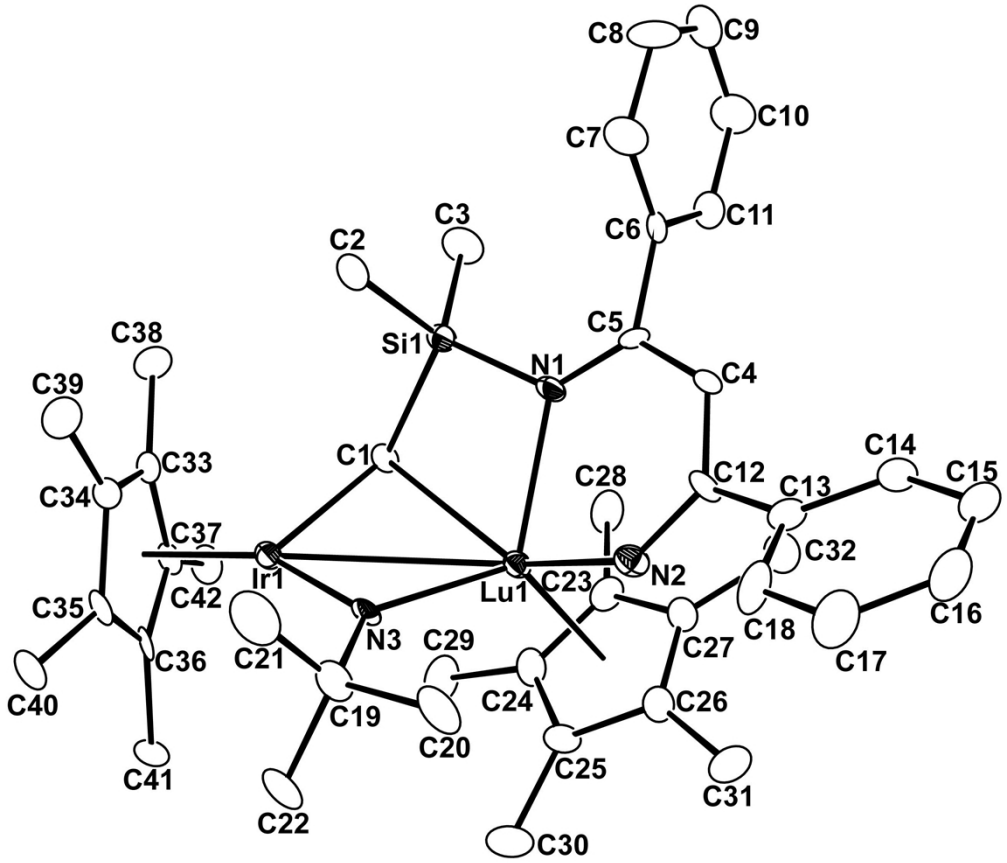

**Table S16.** Crystal data and structure refinement for **5**.

| | | |
|---|---|---|
| Identification code | 16047ts | |
| Empirical formula | C42 H59 Ir Lu N3 Si | |
| Formula weight | 1001.18 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 12.688(7) Å | α= 90°. |
| | b = 15.745(9) Å | β= 95.867(9)°. |
| | c = 20.071(11) Å | γ = 90°. |
| Volume | 3989(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.667 $Mg/m^3$ | |
| Absorption coefficient | 5.856 $mm^{-1}$ | |
| F(000) | 1976 | |
| Crystal size | 0.40 x 0.05 x 0.05 $mm^3$ | |
| Theta range for data collection | 1.65 to 27.50°. | |
| Index ranges | -11<=h<=16, -18<=k<=20, -26<=l<=22 | |
| Reflections collected | 24414 | |
| Independent reflections | 8868 [R(int) = 0.0938] | |
| Completeness to theta = 27.50° | 96.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7584 and 0.2029 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8868 / 0 / 451 | |
| Goodness-of-fit on $F^2$ | 0.963 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0424, wR2 = 0.0698 | |
| R indices (all data) | R1 = 0.1017, wR2 = 0.0824 | |
| Largest diff. peak and hole | 2.441 and -1.567 $e.Å^{-3}$ | |

**Table S17.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 5547(1) | 5812(1) | 2187(1) | 22(1) |
| Lu(1) | 3547(1) | 6200(1) | 2983(1) | 21(1) |
| N(1) | 2232(5) | 5881(4) | 2166(3) | 25(2) |
| N(2) | 2481(6) | 5327(4) | 3527(4) | 28(2) |
| N(3) | 4935(5) | 5366(4) | 2949(4) | 22(2) |
| Si(1) | 2867(2) | 6008(2) | 1458(1) | 25(1) |
| C(1) | 4119(6) | 6527(5) | 1829(4) | 21(2) |
| C(2) | 3107(7) | 4970(6) | 1078(5) | 40(3) |
| C(3) | 2213(7) | 6695(6) | 778(5) | 45(3) |
| C(4) | 882(7) | 5276(5) | 2797(5) | 21(2) |
| C(5) | 1241(7) | 5605(5) | 2228(4) | 22(2) |
| C(6) | 423(6) | 5699(6) | 1644(5) | 26(2) |
| C(7) | 136(8) | 5018(6) | 1219(5) | 44(3) |
| C(8) | -671(10) | 5145(9) | 693(6) | 69(4) |
| C(9) | -1137(9) | 5921(10) | 573(6) | 70(4) |
| C(10) | -868(9) | 6586(8) | 987(6) | 63(4) |
| C(11) | -92(8) | 6474(7) | 1507(5) | 45(3) |
| C(12) | 1471(6) | 5095(5) | 3403(5) | 23(2) |
| C(13) | 964(8) | 4591(5) | 3914(5) | 28(2) |
| C(14) | -79(8) | 4692(6) | 4018(5) | 35(2) |
| C(15) | -535(8) | 4249(7) | 4488(5) | 43(3) |
| C(16) | 51(9) | 3665(6) | 4871(5) | 46(3) |
| C(17) | 1095(10) | 3544(6) | 4790(6) | 52(3) |
| C(18) | 1559(8) | 4003(6) | 4312(5) | 41(3) |
| C(19) | 5421(8) | 4688(6) | 3385(5) | 40(3) |
| C(20) | 4686(8) | 4472(7) | 3913(5) | 55(3) |
| C(21) | 5554(8) | 3894(6) | 2984(6) | 53(3) |
| C(22) | 6498(7) | 5013(6) | 3740(5) | 47(3) |
| C(23) | 3160(8) | 7832(5) | 3103(5) | 31(2) |
| C(24) | 4246(7) | 7707(5) | 3307(5) | 32(2) |
| C(25) | 4318(8) | 7255(6) | 3922(5) | 40(3) |
| C(26) | 3268(8) | 7080(6) | 4072(5) | 33(2) |
| C(27) | 2579(7) | 7435(5) | 3564(5) | 29(2) |
| C(28) | 2711(8) | 8323(6) | 2497(5) | 42(3) |
| C(29) | 5182(8) | 8041(5) | 2998(6) | 46(3) |
| C(30) | 5329(8) | 7077(7) | 4375(5) | 55(3) |
| C(31) | 2961(8) | 6685(7) | 4709(5) | 52(3) |
| C(32) | 1368(7) | 7433(6) | 3537(6) | 46(3) |
| C(33) | 6142(7) | 5992(6) | 1198(5) | 30(2) |
| C(34) | 6443(7) | 5170(6) | 1450(5) | 29(2) |
| C(35) | 7149(6) | 5288(5) | 2059(5) | 26(2) |
| C(36) | 7200(6) | 6165(6) | 2192(5) | 28(2) |
| C(37) | 6626(6) | 6615(5) | 1646(5) | 25(2) |
| C(38) | 5545(7) | 6156(6) | 531(5) | 40(3) |
| C(39) | 6208(8) | 4348(6) | 1111(5) | 52(3) |
| C(40) | 7883(7) | 4611(6) | 2359(5) | 42(3) |
| C(41) | 7889(7) | 6608(6) | 2751(5) | 42(3) |
| C(42) | 6557(7) | 7560(5) | 1561(5) | 35(3) |

