Frustrated Lewis pair behavior of a neutral scandium complex

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Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz and a Bruker 600 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. 2,6-Di-tert-butylphenol was purchased from ACROS. $[Rh(nbd)Cl]_2$ was purchased from Strem. (2, 2-Dimethyl-2-hydroxyethyl) diphenylphosphine[1], $Sc(CH_2SiMe_3)_3(THF)_2$[2] and methyl diazophenylacetate[3] were synthesized by following the literature procedures.

X-ray structure analyses: For compound **7** one toluene molecule was found disordered over two positions in asymmetric unit. Several restraints (SADI, FLAT and DFIX) were used to improve refinement stability. For compound **8** one toluene molecule and part of the six membered ring C31 to C36 were found disordered over two positions in asymmetric unit. Several restraints (SADI, EADP and DFIX) were used to improve refinement stability. For compound **9** one toluene molecule was found in asymmetric unit. Moreover, one toluene molecule and one hexane molecule of compound **10** were found disordered over two positions in asymmetric unit. One restraint (SADI) was used to improve refinement stability.

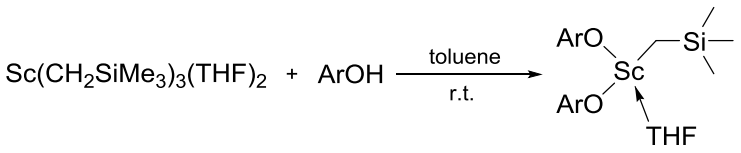
References:

[1] I. Arribas, S. Vargas, M. Rubio, A. Suárez, C. Domene, E. Álvarez, A. Pizzano, *Organometallics*., **2010**, *29*, 5791-5804.

[2] M. F. Lappert, R. Pearce, *J. Chem. Soc. Chem. Commun.*, **1973**, 126-126.

[3] M. Hu, J. Rong, W. Miao, C. Ni, Y. Han, J. Hu, *Org. Lett*., **2014**, *16*, 2030-2033.

Preparation of complex 5:



5

Ar = 2,6-tBu_2-C_6H_3

Scheme S1.

A solution of 2,6-di-tert-butylphenol (1.46 g, 7.1 mmol) in toluene (8 mL) was slowly added to a solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.64 g, 3.6 mmol) in toluene (6 mL). After stirring at room temperature for 1 day, all the volatiles of reaction mixture were removed in vacuo. The residue was washed with hexane (3×2 mL) to give complex **5** as a white solid (1.99 g, 90%).

Elemental Analysis: calcd. for $C_{36}H_{61}O_3SiSc$: C, 70.32; H, 10.00. Found: C, 69.79; H, 9.31.

^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*), 6.85 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*) (O*Ar*), 3.93 (m, 4H, *α*-H_{THF}), 1.57 (s, 36H, C(CH_3)$_3$), 1.11 (m, 4H, *β*-H_{THF}), 0.31 (s, 2H, CH_2SiMe$_3$), 0.28 (s, 9H, Si*Me*$_3$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ =161.4 (*i*), 138.1 (*o*), 125.8 (*m*), 118.8 (*p*) (O*Ar*), 73.4 (*α*-C_{THF}), 39.6(*C*H$_2$SiMe$_3$), 35.4 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 24.7 (*β*-C_{THF}), 4.1 (Si*Me*$_3$).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.31 / 6.85 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.31 / 125.8 (*m*-O*Ar*), 6.85 / 118.8 (*p*-O*Ar*), 3.93 / 73.4 (*α*-CH_2^{THF}), 1.57 / 32.0 (C(*CH*$_3$)$_3$), 1.11 / 24.7 (*β*-CH_2^{THF}), 0.28 / 4.1 (Si*Me*$_3$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.31 / 161.4, 125.8, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.85 / 138.1, (*p*-O*Ar* / *o*-O*Ar*), 1.57 / 138.1, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 0.31 / 4.1 (C*H*$_2$SiMe$_3$ / CH$_2$Si*Me*$_3$), 0.28 / 39.6 (Si*Me*$_3$ / *C*H$_2$SiMe$_3$).

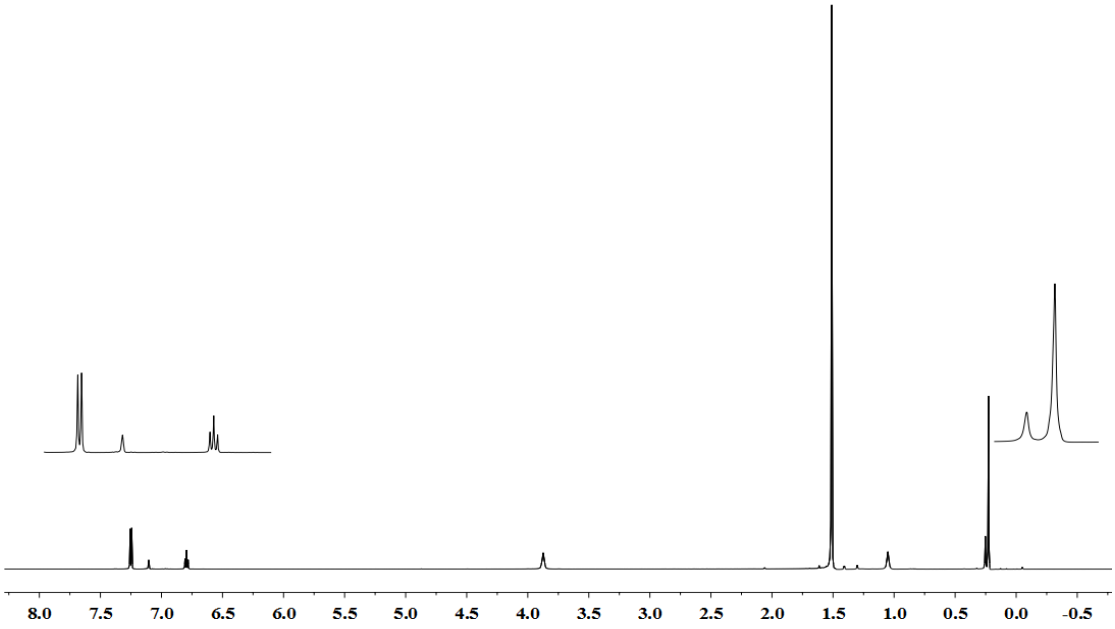


Fig S1. ^{1}H NMR (600 MHz, C_6D_6, 298 K)