**Table S18.** Bond lengths [Å] and angles [°] for **5**.

| | |
|---|---|
| Ir(1)-N(3) | 1.919(7) |
| Ir(1)-C(36) | 2.169(8) |
| Ir(1)-C(1) | 2.191(8) |
| Ir(1)-C(34) | 2.202(9) |
| Ir(1)-C(33) | 2.213(9) |
| Ir(1)-C(37) | 2.226(8) |
| Ir(1)-C(35) | 2.233(8) |
| Ir(1)-Lu(1) | 3.1934(14) |
| Lu(1)-N(3) | 2.204(7) |
| Lu(1)-N(1) | 2.272(6) |
| Lu(1)-N(2) | 2.283(7) |
| Lu(1)-C(1) | 2.549(9) |
| Lu(1)-C(24) | 2.592(8) |
| Lu(1)-C(25) | 2.625(9) |
| Lu(1)-C(23) | 2.631(9) |
| Lu(1)-C(27) | 2.634(9) |
| Lu(1)-C(26) | 2.641(10) |
| Lu(1)-Si(1) | 3.108(3) |
| N(1)-C(5) | 1.348(10) |
| N(1)-Si(1) | 1.715(7) |
| N(2)-C(12) | 1.332(10) |
| N(3)-C(19) | 1.475(10) |
| Si(1)-C(2) | 1.842(9) |
| Si(1)-C(3) | 1.869(9) |
| Si(1)-C(1) | 1.872(8) |
| C(4)-C(5) | 1.373(12) |
| C(4)-C(12) | 1.389(11) |
| C(5)-C(6) | 1.492(11) |
| C(6)-C(7) | 1.394(12) |
| C(6)-C(11) | 1.398(12) |
| C(7)-C(8) | 1.408(14) |
| C(8)-C(9) | 1.367(16) |
| C(9)-C(10) | 1.359(15) |
| C(10)-C(11) | 1.371(13) |
| C(12)-C(13) | 1.493(12) |
| C(13)-C(14) | 1.370(12) |
| C(13)-C(18) | 1.394(12) |
| C(14)-C(15) | 1.351(12) |
| C(15)-C(16) | 1.369(14) |
| C(16)-C(17) | 1.365(13) |
| C(17)-C(18) | 1.380(13) |
| C(19)-C(21) | 1.506(13) |
| C(19)-C(20) | 1.520(13) |
| C(19)-C(22) | 1.561(13) |
| C(23)-C(27) | 1.388(12) |
| C(23)-C(24) | 1.410(12) |
| C(23)-C(28) | 1.503(12) |
| C(24)-C(25) | 1.420(13) |
| C(24)-C(29) | 1.490(12) |
| C(25)-C(26) | 1.422(12) |
| C(25)-C(30) | 1.521(12) |
| C(26)-C(27) | 1.391(12) |
| C(26)-C(31) | 1.509(13) |
| C(27)-C(32) | 1.532(12) |
| C(33)-C(34) | 1.427(12) |
| C(33)-C(37) | 1.428(12) |
| C(33)-C(38) | 1.492(12) |
| C(34)-C(35) | 1.452(12) |
| C(34)-C(39) | 1.476(12) |
| C(35)-C(36) | 1.407(11) |
| C(35)-C(40) | 1.500(11) |
| C(36)-C(37) | 1.438(11) |
| C(36)-C(41) | 1.521(11) |
| C(37)-C(42) | 1.500(11) |
| | |
| N(3)-Ir(1)-C(36) | 124.1(3) |
| N(3)-Ir(1)-C(1) | 93.5(3) |
| C(36)-Ir(1)-C(1) | 129.6(3) |
| N(3)-Ir(1)-C(34) | 130.3(3) |
| C(36)-Ir(1)-C(34) | 63.6(3) |
| C(1)-Ir(1)-C(34) | 118.8(3) |
| N(3)-Ir(1)-C(33) | 164.9(3) |
| C(36)-Ir(1)-C(33) | 63.4(3) |
| C(1)-Ir(1)-C(33) | 89.3(3) |
| C(34)-Ir(1)-C(33) | 37.7(3) |
| N(3)-Ir(1)-C(37) | 156.3(3) |
| C(36)-Ir(1)-C(37) | 38.2(3) |
| C(1)-Ir(1)-C(37) | 94.5(3) |
| C(34)-Ir(1)-C(37) | 63.1(3) |
| C(33)-Ir(1)-C(37) | 37.5(3) |
| N(3)-Ir(1)-C(35) | 113.8(3) |
| C(36)-Ir(1)-C(35) | 37.2(3) |
| C(1)-Ir(1)-C(35) | 152.2(3) |
| C(34)-Ir(1)-C(35) | 38.2(3) |
| C(33)-Ir(1)-C(35) | 63.0(3) |
| C(37)-Ir(1)-C(35) | 62.7(3) |
| N(3)-Ir(1)-Lu(1) | 42.60(19) |
| C(36)-Ir(1)-Lu(1) | 140.0(2) |
| C(1)-Ir(1)-Lu(1) | 52.6(2) |
| C(34)-Ir(1)-Lu(1) | 156.3(2) |
| C(33)-Ir(1)-Lu(1) | 141.8(2) |
| C(37)-Ir(1)-Lu(1) | 134.0(2) |
| C(35)-Ir(1)-Lu(1) | 155.2(2) |
| N(3)-Lu(1)-N(1) | 112.1(3) |
| N(3)-Lu(1)-N(2) | 99.8(2) |
| N(1)-Lu(1)-N(2) | 77.6(3) |
| N(3)-Lu(1)-C(1) | 77.9(3) |
| N(1)-Lu(1)-C(1) | 69.2(3) |
| N(2)-Lu(1)-C(1) | 142.5(3) |
| N(3)-Lu(1)-C(24) | 107.4(3) |
| N(1)-Lu(1)-C(24) | 126.2(3) |
| N(2)-Lu(1)-C(24) | 129.5(3) |
| C(1)-Lu(1)-C(24) | 85.5(3) |
| N(3)-Lu(1)-C(25) | 99.1(3) |
| N(1)-Lu(1)-C(25) | 148.2(3) |
| N(2)-Lu(1)-C(25) | 103.5(3) |
| C(1)-Lu(1)-C(25) | 113.9(3) |
| C(24)-Lu(1)-C(25) | 31.6(3) |
| N(3)-Lu(1)-C(23) | 137.9(3) |
| N(1)-Lu(1)-C(23) | 98.8(3) |
| N(2)-Lu(1)-C(23) | 114.8(3) |
| C(1)-Lu(1)-C(23) | 87.7(3) |
| C(24)-Lu(1)-C(23) | 31.3(3) |
| C(25)-Lu(1)-C(23) | 51.4(3) |
| N(3)-Lu(1)-C(27) | 149.7(3) |
| N(1)-Lu(1)-C(27) | 98.2(3) |
| N(2)-Lu(1)-C(27) | 84.7(3) |
| C(1)-Lu(1)-C(27) | 116.3(3) |