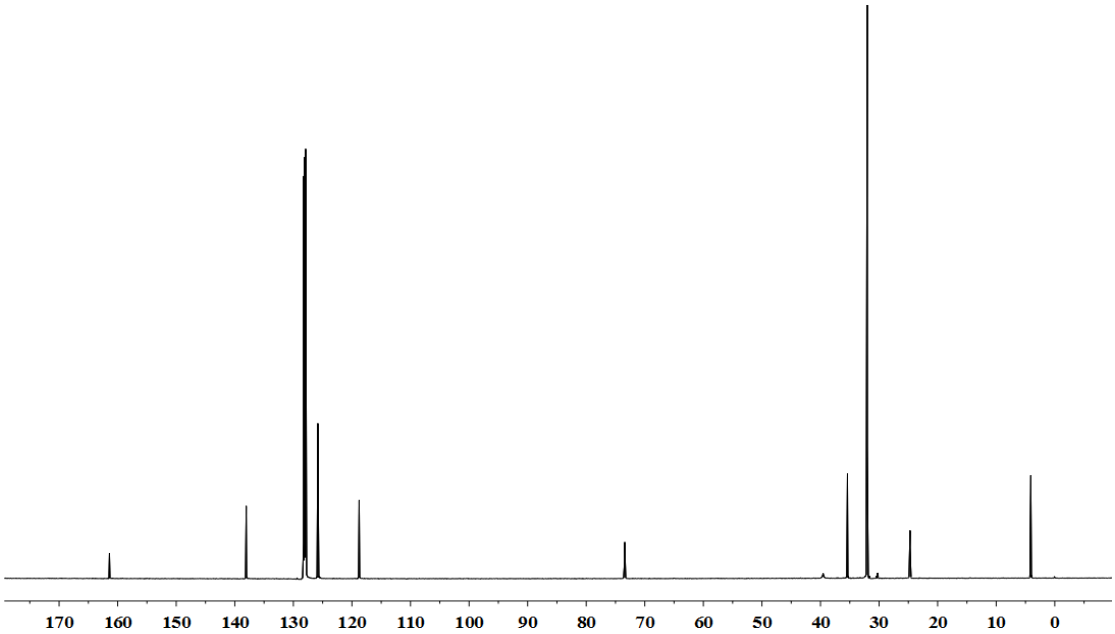
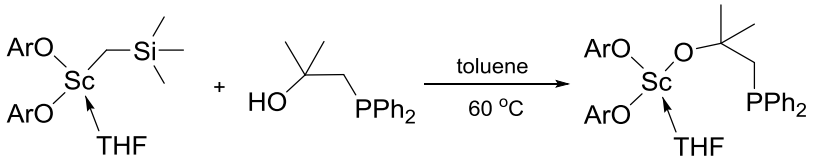


Fig S2. ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K)

Preparation of complex 6:



Ar = 2,6-tBu_2-C_6H_3

Scheme S2.

Complex **5** (2.03 g, 3.3 mmol) and (2,2-dimethyl-2-hydroxyethyl)diphenylphosphine (0.85 g, 3.3 mmol) were mixed in toluene (10 mL), and then the reaction mixture was stirred at 60°C overnight. After all volatiles were removed, the residue was recrystallized from hexane (2 mL) at -35°C for 1 day to eventually afford complex **6** as a white solid (2.38 g, 92%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered fluorobenzene / hexane (v/v: 1:1) solution at -35°C.

Elemental Analysis: calcd. for $C_{48}H_{68}O_4PSc$: C, 73.44; H, 8.73. Found: C, 72.84; H, 8.92.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.51 (4H, *o*), 7.08 (4H, *m*), 7.04 (2H, *p*) (each m, *Ph*$_2$P), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*), 6.87 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*) (O*Ar*), 3.95 (m, 4H, *α*-H_{THF}), 2.67 (d, $^2J_{PH}$ = 3.4 Hz, 2H, PCH_2), 1.61 (s, 36H, C(CH_3)$_3$), 1.41 (br s, 6H, CH_3), 1.15 (m, 4H, *β*-H_{THF}).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 161.7 (*i*), 138.2 (*o*), 125.7 (*m*), 118.0 (*p*) (O*Ar*), 140.9 (br, *i*), 133.4 (d, $^2J_{PC}$ = 19.3 Hz, *o*), 128.7 (d, $^3J_{PC}$ = 6.9 Hz, *m*), 128.6 (overlapped, *p*) (*Ph*$_2$P), 77.6 (d, $^2J_{PC}$ = 17.4 Hz, O*C*(CH$_3$)$_2$), 73.5 (*α*-C_{THF}), 47.5 (d, $^1J_{PC}$ =16.7 Hz, P*C*H$_2$), 35.4 (*C*(CH$_3$)$_3$), 33.1 (d, $^3J_{PC}$ = 7.1 Hz, *C*H$_3$), 32.1 (C(*C*H$_3$)$_3$), 24.9 (*β*-C_{THF}).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -22.3 ($\nu_{1/2}$ ~ 58 Hz).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.51 / 7.08 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.35 / 6.87 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.51 / 133.4 (*o*-*Ph*$_2$P), 7.35 / 125.7 (*m*-O*Ar*), 7.08 / 128.7 (*m*-*Ph*$_2$P), 7.04 / 128.6 (*p*-*Ph*$_2$P), 6.87 /

118.0 (*p*-O*Ar*), 3.95 / 73.5 (*α*-CH_2^{THF}), 2.67 / 47.5 (PCH_2), 1.61 / 32.1 (C(CH_3)$_3$), 1.41 / 33.1 (OC(CH_3)$_2$), 1.15 / 24.9 (*β*-CH_2^{THF}).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.51 / 128.6 (*o*-Ph_2P / *p*- Ph_2P), 7.35 / 161.7, 125.7, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH_3)$_3$), 7.08 / 140.9 (*m*-Ph_2P / *i*-Ph_2P), 6.87 / 138.2 (*p*-O*Ar* / *o*-O*Ar*), 2.67 / 140.9, 77.6, 33.1 (PCH_2 / *i*-Ph_2P, O*C*(CH_3)$_2$, OC(*C*H_3)$_2$), 1.61 / 138.2, 125.7, 35.4 (C(CH_3)$_3$ / *o*-O*Ar*, *m*-O*Ar*, *C*(CH_3)$_3$), 1.41 / 77.6, 47.5 (OC(CH_3)$_2$ / O*C*(CH_3)$_2$, PCH_2).

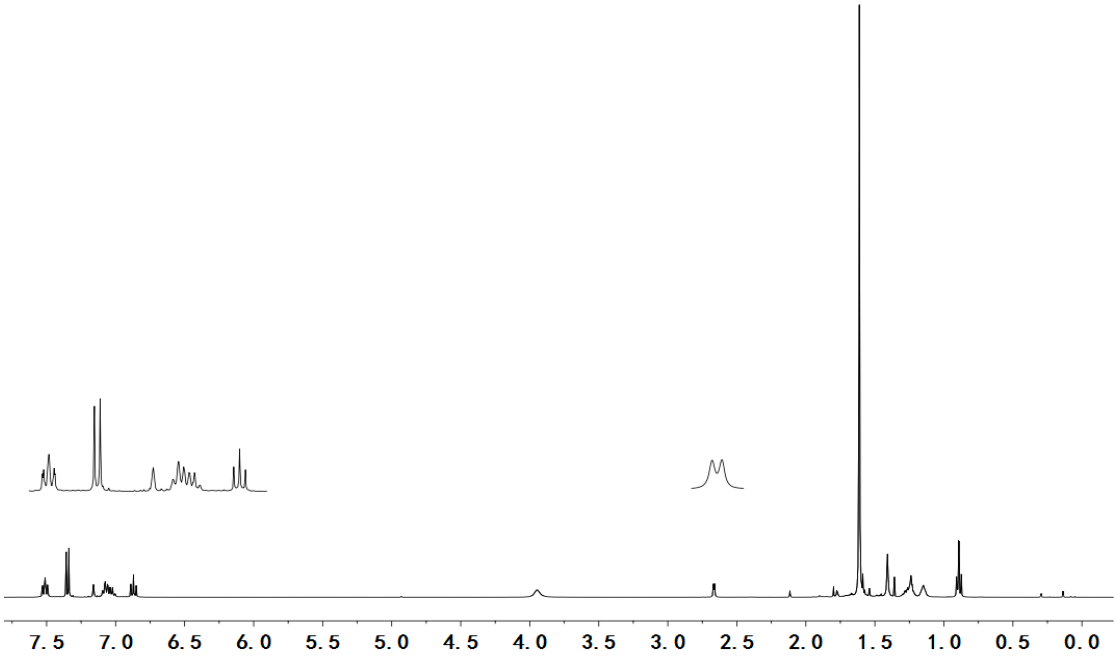


Fig S3. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

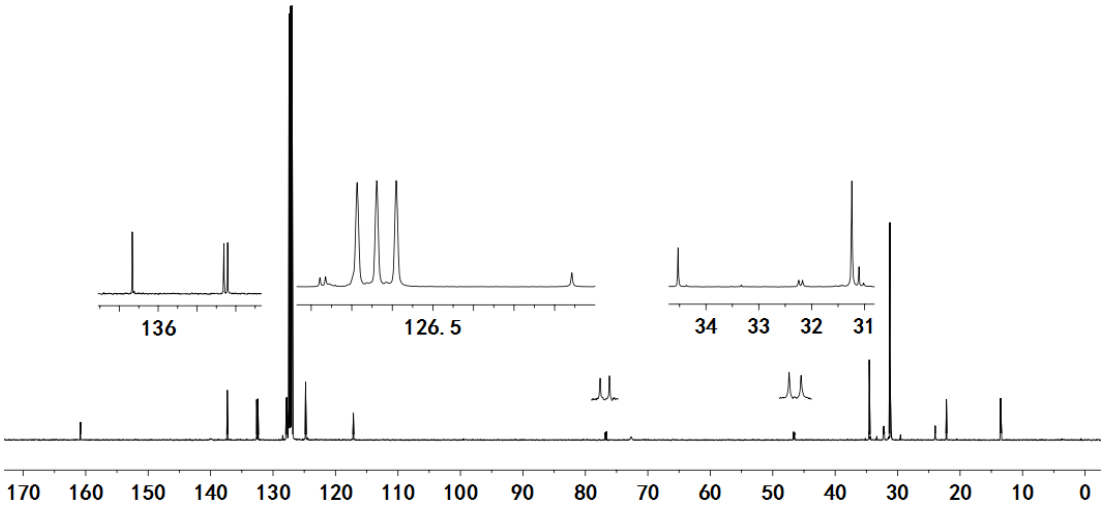


Fig S4. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

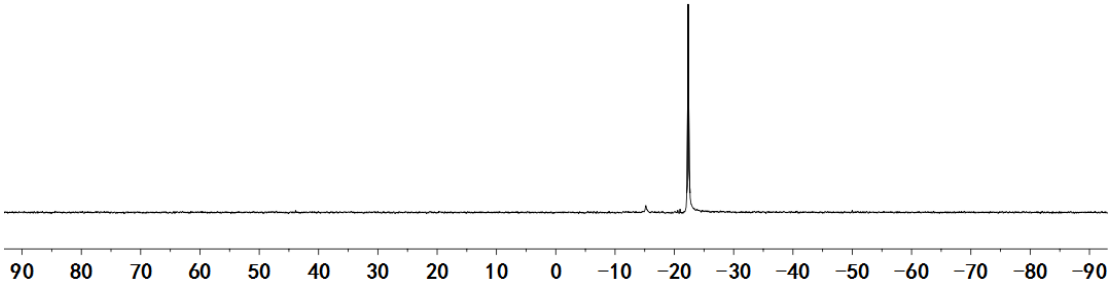


Fig S5. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

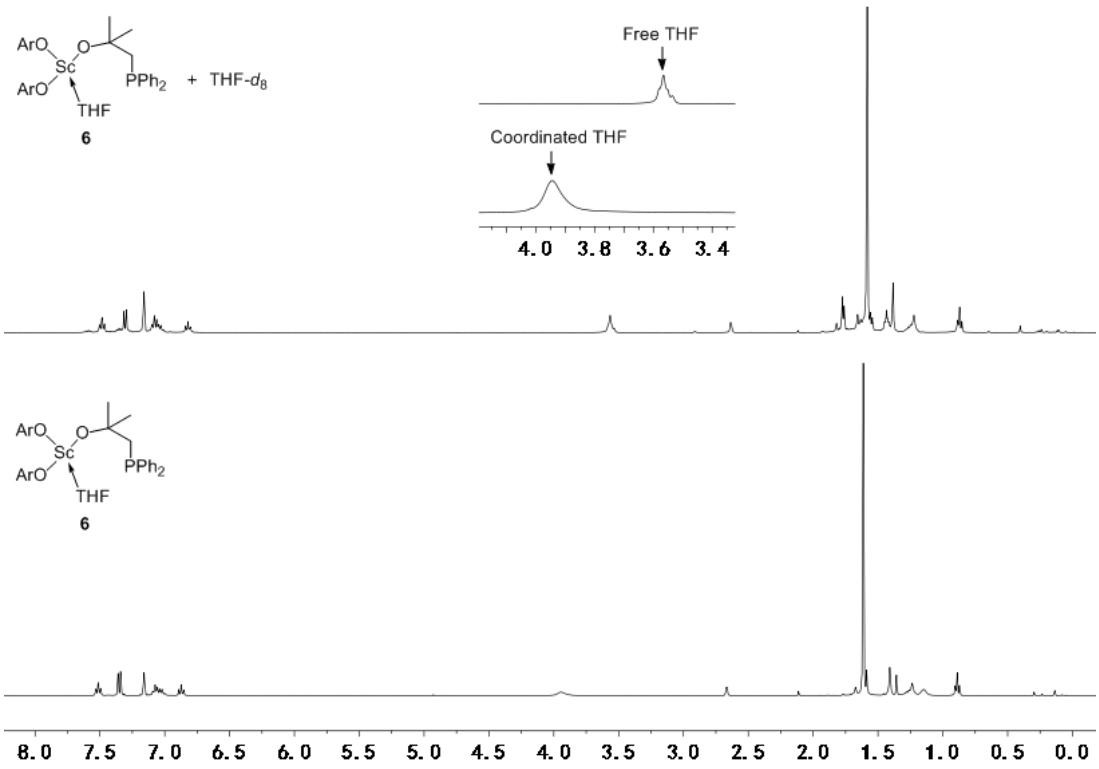


Fig S6. Comparison of ^{1}H NMR of complex **6**

(400 MHz, C_6D_6, 298 K. Above: **6** + one drop of THF-d_8; blow: **6**).