| | | | |
|---|---|---|---|
| C(24)-Lu(1)-C(27) | 51.4(3) | C(9)-C(10)-C(11) | 118.8(11) |
| C(25)-Lu(1)-C(27) | 51.1(3) | C(10)-C(11)-C(6) | 123.2(11) |
| C(23)-Lu(1)-C(27) | 30.6(3) | N(2)-C(12)-C(4) | 121.9(8) |
| N(3)-Lu(1)-C(26) | 120.8(3) | N(2)-C(12)-C(13) | 119.4(8) |
| N(1)-Lu(1)-C(26) | 124.2(3) | C(4)-C(12)-C(13) | 118.7(8) |
| N(2)-Lu(1)-C(26) | 77.5(3) | C(14)-C(13)-C(18) | 117.7(9) |
| C(1)-Lu(1)-C(26) | 136.1(3) | C(14)-C(13)-C(12) | 122.2(8) |
| C(24)-Lu(1)-C(26) | 52.0(3) | C(18)-C(13)-C(12) | 120.0(9) |
| C(25)-Lu(1)-C(26) | 31.3(3) | C(15)-C(14)-C(13) | 122.4(10) |
| C(23)-Lu(1)-C(26) | 51.0(3) | C(14)-C(15)-C(16) | 119.5(11) |
| C(27)-Lu(1)-C(26) | 30.6(3) | C(17)-C(16)-C(15) | 120.4(10) |
| N(3)-Lu(1)-Si(1) | 93.10(19) | C(16)-C(17)-C(18) | 119.9(11) |
| N(1)-Lu(1)-Si(1) | 32.73(18) | C(17)-C(18)-C(13) | 120.1(10) |
| N(2)-Lu(1)-Si(1) | 107.08(19) | N(3)-C(19)-C(21) | 110.3(9) |
| C(1)-Lu(1)-Si(1) | 37.00(18) | N(3)-C(19)-C(20) | 109.0(8) |
| C(24)-Lu(1)-Si(1) | 112.9(2) | C(21)-C(19)-C(20) | 107.3(9) |
| C(25)-Lu(1)-Si(1) | 144.5(2) | N(3)-C(19)-C(22) | 109.1(8) |
| C(23)-Lu(1)-Si(1) | 98.6(2) | C(21)-C(19)-C(22) | 112.1(8) |
| C(27)-Lu(1)-Si(1) | 114.4(2) | C(20)-C(19)-C(22) | 109.0(9) |
| C(26)-Lu(1)-Si(1) | 144.9(2) | C(27)-C(23)-C(24) | 108.3(9) |
| N(3)-Lu(1)-Ir(1) | 36.10(18) | C(27)-C(23)-C(28) | 125.9(9) |
| N(1)-Lu(1)-Ir(1) | 99.15(18) | C(24)-C(23)-C(28) | 125.8(9) |
| N(2)-Lu(1)-Ir(1) | 131.58(18) | C(27)-C(23)-Lu(1) | 74.8(5) |
| C(1)-Lu(1)-Ir(1) | 43.05(18) | C(24)-C(23)-Lu(1) | 72.8(5) |
| C(24)-Lu(1)-Ir(1) | 91.8(2) | C(28)-C(23)-Lu(1) | 119.1(6) |
| C(25)-Lu(1)-Ir(1) | 102.9(2) | C(23)-C(24)-C(25) | 107.2(9) |
| C(23)-Lu(1)-Ir(1) | 113.5(2) | C(23)-C(24)-C(29) | 128.8(10) |
| C(27)-Lu(1)-Ir(1) | 142.5(2) | C(25)-C(24)-C(29) | 123.7(9) |
| C(26)-Lu(1)-Ir(1) | 134.0(2) | C(23)-C(24)-Lu(1) | 75.9(5) |
| Si(1)-Lu(1)-Ir(1) | 69.12(6) | C(25)-C(24)-Lu(1) | 75.5(5) |
| C(5)-N(1)-Si(1) | 129.5(6) | C(29)-C(24)-Lu(1) | 119.1(6) |
| C(5)-N(1)-Lu(1) | 128.9(6) | C(24)-C(25)-C(26) | 107.6(9) |
| Si(1)-N(1)-Lu(1) | 101.5(3) | C(24)-C(25)-C(30) | 126.0(9) |
| C(12)-N(2)-Lu(1) | 133.0(6) | C(26)-C(25)-C(30) | 126.1(10) |
| C(19)-N(3)-Ir(1) | 124.0(6) | C(24)-C(25)-Lu(1) | 72.9(5) |
| C(19)-N(3)-Lu(1) | 134.5(6) | C(26)-C(25)-Lu(1) | 74.9(5) |
| Ir(1)-N(3)-Lu(1) | 101.3(3) | C(30)-C(25)-Lu(1) | 122.8(7) |
| N(1)-Si(1)-C(2) | 110.6(4) | C(27)-C(26)-C(25) | 107.4(9) |
| N(1)-Si(1)-C(3) | 117.5(4) | C(27)-C(26)-C(31) | 126.1(9) |
| C(2)-Si(1)-C(3) | 106.9(5) | C(25)-C(26)-C(31) | 126.0(9) |
| N(1)-Si(1)-C(1) | 100.0(4) | C(27)-C(26)-Lu(1) | 74.4(6) |
| C(2)-Si(1)-C(1) | 112.5(4) | C(25)-C(26)-Lu(1) | 73.7(6) |
| C(3)-Si(1)-C(1) | 109.5(4) | C(31)-C(26)-Lu(1) | 123.6(6) |
| N(1)-Si(1)-Lu(1) | 45.8(2) | C(23)-C(27)-C(26) | 109.4(9) |
| C(2)-Si(1)-Lu(1) | 116.9(3) | C(23)-C(27)-C(32) | 125.2(9) |
| C(3)-Si(1)-Lu(1) | 136.1(3) | C(26)-C(27)-C(32) | 125.3(9) |
| C(1)-Si(1)-Lu(1) | 55.1(3) | C(23)-C(27)-Lu(1) | 74.6(5) |
| Si(1)-C(1)-Ir(1) | 123.1(4) | C(26)-C(27)-Lu(1) | 75.0(5) |
| Si(1)-C(1)-Lu(1) | 87.9(3) | C(32)-C(27)-Lu(1) | 119.6(6) |
| Ir(1)-C(1)-Lu(1) | 84.4(3) | C(34)-C(33)-C(37) | 108.5(8) |
| C(5)-C(4)-C(12) | 127.6(8) | C(34)-C(33)-C(38) | 124.6(8) |
| N(1)-C(5)-C(4) | 126.2(8) | C(37)-C(33)-C(38) | 126.4(8) |
| N(1)-C(5)-C(6) | 118.4(8) | C(34)-C(33)-Ir(1) | 70.7(5) |
| C(4)-C(5)-C(6) | 115.3(8) | C(37)-C(33)-Ir(1) | 71.7(5) |
| C(7)-C(6)-C(11) | 117.6(9) | C(38)-C(33)-Ir(1) | 129.7(6) |
| C(7)-C(6)-C(5) | 121.4(9) | C(33)-C(34)-C(35) | 107.6(8) |
| C(11)-C(6)-C(5) | 121.0(8) | C(33)-C(34)-C(39) | 126.7(9) |
| C(6)-C(7)-C(8) | 118.3(10) | C(35)-C(34)-C(39) | 125.3(8) |
| C(9)-C(8)-C(7) | 121.8(11) | C(33)-C(34)-Ir(1) | 71.6(5) |
| C(10)-C(9)-C(8) | 120.3(12) | C(35)-C(34)-Ir(1) | 72.0(5) |

| | |
|---|---|
| C(39)-C(34)-Ir(1) | 128.1(7) |
| C(36)-C(35)-C(34) | 107.3(8) |
| C(36)-C(35)-C(40) | 127.4(8) |
| C(34)-C(35)-C(40) | 123.5(8) |
| C(36)-C(35)-Ir(1) | 68.9(4) |
| C(34)-C(35)-Ir(1) | 69.7(5) |
| C(40)-C(35)-Ir(1) | 138.7(7) |
| C(35)-C(36)-C(37) | 109.3(8) |
| C(35)-C(36)-C(41) | 127.0(8) |
| C(37)-C(36)-C(41) | 123.0(9) |
| C(35)-C(36)-Ir(1) | 73.8(5) |
| C(37)-C(36)-Ir(1) | 73.1(5) |
| C(41)-C(36)-Ir(1) | 127.1(6) |
| C(33)-C(37)-C(36) | 107.1(8) |
| C(33)-C(37)-C(42) | 126.4(8) |
| C(36)-C(37)-C(42) | 126.5(8) |
| C(33)-C(37)-Ir(1) | 70.8(5) |
| C(36)-C(37)-Ir(1) | 68.8(5) |
| C(42)-C(37)-Ir(1) | 126.0(6) |

Symmetry transformations used to generate equivalent atoms:

**Table S19.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 17(1) | 25(1) | 23(1) | 1(1) | 1(1) | 1(1) |
| Lu(1) | 17(1) | 24(1) | 22(1) | 1(1) | 1(1) | -2(1) |
| N(1) | 16(4) | 36(4) | 20(4) | 4(3) | -4(3) | 2(3) |
| N(2) | 26(5) | 28(4) | 27(5) | 7(3) | -1(4) | -1(3) |
| N(3) | 15(4) | 31(4) | 20(4) | 12(3) | -4(3) | 7(3) |
| Si(1) | 20(1) | 32(2) | 22(2) | 1(1) | 0(1) | -1(1) |
| C(1) | 16(5) | 27(5) | 21(5) | 9(4) | 5(4) | -7(4) |
| C(2) | 21(6) | 48(6) | 52(8) | -16(5) | 3(5) | -2(4) |
| C(3) | 38(7) | 57(7) | 39(7) | 14(5) | -2(5) | -5(5) |
| C(4) | 12(5) | 28(5) | 24(6) | -5(4) | -1(4) | -10(4) |
| C(5) | 26(5) | 28(5) | 11(5) | -4(4) | -4(4) | 3(4) |
| C(6) | 13(5) | 42(6) | 25(6) | -3(5) | 10(4) | -5(4) |
| C(7) | 39(7) | 48(7) | 45(8) | 5(6) | 1(6) | -16(5) |
| C(8) | 60(9) | 112(12) | 35(8) | -18(8) | -3(7) | -51(8) |
| C(9) | 29(7) | 130(14) | 48(9) | -6(9) | -5(6) | 30(8) |
| C(10) | 48(8) | 87(10) | 51(9) | -5(7) | -11(7) | 19(7) |
| C(11) | 31(6) | 72(8) | 33(7) | -2(6) | 5(5) | 12(5) |
| C(12) | 12(5) | 19(5) | 36(6) | 2(4) | -4(4) | 1(3) |
| C(13) | 36(6) | 24(5) | 24(6) | -3(4) | 4(5) | -16(4) |
| C(14) | 35(6) | 41(6) | 28(6) | -2(5) | 2(5) | -14(5) |
| C(15) | 48(7) | 50(7) | 34(7) | -14(6) | 12(5) | -21(6) |
| C(16) | 61(8) | 40(7) | 43(8) | -4(5) | 26(6) | -19(6) |
| C(17) | 69(9) | 34(6) | 56(9) | 2(5) | 22(7) | 6(5) |
| C(18) | 54(7) | 32(6) | 42(7) | 1(5) | 29(6) | 4(5) |
| C(19) | 29(6) | 54(7) | 36(7) | 24(5) | 4(5) | 9(5) |
| C(20) | 27(6) | 87(9) | 51(8) | 46(6) | 3(5) | 13(5) |
| C(21) | 48(7) | 27(6) | 83(10) | 16(6) | 1(6) | 3(5) |
| C(22) | 21(6) | 70(8) | 49(8) | 25(6) | -4(5) | 12(5) |
| C(23) | 42(6) | 24(5) | 27(6) | 4(4) | 9(5) | -3(4) |
| C(24) | 29(6) | 22(5) | 47(7) | -8(5) | 11(5) | -4(4) |
| C(25) | 28(6) | 56(7) | 35(7) | -13(5) | -4(5) | -15(5) |
| C(26) | 29(6) | 32(6) | 38(7) | -6(5) | 7(5) | -4(4) |
| C(27) | 26(6) | 21(5) | 40(7) | -9(4) | 4(5) | 1(4) |
| C(28) | 48(7) | 36(6) | 44(7) | 9(5) | 18(6) | 7(5) |
| C(29) | 54(7) | 24(5) | 64(8) | -13(5) | 28(6) | -16(5) |
| C(30) | 47(8) | 73(9) | 41(8) | -7(6) | -12(6) | -12(6) |
| C(31) | 54(8) | 73(8) | 30(7) | -7(6) | 8(6) | -18(6) |
| C(32) | 40(7) | 41(6) | 57(8) | -16(5) | 6(6) | 7(5) |
| C(33) | 17(5) | 49(7) | 24(6) | 0(4) | 9(4) | 1(4) |
| C(34) | 22(5) | 36(6) | 28(6) | -3(4) | 3(4) | 2(4) |
| C(35) | 9(5) | 26(5) | 42(7) | 0(4) | 4(4) | 3(4) |
| C(36) | 9(4) | 44(6) | 33(6) | 1(5) | 8(4) | 12(4) |
| C(37) | 13(5) | 35(5) | 27(6) | 10(4) | 8(4) | -1(4) |
| C(38) | 45(7) | 50(6) | 25(6) | 1(5) | 4(5) | -2(5) |
| C(39) | 50(8) | 54(8) | 50(8) | -16(6) | 5(6) | 5(5) |
| C(40) | 18(5) | 51(7) | 55(8) | -6(5) | -1(5) | 9(4) |
| C(41) | 19(6) | 67(8) | 37(7) | -15(5) | -7(5) | -8(5) |
| C(42) | 31(6) | 35(6) | 42(7) | 12(5) | 14(5) | -4(4) |

**Table S20.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **5**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 2803 | 5097 | 3892 | 33 |
| H(2A) | 3586 | 4634 | 1389 | 61 |
| H(2B) | 3429 | 5056 | 660 | 61 |
| H(2C) | 2433 | 4668 | 984 | 61 |
| H(3A) | 1558 | 6423 | 583 | 68 |
| H(3B) | 2692 | 6774 | 430 | 68 |
| H(3C) | 2045 | 7248 | 964 | 68 |
| H(7) | 475 | 4483 | 1283 | 53 |
| H(8) | -897 | 4680 | 413 | 83 |
| H(9) | -1652 | 5995 | 200 | 84 |
| H(10) | -1211 | 7120 | 918 | 76 |
| H(11) | 105 | 6945 | 1788 | 54 |
| H(14) | -497 | 5089 | 3749 | 42 |
| H(15) | -1258 | 4342 | 4552 | 52 |
| H(16) | -271 | 3342 | 5195 | 56 |
| H(17) | 1502 | 3145 | 5062 | 62 |
| H(18) | 2285 | 3917 | 4253 | 49 |
| H(20A) | 4625 | 4964 | 4206 | 83 |
| H(20B) | 4975 | 3988 | 4180 | 83 |
| H(20C) | 3984 | 4325 | 3693 | 83 |
| H(21A) | 4858 | 3693 | 2791 | 80 |
| H(21B) | 5895 | 3454 | 3277 | 80 |
| H(21C) | 5997 | 4018 | 2624 | 80 |
| H(22A) | 6928 | 5248 | 3406 | 71 |
| H(22B) | 6878 | 4539 | 3973 | 71 |
| H(22C) | 6364 | 5454 | 4065 | 71 |
| H(28A) | 2131 | 8000 | 2258 | 63 |
| H(28B) | 3267 | 8418 | 2201 | 63 |
| H(28C) | 2443 | 8871 | 2639 | 63 |
| H(29A) | 5562 | 8449 | 3304 | 68 |
| H(29B) | 4944 | 8325 | 2575 | 68 |
| H(29C) | 5655 | 7570 | 2913 | 68 |
| H(30A) | 5933 | 7072 | 4107 | 82 |
| H(30B) | 5272 | 6523 | 4592 | 82 |
| H(30C) | 5434 | 7521 | 4718 | 82 |
| H(31A) | 2812 | 7134 | 5024 | 78 |
| H(31B) | 3543 | 6329 | 4909 | 78 |
| H(31C) | 2326 | 6334 | 4607 | 78 |
| H(32A) | 1115 | 6848 | 3565 | 69 |
| H(32B) | 1065 | 7688 | 3114 | 69 |
| H(32C) | 1150 | 7764 | 3913 | 69 |
| H(38A) | 6029 | 6120 | 181 | 60 |
| H(38B) | 5231 | 6725 | 527 | 60 |
| H(38C) | 4982 | 5732 | 445 | 60 |
| H(39A) | 5526 | 4384 | 837 | 77 |
| H(39B) | 6177 | 3901 | 1448 | 77 |
| H(39C) | 6767 | 4215 | 825 | 77 |
| H(40A) | 8452 | 4519 | 2072 | 62 |
| H(40B) | 7487 | 4081 | 2397 | 62 |
| H(40C) | 8188 | 4790 | 2805 | 62 |
| H(41A) | 8058 | 6211 | 3123 | 62 |
| H(41B) | 7507 | 7097 | 2909 | 62 |
| H(41C) | 8546 | 6802 | 2583 | 62 |
| H(42A) | 6789 | 7838 | 1988 | 53 |
| H(42B) | 5822 | 7721 | 1417 | 53 |