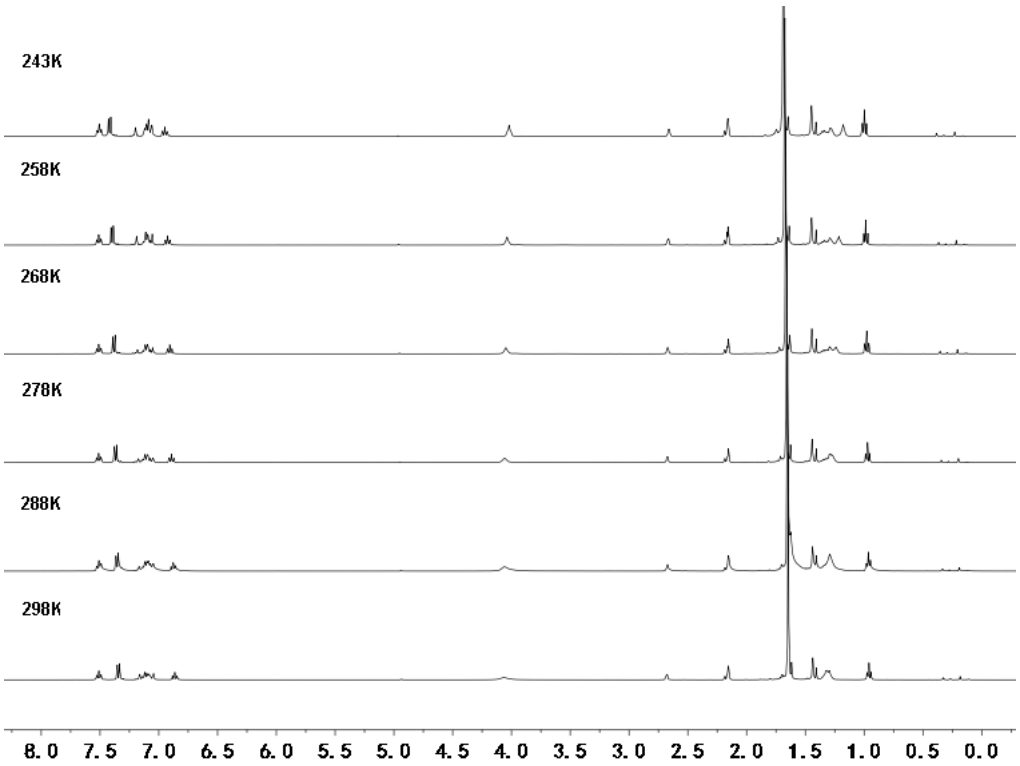


Fig S7. VT ^{1}H NMR of complex **6** (400 MHz, Tol-d_8).

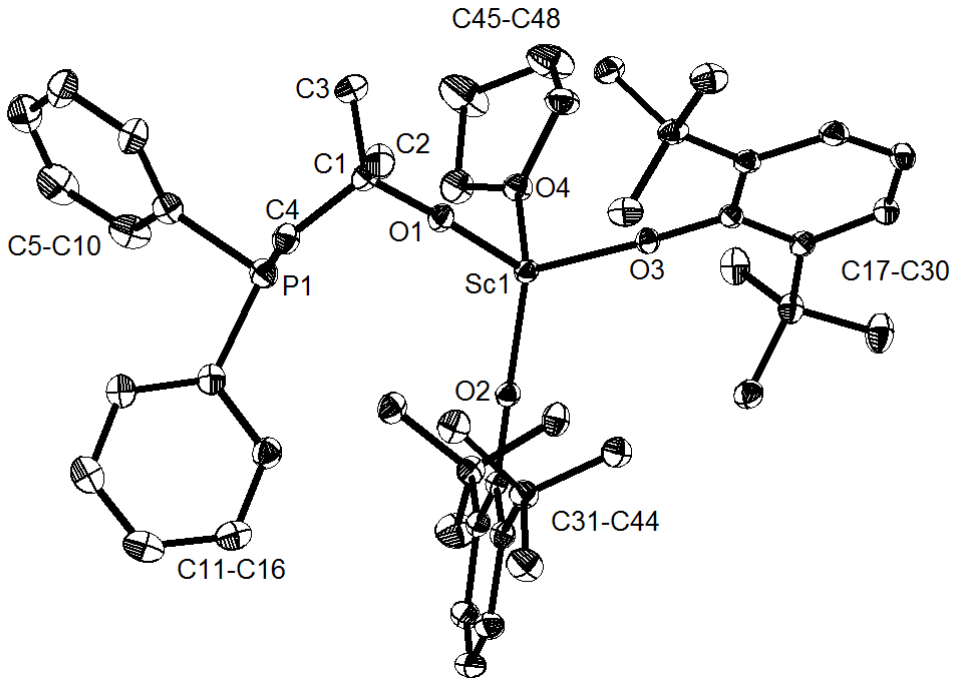
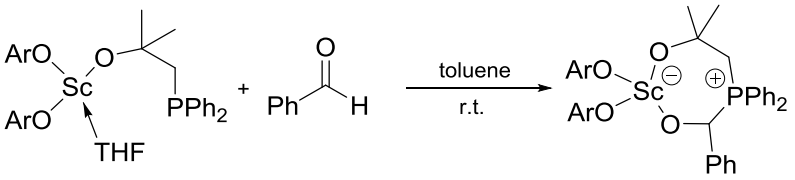


Fig S8. Crystal structure of complex **6**.

Preparation of complex 7:



6 **7**

Ar = 2,6-tBu_2-C_6H_3

Scheme S3.

A solution of phenylaldehyde (12 mg, 0.11 mmol) in toluene (1 mL) was added to a solution of **6** (89 mg, 0.11 mmol) in toluene (1 mL). The reaction mixture was stirred at room temperature for 15 min and then all volatiles were removed in vacuo. The residue was washed with hexane (3×2 mL) and finally gave complex **7** as a yellow crystalline solid (70 mg, 76%). Crystals suitable for the X-ray crystal structure analysis were grown from a mixture of C_6D_6 and C_6D_5Br (v/v: 5: 1) at room temperature.

Elemental Analysis: calcd. for $C_{51}H_{66}O_4PSc$: C, 74.79; H, 8.12. Found: C, 75.55; H, 8.28.