| | | | | |
|---|---|---|---|---|
| H(42C) | 7014 | 7740 | 1221 | 53 |
| H(4) | 180(70) | 5070(50) | 2710(50) | 50 |

**Figure S5.** ORTEP drawing of [($C_5Me_5$)Ir($\mu$-N$^t$Bu)($\mu$-$CH_2SiMe_2C(=CH_2)O$)Lu(NCPh)($C_5Me_5$)] (**6'**)

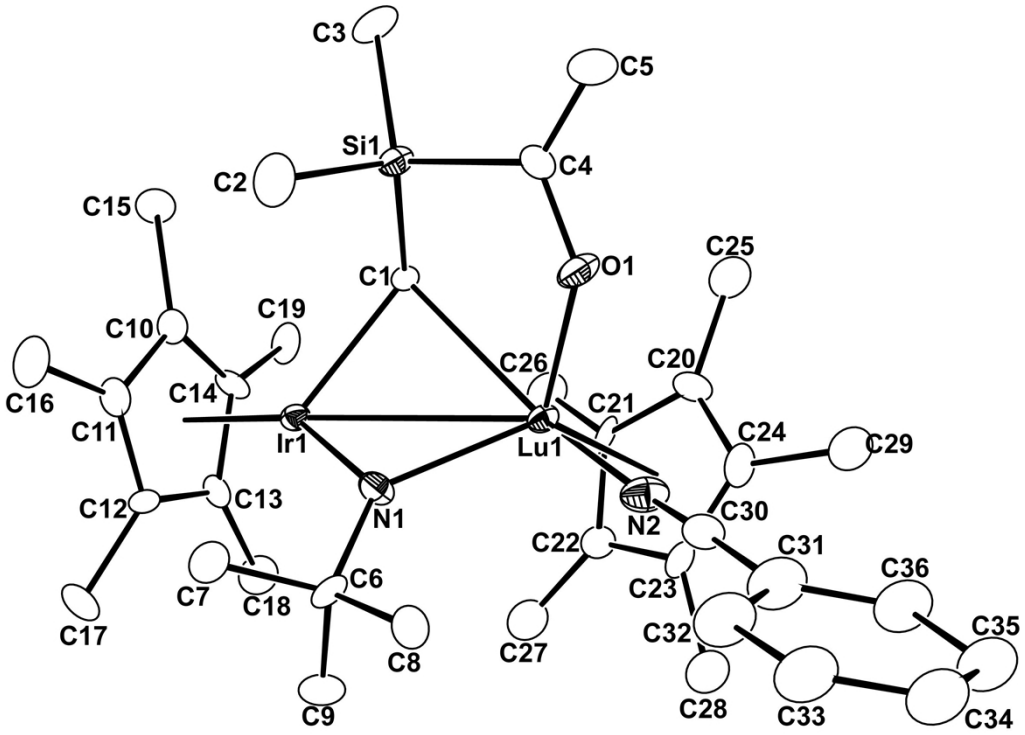

**Table S21.** Crystal data and structure refinement for **6'**.

| | | |
|---|---|---|
| Identification code | 16109ts | |
| Empirical formula | C36 H54 Ir Lu N2 O Si | |
| Formula weight | 926.07 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.431(2) Å | $\alpha$= 85.387(4)°. |
| | b = 10.568(3) Å | $\beta$= 79.968(3)°. |
| | c = 18.813(5) Å | $\gamma$ = 74.367(3)°. |
| Volume | 1776.9(8) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.731 $Mg/m^3$ | |
| Absorption coefficient | 6.565 $mm^{-1}$ | |
| F(000) | 908 | |
| Crystal size | 0.40 x 0.20 x 0.10 $mm^3$ | |
| Theta range for data collection | 2.00 to 26.50°. | |
| Index ranges | -11<=h<=11, -9<=k<=13, -23<=l<=22 | |
| Reflections collected | 10513 | |
| Independent reflections | 7120 [R(int) = 0.0788] | |
| Completeness to theta = 26.50° | 96.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.5597 and 0.1787 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7120 / 0 / 340 | |
| Goodness-of-fit on $F^2$ | 0.924 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0715, wR2 = 0.1669 | |
| R indices (all data) | R1 = 0.0972, wR2 = 0.1743 | |
| Largest diff. peak and hole | 5.223 and -4.148 $e.Å^{-3}$ | |