^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*), 6.85 (m, 2H, *p*) (O*Ar*), 7.24 (4H, *o*), 6.83 (6H, *m*, *p*) (each m, *Ph*$_2$P), 7.21 (overlapped, 1H, C*H*Ph), 7.00 (2H, *o*), 6.98 (2H, *m*), 6.97 (1H, *p*) (each m, CH*Ph*), 2.95 (d, $^2J_{PH}$ = 12.5 Hz, 2H, PC*H*$_2$), 1.74 (s, 36H, C(C*H*$_3$)$_3$), 1.19 (s, 6H, OC(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 162.9 (*i*), 138.6 (*o*), 125.0 (*m*), 116.7 (*p*) (O*Ar*), 133.9 (d, $^2J_{PC}$ = 7.4 Hz, *o*), 129.3 (*m*), 128.3 (overlapped with solvent, *p*), 121.8 (d, $^1J_{PC}$ = 65.0 Hz, *i*) (*Ph*$_2$P), n.o. (*i*), 133.4 (d, $^3J_{PC}$ = 2.7 Hz, *o*), 129.2 (*p*), 128.2 (overlapped with solvent, *m*) (CH*Ph*), 84.9 (d, $^1J_{PC}$ = 35.4 Hz, *C*HPh), 74.2 (d, $^2J_{PC}$ = 5.3 Hz, O*C*(CH$_3$)$_2$), 44.0 (d, $^1J_{PC}$ = 37.0 Hz, P*C*H$_2$), 35.4 (*C*(CH$_3$)$_3$), 34.6 (d, $^3J_{PC}$ = 8.6 Hz, OC(*C*H$_3$)$_2$), 31.8 (C(*C*H$_3$)$_3$). [n.o.: not observed]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 14.4 ($\nu_{1/2}$ ~ 12 Hz).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.39 / 6.85 (*m*-O*Ar* / *p*-O*Ar*), 7.24 / 6.83 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.39 / 125.0 (*m*-O*Ar*), 7.24 / 133.9 (*o*-*Ph*$_2$P), 7.21 / 84.9 (*CH*Ph), 6.97 / 129.2 (*p*-CH*Ph*), 6.85 / 116.7 (*p*-O*Ar*), 2.95 / 44.0 (P*CH*$_2$), 1.74 / 31.8 (C(*CH*$_3$)$_3$), 1.19 / 34.6 (OC(*CH*$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.39 / 162.9, 125.0, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.85 / 138.6 (*p*-O*Ar* / *o*-O*Ar*), 2.95 / 121.8, 74.2, 34.6 (PC*H*$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.74 / 138.6, 125.0, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 1.19 / 74.2, 44.0 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

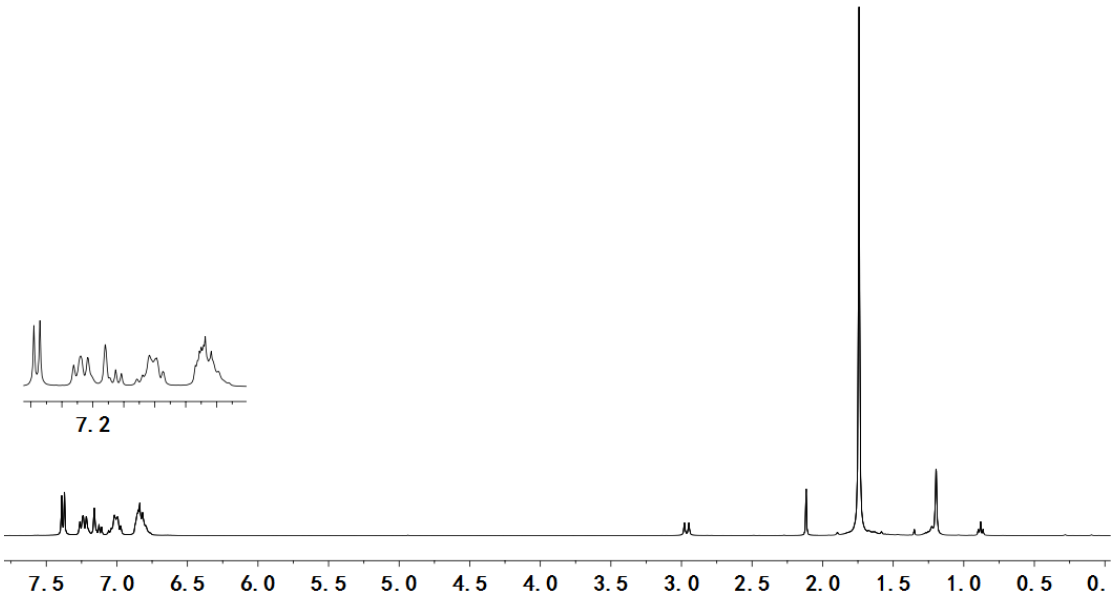


Fig S9. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

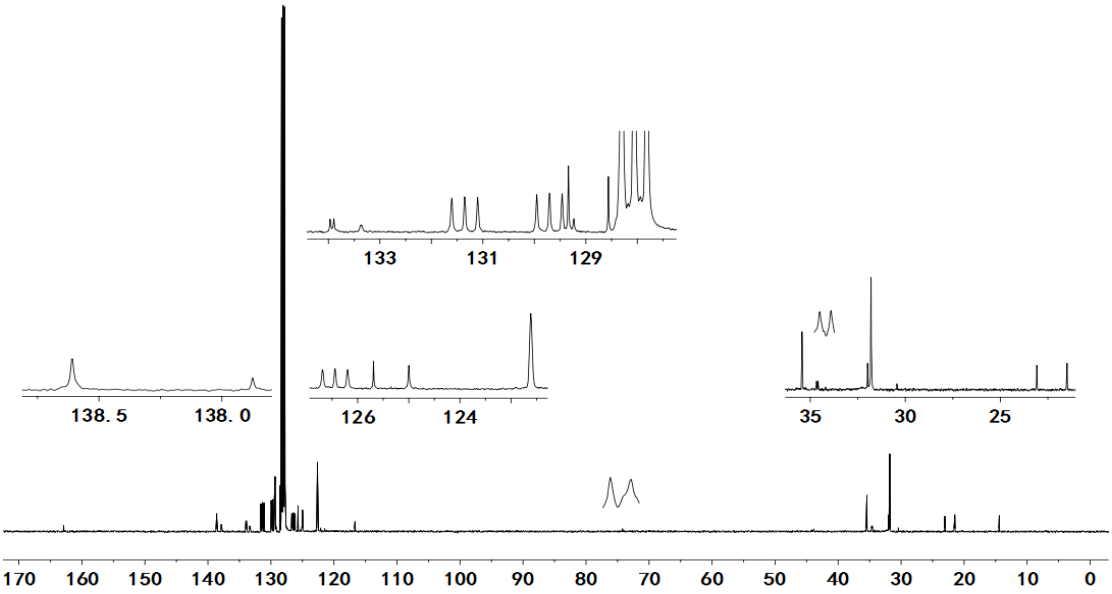


Fig S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

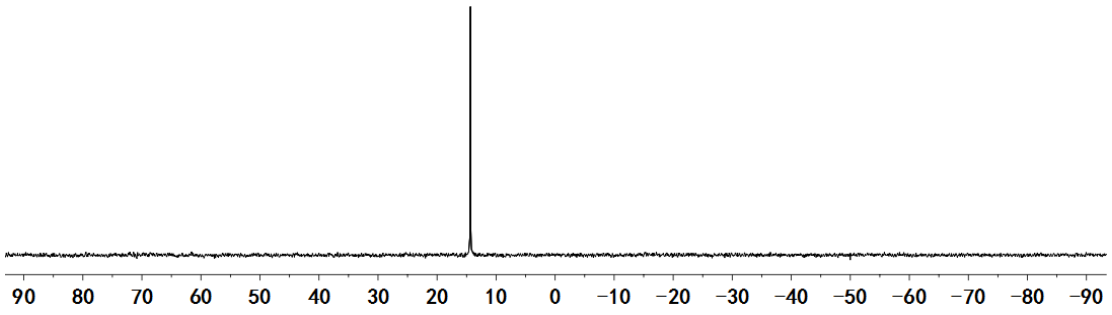


Fig S11. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

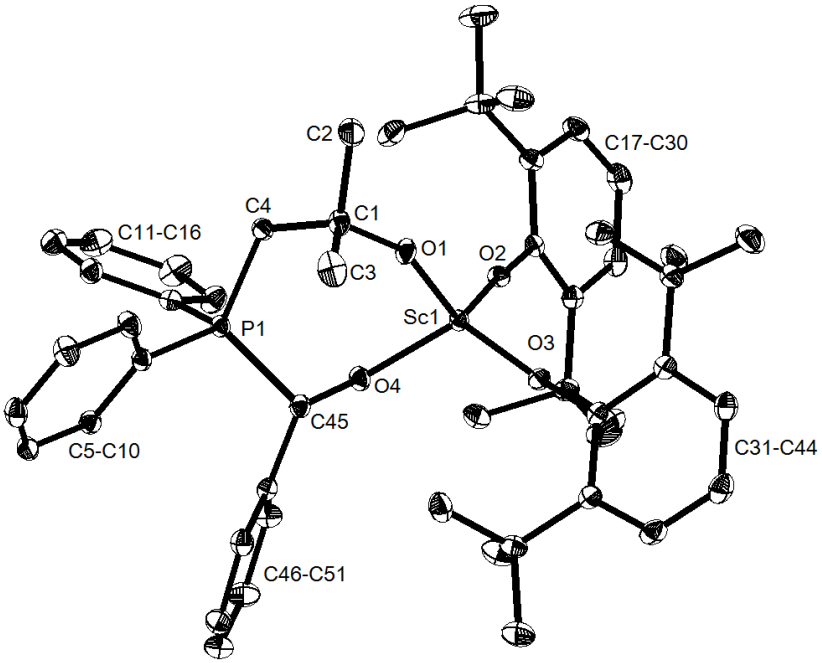
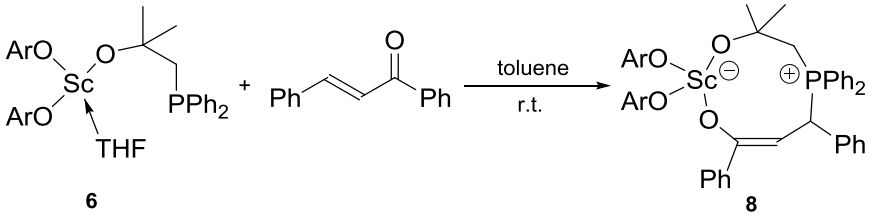


Fig S12. Crystal structure of complex **7**.

Preparation of complex 8:



Ar = 2,6-tBu_2-C_6H_3

Scheme S4.

Following the procedure described for **7**, reaction of complex **6** (89 mg, 0.11 mmol) and chalcone (23 mg, 0.11 mmol) gave complex **8** as a white crystalline solid (86 mg, 83%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{59}H_{72}O_4PSc{\cdot}C_7H_8$: C, 78.23; H, 7.96. Found: C, 77.80; H, 7.79.

^{1}H NMR (400 MHz, Tol-d_8, 243 K): δ = 8.02 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*), 7.33 (m, 2H, *m*), 7.32 (m, 1H, *p*) (=C*Ph*), 7.50 (br, 2H, *m*), 6.94 (overlapped with solvent, 1H, *p*) (O*Ar*), 7.38 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*), 6.83 (overlapped, 1H, *p*) (O*Ar*'), 7.18 (2H, *o*), 6.82 (3H, *m*, *p*)^t (each m, *Ph*P), 7.15 (2H, *o*), 6.81 (1H, *p*), 6.79 (2H, *m*) (each m, *Ph*'P), 7.01 (m, 1H, *p*)^t, 6.96 (m, 2H, *o*), 6.61 (m, 2H, *m*) (CH*Ph*), 6.90 (overlapped, 1H, C*H*Ph), 4.24 (dd, $^3J_{PH}$ = 4.2 Hz, $^3J_{HH}$ = 10.5 Hz, 1H, C*H*=), 3.34 (dd, $^2J_{PH}$ = 13.9 Hz, $^2J_{HH}$ = 16.4 Hz, 1H, PCH_2), 1.96 (br, 18H, C(CH_3)$_3$), 1.79 (overlapped, 1H, PCH_2), 1.72 (s, 18H, C(CH_3)$_3$'), 1.50 (d, $^4J_{PH}$ = 4.1 Hz, 3H, OC(CH_3)$_2$), 0.55 (br, 3H, OC(CH_3)$_2$) [^{t} tentative assignment].

^{13}C{^{1}H} NMR (101 MHz, Tol-d_8, 243 K): δ = 165.0 (d, $^3J_{PC}$ = 9.2 Hz, O*C*=), 163.2 (*i*), 137.8 (*o*), 125.2 (*m*), 116.8 (*p*) (O*Ar*), 163.1 (*i*), 138.8 (*o*), 125.0(*m*), 116.7 (*p*) (O*Ar*'), 142.1 (d, $^4J_{PC}$ = 2.9 Hz, *i*), 129.3 (*p*), 128.0 (overlapped with solvent, *m*), 127.4 (*o*), (C*Ph*), 133.8 (d, $^3J_{PC}$ = 2.0 Hz, *o*), 137.7 (d, $^2J_{PC}$ = 10.5 Hz, *i*), 129.4 (overlapped with solvent, *m*), 128.7 (overlapped with solvent, *p*)^t (CH*Ph*), 134.3 (d, $^3J_{PC}$ = 7.3 Hz, *m*), 125.6 (d, $^4J_{PC}$ = 2.0 Hz, *p*) 125.3 (overlapped with solvent, *o*), 122.6 (*i*) (*Ph*P), 134.1 (d, $^3J_{PC}$ = 8.5 Hz, *m*), 128.4 (overlapped with solvent, *o*), 127.6 (*p*)^t, 123.6 (*i*)^t (*Ph*'P), 91.3 (*C*H=), 75.9 (d, $^2J_{PC}$ = 4.8 Hz, O*C*(CH$_3$)$_2$), 39.2 (d, $^1J_{PC}$ =

40.9 Hz, *C*HPh)[1], 38.6 (d, $^{1}J_{PC}$ = 29.1 Hz, P*C*H$_2$)[1], 38.4 (OC(*C*H$_3$)$_2$), 35.5 (*C*(CH$_3$)$_3$'), 34.2 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$'), 30.7 (OC(*C*H$_3$)$_2$), [[t] tentative assignment] [[1]from the GHSQC experiment].