**Table S22.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **6'**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 3576(1) | 7408(1) | 3409(1) | 22(1) |
| Lu(1) | 3114(1) | 9838(1) | 2262(1) | 23(1) |
| N(1) | 2074(12) | 8374(12) | 2854(6) | 29(3) |
| N(2) | 1307(13) | 10738(14) | 1470(7) | 37(3) |
| O(1) | 4294(11) | 9241(10) | 1253(5) | 37(2) |
| Si(1) | 6043(4) | 7013(4) | 1750(2) | 27(1) |
| C(1) | 5366(14) | 7902(12) | 2619(6) | 20(3) |
| C(2) | 5080(20) | 5702(16) | 1699(8) | 46(4) |
| C(3) | 8113(17) | 6227(16) | 1606(8) | 42(4) |
| C(4) | 5570(15) | 8327(14) | 1031(7) | 29(3) |
| C(5) | 6389(18) | 8338(18) | 393(8) | 48(5) |
| C(6) | 497(15) | 8233(13) | 3012(8) | 31(3) |
| C(7) | 516(17) | 6781(15) | 2980(9) | 40(4) |
| C(8) | -371(16) | 8975(16) | 2433(10) | 45(4) |
| C(9) | -289(16) | 8806(17) | 3740(8) | 43(4) |
| C(10) | 5185(15) | 5735(14) | 3867(8) | 31(3) |
| C(11) | 3808(16) | 5374(14) | 3911(7) | 30(3) |
| C(12) | 2721(15) | 6263(13) | 4366(7) | 28(3) |
| C(13) | 3405(15) | 7167(13) | 4587(6) | 23(3) |
| C(14) | 4966(14) | 6829(15) | 4288(6) | 26(3) |
| C(15) | 6707(16) | 4928(16) | 3487(9) | 42(4) |
| C(16) | 3650(20) | 4216(16) | 3570(9) | 50(5) |
| C(17) | 1269(17) | 6035(17) | 4745(9) | 46(4) |
| C(18) | 2704(19) | 8213(17) | 5117(8) | 42(4) |
| C(19) | 6152(16) | 7390(14) | 4453(9) | 36(4) |
| C(20) | 4414(16) | 11717(15) | 2347(8) | 34(3) |
| C(21) | 4133(16) | 11188(12) | 3057(8) | 30(3) |
| C(22) | 2549(17) | 11546(14) | 3295(7) | 33(3) |
| C(23) | 1875(16) | 12232(13) | 2697(9) | 34(3) |
| C(24) | 2995(18) | 12363(14) | 2140(8) | 34(3) |
| C(25) | 5921(18) | 11623(17) | 1920(10) | 52(2) |
| C(26) | 5259(19) | 10581(17) | 3537(10) | 52(2) |
| C(27) | 1784(19) | 11315(18) | 4027(10) | 52(2) |
| C(28) | 255(18) | 12904(17) | 2767(10) | 52(2) |
| C(29) | 2801(19) | 13179(17) | 1431(10) | 52(2) |
| C(30) | 488(16) | 11222(15) | 1082(8) | 31(3) |
| C(31) | -570(20) | 11790(20) | 608(10) | 61(2) |
| C(32) | -1460(20) | 11100(20) | 407(10) | 61(2) |
| C(33) | -2450(20) | 11670(20) | -65(10) | 61(2) |
| C(34) | -2590(20) | 12940(20) | -270(10) | 61(2) |
| C(35) | -1780(20) | 13700(20) | -55(10) | 61(2) |
| C(36) | -740(20) | 13090(20) | 382(10) | 61(2) |

**Table S23.** Bond lengths [Å] and angles [°] for **6'**.

| | |
|---|---|
| Ir(1)-N(1) | 1.925(11) |
| Ir(1)-C(13) | 2.192(11) |
| Ir(1)-C(1) | 2.194(12) |
| Ir(1)-C(10) | 2.222(13) |
| Ir(1)-C(14) | 2.233(12) |
| Ir(1)-C(12) | 2.240(13) |
| Ir(1)-C(11) | 2.247(14) |
| Ir(1)-Lu(1) | 3.2063(9) |
| Lu(1)-O(1) | 2.077(9) |
| Lu(1)-N(1) | 2.181(11) |
| Lu(1)-N(2) | 2.410(12) |
| Lu(1)-C(21) | 2.604(14) |
| Lu(1)-C(23) | 2.617(14) |
| Lu(1)-C(20) | 2.628(14) |
| Lu(1)-C(24) | 2.634(14) |
| Lu(1)-C(22) | 2.646(13) |
| Lu(1)-C(1) | 2.661(12) |
| N(1)-C(6) | 1.510(17) |
| N(2)-C(30) | 1.146(18) |
| O(1)-C(4) | 1.349(16) |
| Si(1)-C(2) | 1.864(17) |
| Si(1)-C(1) | 1.876(13) |
| Si(1)-C(4) | 1.879(14) |
| Si(1)-C(3) | 1.885(15) |
| C(4)-C(5) | 1.310(19) |
| C(6)-C(8) | 1.516(19) |
| C(6)-C(9) | 1.53(2) |
| C(6)-C(7) | 1.535(19) |
| C(10)-C(14) | 1.40(2) |
| C(10)-C(11) | 1.437(19) |
| C(10)-C(15) | 1.54(2) |
| C(11)-C(12) | 1.404(19) |
| C(11)-C(16) | 1.48(2) |
| C(12)-C(13) | 1.411(19) |
| C(12)-C(17) | 1.501(19) |
| C(13)-C(14) | 1.439(17) |
| C(13)-C(18) | 1.48(2) |
| C(14)-C(19) | 1.486(18) |
| C(20)-C(21) | 1.414(19) |
| C(20)-C(24) | 1.43(2) |
| C(20)-C(25) | 1.49(2) |
| C(21)-C(22) | 1.44(2) |
| C(21)-C(26) | 1.49(2) |
| C(22)-C(23) | 1.44(2) |
| C(22)-C(27) | 1.47(2) |
| C(23)-C(24) | 1.38(2) |
| C(23)-C(28) | 1.49(2) |
| C(24)-C(29) | 1.54(2) |
| C(30)-C(31) | 1.43(2) |
| C(31)-C(32) | 1.37(3) |
| C(31)-C(36) | 1.38(3) |
| C(32)-C(33) | 1.39(2) |
| C(33)-C(34) | 1.34(3) |
| C(34)-C(35) | 1.37(3) |
| C(35)-C(36) | 1.38(2) |
| | |
| N(1)-Ir(1)-C(13) | 128.1(5) |
| N(1)-Ir(1)-C(1) | 92.0(4) |
| C(13)-Ir(1)-C(1) | 129.0(5) |
| N(1)-Ir(1)-C(10) | 160.5(5) |
| C(13)-Ir(1)-C(10) | 61.6(5) |
| C(1)-Ir(1)-C(10) | 91.5(5) |
| N(1)-Ir(1)-C(14) | 161.4(5) |
| C(13)-Ir(1)-C(14) | 38.0(5) |
| C(1)-Ir(1)-C(14) | 94.3(5) |
| C(10)-Ir(1)-C(14) | 36.7(5) |
| N(1)-Ir(1)-C(12) | 114.4(5) |
| C(13)-Ir(1)-C(12) | 37.1(5) |
| C(1)-Ir(1)-C(12) | 152.9(5) |
| C(10)-Ir(1)-C(12) | 61.6(5) |
| C(14)-Ir(1)-C(12) | 62.7(5) |
| N(1)-Ir(1)-C(11) | 127.3(5) |
| C(13)-Ir(1)-C(11) | 61.7(5) |
| C(1)-Ir(1)-C(11) | 121.7(5) |
| C(10)-Ir(1)-C(11) | 37.5(5) |
| C(14)-Ir(1)-C(11) | 62.6(5) |
| C(12)-Ir(1)-C(11) | 36.5(5) |
| N(1)-Ir(1)-Lu(1) | 41.6(3) |
| C(13)-Ir(1)-Lu(1) | 136.0(4) |
| C(1)-Ir(1)-Lu(1) | 55.3(3) |
| C(10)-Ir(1)-Lu(1) | 146.7(4) |
| C(14)-Ir(1)-Lu(1) | 133.2(4) |
| C(12)-Ir(1)-Lu(1) | 151.4(3) |
| C(11)-Ir(1)-Lu(1) | 161.5(4) |
| O(1)-Lu(1)-N(1) | 113.5(4) |
| O(1)-Lu(1)-N(2) | 77.2(4) |
| N(1)-Lu(1)-N(2) | 98.8(4) |
| O(1)-Lu(1)-C(21) | 120.3(4) |
| N(1)-Lu(1)-C(21) | 114.9(4) |
| N(2)-Lu(1)-C(21) | 125.7(4) |
| O(1)-Lu(1)-C(23) | 128.4(4) |
| N(1)-Lu(1)-C(23) | 113.5(4) |
| N(2)-Lu(1)-C(23) | 75.9(5) |
| C(21)-Lu(1)-C(23) | 52.5(4) |
| O(1)-Lu(1)-C(20) | 95.2(4) |
| N(1)-Lu(1)-C(20) | 146.2(4) |
| N(2)-Lu(1)-C(20) | 104.9(5) |
| C(21)-Lu(1)-C(20) | 31.4(4) |
| C(23)-Lu(1)-C(20) | 51.9(4) |
| O(1)-Lu(1)-C(24) | 100.1(4) |
| N(1)-Lu(1)-C(24) | 144.0(5) |
| N(2)-Lu(1)-C(24) | 75.6(5) |
| C(21)-Lu(1)-C(24) | 51.9(4) |
| C(23)-Lu(1)-C(24) | 30.5(5) |
| C(20)-Lu(1)-C(24) | 31.6(5) |
| O(1)-Lu(1)-C(22) | 147.0(4) |
| N(1)-Lu(1)-C(22) | 98.7(4) |
| N(2)-Lu(1)-C(22) | 105.8(5) |
| C(21)-Lu(1)-C(22) | 31.8(4) |
| C(23)-Lu(1)-C(22) | 31.7(4) |
| C(20)-Lu(1)-C(22) | 51.9(4) |
| C(24)-Lu(1)-C(22) | 51.3(4) |
| O(1)-Lu(1)-C(1) | 78.4(4) |
| N(1)-Lu(1)-C(1) | 74.9(4) |
| N(2)-Lu(1)-C(1) | 149.7(4) |
| C(21)-Lu(1)-C(1) | 82.5(4) |
| C(23)-Lu(1)-C(1) | 134.1(4) |
| C(20)-Lu(1)-C(1) | 95.0(4) |