^{31}P{^{1}H} NMR (162 MHz, Tol-d$_8$, 243 K): δ = 18.0 ($\nu_{1/2}$ ~ 13 Hz).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, Tol-d$_8$, 243 K) [selected traces]: δ ^{1}H / δ ^{1}H = 8.02 / 7.33 (*o*-C*Ph* / *m*-C*Ph*), 7.50 / 6.94 (*m*-O*Ar* / *p*-O*Ar*), 7.38 / 6.83 (*m*-O*Ar*'/ *p*-O*Ar*'), 7.18 / 6.82 (*o*-*Ph*P / *m*-*Ph*P), 7.15 / 6.79 (*o*-*Ph*'P / *m*-*Ph*'P), 7.01 / 6.61 (*p*-CH*Ph* / *m*-CH*Ph*), 6.90 / 4.24 (C*H*Ph / C*H*=), 3.34 / 1.79 (PC*H*$_2$ / PC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, Tol-d$_8$, 243 K): δ ^{1}H / δ ^{13}C = 8.02 / 127.4 (*o*-C*Ph*), 7.50 / 125.2 (*m*-O*Ar*), 7.38 / 125.0 (*m*-O*Ar*'), 7.33 / 128.0 (*m*-C*Ph*), 7.18 / 128.4 (*o*-*Ph*P), 7.15 / 125.3 (*o*-*Ph*'P), 6.96 / 133.8 (*o*-CH*Ph*), 6.94 /116.8 (*p*-O*Ar*), 6.90 / 39.2 (*CH*Ph), 6.83 / 116.7 (*p*-O*Ar*'), 6.82 / 134.07 (*m*-*Ph*P), 6.81 / 125.6 (*p*-*Ph*'P), 6.79 / 134.3 (*m*-*Ph*'P), 6.61 / 129.4 (*m*-CH*Ph*), 4.24 / 91.3 (C*H*=), 1.96 / 31.8 (C(*CH*$_3$)$_3$), 1.79, 3.34 / 38.6 (P*CH*$_2$), 1.72 / 31.4 (C(*CH*$_3$)$_3$'), 1.50 / 38.4 (OC(*CH*$_3$)$_2$), 0.55 / 30.7 (OC(*CH*$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, Tol-d$_8$, 243 K) [selected traces]: δ ^{1}H / δ ^{13}C = 8.02 / 165.0 (*o*-C*Ph* / O*C*=), 7.38 / 163.1, 125.0 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*'), 7.33 / 142.1 (*m*-C*Ph* / *i*-C*Ph*), 7.18 / 127.6 (*o*-*Ph*P / (*p*-*Ph*P), 7.15 / 125.6 (*o*-*Ph*'P / *p*-*Ph*'P), 7.01 / 133.8 (*p*-CH*Ph* / *o*-CH*Ph*), 6.94 / 137.8 (*p*-O*Ar* / *o*-O*Ar*), 6.90 / 165.0 (C*H*Ph / O*C*=), 6.83 / 138.8 (*p*-O*Ar*' / *o*-O*Ar*'), 6.82 / 123.6 (*m*-*Ph*P / *i*-*Ph*P), 6.79 / 122.6 (*m*-*Ph*'P / *i*-*Ph*'P), 6.61 / 137.7 (*m*-CH*Ph* / *i*-CH*Ph*), 4.24 / 165.0 (C*H*= / O*C*=), 1.72 / 138.8, 35.5 (C(C*H*$_3$)$_3$ / *o*-O*Ar*', *C*(CH$_3$)$_3$').

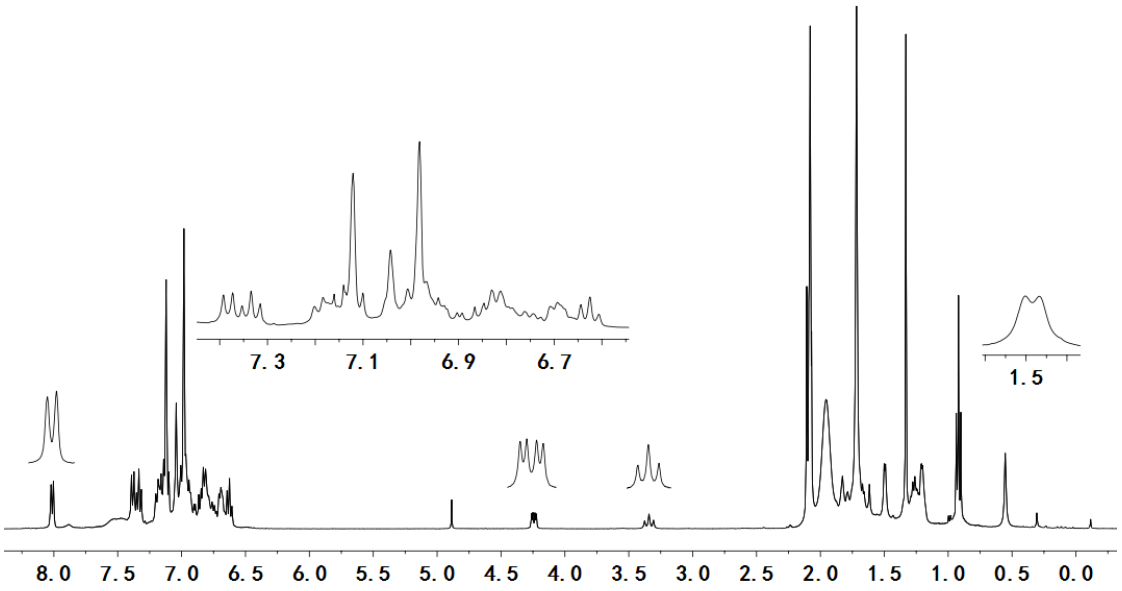


Fig S13. ^{1}H NMR (400 MHz, Tol-d_8, 243 K)

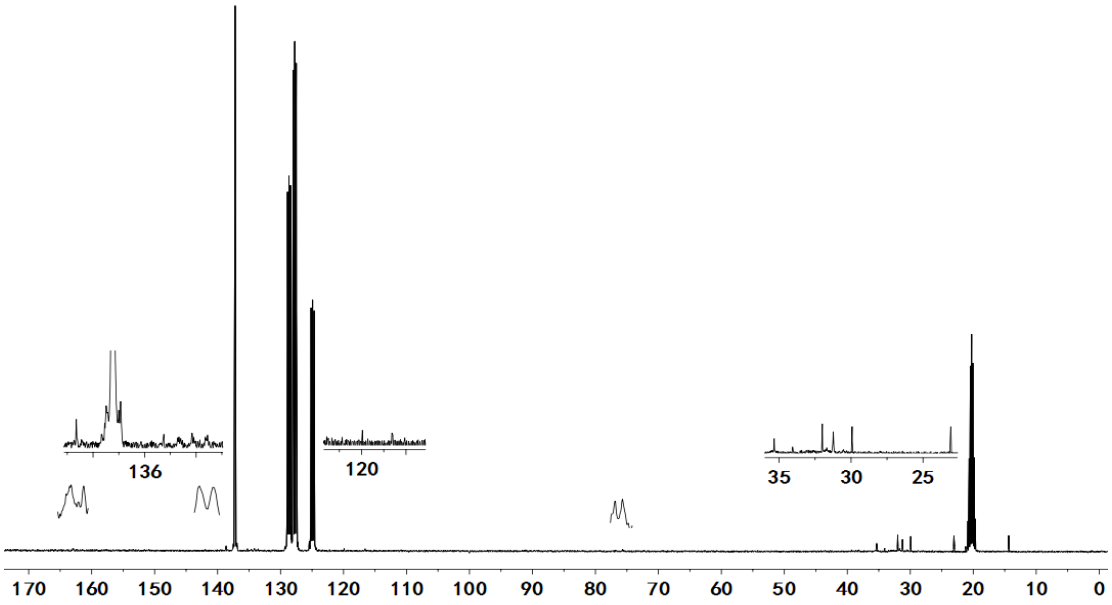


Fig S14. ^{13}C{^{1}H} NMR (101 MHz, Tol-d_8, 243 K)