| | |
|---|---|
| C(24)-Lu(1)-C(1) | 126.6(4) |
| C(22)-Lu(1)-C(1) | 104.5(4) |
| O(1)-Lu(1)-Ir(1) | 110.0(3) |
| N(1)-Lu(1)-Ir(1) | 35.9(3) |
| N(2)-Lu(1)-Ir(1) | 134.2(3) |
| C(21)-Lu(1)-Ir(1) | 90.7(3) |
| C(23)-Lu(1)-Ir(1) | 120.4(3) |
| C(20)-Lu(1)-Ir(1) | 118.7(3) |
| C(24)-Lu(1)-Ir(1) | 140.9(3) |
| C(22)-Lu(1)-Ir(1) | 91.6(3) |
| C(1)-Lu(1)-Ir(1) | 42.7(3) |
| C(6)-N(1)-Ir(1) | 121.7(8) |
| C(6)-N(1)-Lu(1) | 134.0(8) |
| Ir(1)-N(1)-Lu(1) | 102.5(5) |
| C(30)-N(2)-Lu(1) | 176.1(13) |
| C(4)-O(1)-Lu(1) | 133.7(8) |
| C(2)-Si(1)-C(1) | 112.0(7) |
| C(2)-Si(1)-C(4) | 110.1(6) |
| C(1)-Si(1)-C(4) | 104.3(6) |
| C(2)-Si(1)-C(3) | 107.7(8) |
| C(1)-Si(1)-C(3) | 112.9(6) |
| C(4)-Si(1)-C(3) | 109.9(7) |
| Si(1)-C(1)-Ir(1) | 120.3(6) |
| Si(1)-C(1)-Lu(1) | 101.3(5) |
| Ir(1)-C(1)-Lu(1) | 82.1(4) |
| C(5)-C(4)-O(1) | 124.8(14) |
| C(5)-C(4)-Si(1) | 123.5(12) |
| O(1)-C(4)-Si(1) | 111.7(9) |
| N(1)-C(6)-C(8) | 109.6(11) |
| N(1)-C(6)-C(9) | 110.6(12) |
| C(8)-C(6)-C(9) | 108.2(12) |
| N(1)-C(6)-C(7) | 109.6(11) |
| C(8)-C(6)-C(7) | 106.8(12) |
| C(9)-C(6)-C(7) | 112.0(13) |
| C(14)-C(10)-C(11) | 110.0(13) |
| C(14)-C(10)-C(15) | 125.3(13) |
| C(11)-C(10)-C(15) | 124.3(14) |
| C(14)-C(10)-Ir(1) | 72.1(8) |
| C(11)-C(10)-Ir(1) | 72.2(8) |
| C(15)-C(10)-Ir(1) | 127.9(9) |
| C(12)-C(11)-C(10) | 107.1(13) |
| C(12)-C(11)-C(16) | 128.3(14) |
| C(10)-C(11)-C(16) | 124.5(14) |
| C(12)-C(11)-Ir(1) | 71.5(8) |
| C(10)-C(11)-Ir(1) | 70.3(8) |
| C(16)-C(11)-Ir(1) | 126.5(10) |
| C(11)-C(12)-C(13) | 108.0(12) |
| C(11)-C(12)-C(17) | 125.2(14) |
| C(13)-C(12)-C(17) | 123.9(13) |
| C(11)-C(12)-Ir(1) | 72.0(8) |
| C(13)-C(12)-Ir(1) | 69.6(7) |
| C(17)-C(12)-Ir(1) | 139.2(10) |
| C(12)-C(13)-C(14) | 109.5(12) |
| C(12)-C(13)-C(18) | 126.4(13) |
| C(14)-C(13)-C(18) | 123.7(13) |
| C(12)-C(13)-Ir(1) | 73.3(7) |
| C(14)-C(13)-Ir(1) | 72.5(7) |
| C(18)-C(13)-Ir(1) | 126.3(10) |
| C(10)-C(14)-C(13) | 105.4(12) |
| C(10)-C(14)-C(19) | 126.0(13) |
| C(13)-C(14)-C(19) | 128.2(13) |
| C(10)-C(14)-Ir(1) | 71.2(7) |
| C(13)-C(14)-Ir(1) | 69.5(6) |
| C(19)-C(14)-Ir(1) | 129.3(9) |
| C(21)-C(20)-C(24) | 107.1(12) |
| C(21)-C(20)-C(25) | 125.1(14) |
| C(24)-C(20)-C(25) | 127.8(14) |
| C(21)-C(20)-Lu(1) | 73.4(8) |
| C(24)-C(20)-Lu(1) | 74.4(8) |
| C(25)-C(20)-Lu(1) | 118.8(10) |
| C(20)-C(21)-C(22) | 108.1(12) |
| C(20)-C(21)-C(26) | 126.8(14) |
| C(22)-C(21)-C(26) | 124.2(14) |
| C(20)-C(21)-Lu(1) | 75.2(8) |
| C(22)-C(21)-Lu(1) | 75.7(8) |
| C(26)-C(21)-Lu(1) | 123.6(10) |
| C(23)-C(22)-C(21) | 106.9(12) |
| C(23)-C(22)-C(27) | 127.0(14) |
| C(21)-C(22)-C(27) | 126.0(14) |
| C(23)-C(22)-Lu(1) | 73.0(8) |
| C(21)-C(22)-Lu(1) | 72.5(8) |
| C(27)-C(22)-Lu(1) | 122.5(10) |
| C(24)-C(23)-C(22) | 108.4(13) |
| C(24)-C(23)-C(28) | 128.0(14) |
| C(22)-C(23)-C(28) | 122.4(14) |
| C(24)-C(23)-Lu(1) | 75.4(9) |
| C(22)-C(23)-Lu(1) | 75.3(8) |
| C(28)-C(23)-Lu(1) | 125.3(11) |
| C(23)-C(24)-C(20) | 109.3(13) |
| C(23)-C(24)-C(29) | 126.5(14) |
| C(20)-C(24)-C(29) | 124.0(14) |
| C(23)-C(24)-Lu(1) | 74.1(8) |
| C(20)-C(24)-Lu(1) | 74.0(8) |
| C(29)-C(24)-Lu(1) | 122.9(10) |
| N(2)-C(30)-C(31) | 177.7(18) |
| C(32)-C(31)-C(36) | 119.5(17) |
| C(32)-C(31)-C(30) | 121.6(19) |
| C(36)-C(31)-C(30) | 118.8(19) |
| C(31)-C(32)-C(33) | 120(2) |
| C(34)-C(33)-C(32) | 118(2) |
| C(33)-C(34)-C(35) | 123.8(18) |
| C(34)-C(35)-C(36) | 117(2) |
| C(35)-C(36)-C(31) | 121(2) |

Symmetry transformations used to generate equivalent atoms:

**Table S24.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 17(1) | 23(1) | 24(1) | -1(1) | -3(1) | -2(1) |
| Lu(1) | 19(1) | 22(1) | 25(1) | -1(1) | -5(1) | 0(1) |
| N(1) | 20(6) | 41(7) | 26(6) | 11(6) | -6(5) | -8(5) |
| N(2) | 26(7) | 49(8) | 34(7) | -8(7) | -7(6) | -2(6) |
| O(1) | 38(6) | 32(5) | 30(5) | -5(5) | -6(5) | 12(5) |
| Si(1) | 25(2) | 25(2) | 26(2) | -4(2) | -4(2) | 2(2) |
| C(1) | 20(7) | 19(6) | 17(6) | -1(5) | -1(5) | 0(5) |
| C(2) | 78(13) | 41(9) | 22(8) | 2(7) | -20(8) | -13(9) |
| C(3) | 40(9) | 36(8) | 38(9) | -7(8) | -16(7) | 16(7) |
| C(4) | 27(8) | 36(8) | 24(7) | 3(6) | -1(6) | -10(7) |
| C(5) | 45(10) | 61(11) | 21(8) | 2(8) | -4(7) | 14(9) |
| C(6) | 20(7) | 21(7) | 47(9) | 0(7) | -12(6) | 6(6) |
| C(7) | 33(9) | 32(8) | 56(10) | -2(8) | -11(8) | -7(7) |
| C(8) | 18(7) | 44(9) | 76(12) | 24(9) | -19(8) | -13(7) |
| C(9) | 24(8) | 52(10) | 46(10) | -3(9) | 0(7) | -1(8) |
| C(10) | 25(8) | 31(7) | 35(8) | 15(7) | -11(6) | -3(6) |
| C(11) | 39(9) | 31(7) | 23(7) | 7(6) | -9(6) | -13(7) |
| C(12) | 21(7) | 25(7) | 27(7) | 4(6) | 4(6) | 5(6) |
| C(13) | 31(8) | 30(7) | 9(6) | 7(6) | -5(5) | -12(6) |
| C(14) | 15(7) | 48(9) | 13(6) | 15(6) | -7(5) | -7(6) |
| C(15) | 20(8) | 49(10) | 45(9) | 23(8) | -10(7) | 9(7) |
| C(16) | 73(13) | 33(8) | 43(10) | 10(8) | -14(9) | -10(9) |
| C(17) | 35(9) | 54(10) | 44(10) | 18(9) | 7(8) | -17(8) |
| C(18) | 52(10) | 44(9) | 27(8) | -4(7) | -8(7) | -6(8) |
| C(19) | 32(8) | 29(7) | 53(10) | 15(7) | -28(7) | -8(7) |
| C(20) | 31(8) | 38(8) | 33(8) | -12(7) | 8(6) | -15(7) |
| C(21) | 34(8) | 14(6) | 37(8) | 10(6) | -18(7) | 3(6) |
| C(22) | 44(9) | 26(7) | 23(7) | -11(6) | 5(6) | -4(7) |
| C(23) | 32(8) | 18(6) | 49(9) | 5(7) | -10(7) | -1(6) |
| C(24) | 47(10) | 26(7) | 33(8) | 5(7) | -18(7) | -10(7) |
| C(25) | 45(5) | 43(4) | 65(5) | 0(4) | -8(4) | -6(4) |
| C(26) | 45(5) | 43(4) | 65(5) | 0(4) | -8(4) | -6(4) |
| C(27) | 45(5) | 43(4) | 65(5) | 0(4) | -8(4) | -6(4) |
| C(28) | 45(5) | 43(4) | 65(5) | 0(4) | -8(4) | -6(4) |
| C(29) | 45(5) | 43(4) | 65(5) | 0(4) | -8(4) | -6(4) |
| C(30) | 25(8) | 36(8) | 33(8) | -6(7) | -2(7) | -10(7) |
| C(31) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |
| C(32) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |
| C(33) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |
| C(34) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |
| C(35) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |
| C(36) | 46(4) | 78(6) | 52(5) | 7(5) | -23(3) | 2(4) |

**Table S25.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **6'**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 4026 | 6016 | 1902 | 70 |
| H(2B) | 5542 | 4917 | 1976 | 70 |
| H(2C) | 5180 | 5482 | 1194 | 70 |
| H(3A) | 8436 | 5924 | 1111 | 63 |
| H(3B) | 8337 | 5477 | 1947 | 63 |
| H(3C) | 8641 | 6873 | 1685 | 63 |
| H(5A) | 6096 | 9025 | 49 | 58 |
| H(5B) | 7277 | 7659 | 275 | 58 |
| H(7A) | -458 | 6655 | 3202 | 60 |
| H(7B) | 1290 | 6234 | 3241 | 60 |
| H(7C) | 730 | 6528 | 2475 | 60 |
| H(8A) | -420 | 9912 | 2439 | 68 |
| H(8B) | -1384 | 8857 | 2527 | 68 |
| H(8C) | 129 | 8635 | 1959 | 68 |
| H(9A) | -384 | 9755 | 3720 | 65 |
| H(9B) | 296 | 8384 | 4118 | 65 |
| H(9C) | -1282 | 8648 | 3850 | 65 |
| H(15A) | 7366 | 5509 | 3335 | 63 |
| H(15B) | 6564 | 4525 | 3062 | 63 |
| H(15C) | 7158 | 4239 | 3821 | 63 |
| H(16A) | 4198 | 3410 | 3801 | 76 |
| H(16B) | 4060 | 4239 | 3054 | 76 |
| H(16C) | 2595 | 4230 | 3628 | 76 |
| H(17A) | 864 | 5583 | 4425 | 70 |
| H(17B) | 561 | 6881 | 4872 | 70 |
| H(17C) | 1435 | 5491 | 5185 | 70 |
| H(18A) | 1659 | 8591 | 5060 | 63 |
| H(18B) | 3238 | 8902 | 5033 | 63 |
| H(18C) | 2753 | 7834 | 5608 | 63 |
| H(19A) | 6752 | 6773 | 4772 | 54 |
| H(19B) | 5693 | 8224 | 4694 | 54 |
| H(19C) | 6793 | 7543 | 4003 | 54 |
| H(25A) | 6643 | 11541 | 2248 | 78 |
| H(25B) | 5897 | 12417 | 1609 | 78 |
| H(25C) | 6214 | 10850 | 1620 | 78 |
| H(26A) | 5920 | 9769 | 3328 | 78 |
| H(26B) | 4747 | 10379 | 4015 | 78 |
| H(26C) | 5848 | 11196 | 3584 | 78 |
| H(27A) | 2047 | 11831 | 4370 | 78 |
| H(27B) | 2093 | 10379 | 4164 | 78 |
| H(27C) | 702 | 11583 | 4034 | 78 |
| H(28A) | 75 | 13790 | 2944 | 78 |
| H(28B) | -311 | 12400 | 3109 | 78 |
| H(28C) | -66 | 12965 | 2295 | 78 |
| H(29A) | 3705 | 12899 | 1075 | 78 |
| H(29B) | 2626 | 14112 | 1522 | 78 |
| H(29C) | 1947 | 13044 | 1244 | 78 |
| H(32) | -1402 | 10226 | 591 | 73 |
| H(33) | -3015 | 11178 | -240 | 73 |
| H(34) | -3286 | 13337 | -583 | 73 |
| H(35) | -1929 | 14599 | -199 | 73 |
| H(36) | -135 | 13575 | 530 | 73 |