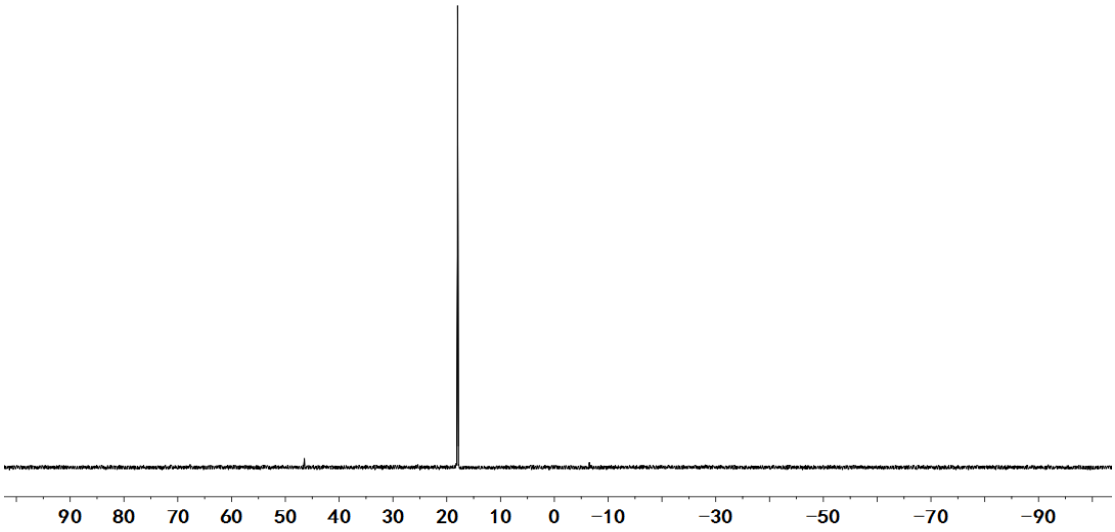


Fig S15. $^{31}P\{^{1}H\}$ NMR (162 MHz, Tol-d_8, 243 K)

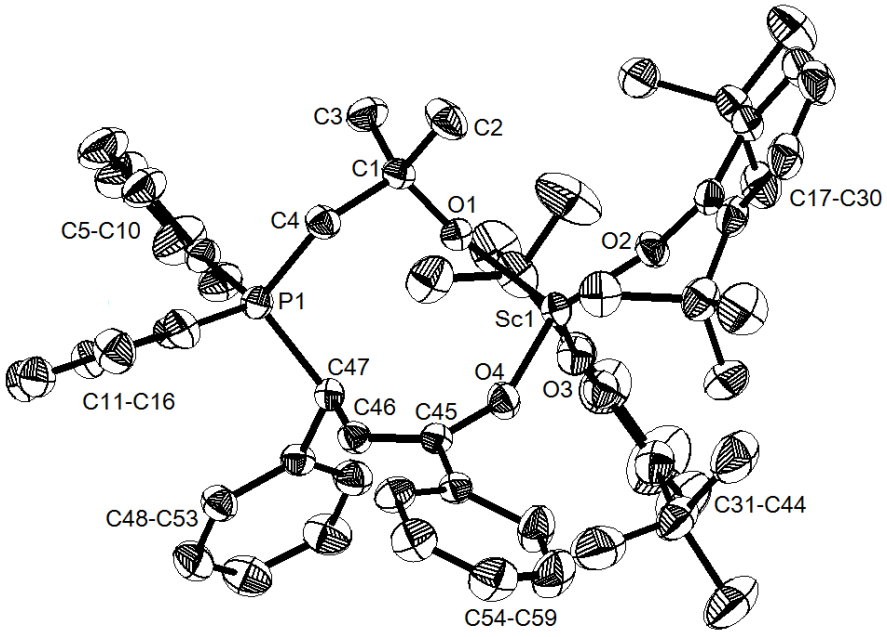
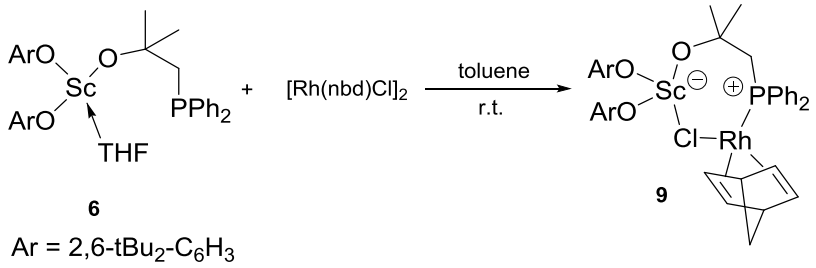


Fig S16. Crystal structure of complex **8**.

Preparation of complex 9:



6

Ar = 2,6-tBu_2-C_6H_3

9

Scheme S5.

Following the procedure described for **7**, reaction of complex **6** (89 mg, 0.11 mmol) and $[Rh(nbd)Cl]_2$ (26 mg, 0.06 mmol) gave complex **9** as a yellow crystalline solid (80 mg, 75%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of hexane into a solution of complex **9** in toluene at room temperature.

Elemental Analysis: calcd. for $C_{51}H_{68}O_3PClRhSc$: C, 64.93; H, 7.27. Found: C, 65.54; H, 7.22.

^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ = 7.43 (4H, *o*), 7.18 (4H, *m*), 7.17 (2H, *p*), (each m, *Ph*$_2$P), 7.22 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*), 6.71 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*) (O*Ar*), 3.99 (br, 4H, =C*H*^{nbd}), 3.27 (s, 2H, C*H*^{nbd}), 2.63 (d, $^2J_{PH}$ = 10.3 Hz, 2H, PCH_2), 1.58 (s, 36H, C(CH_3)$_3$), 1.41 (s, 6H, OC(CH_3)$_2$), 0.78 (s, 2H, CH_2^{nbd}).

^{13}C {^{1}H} NMR (101 MHz, C_6D_5Br, 298 K): δ = 162.3 (*i*), 138.5 (*o*), 125.0 (*m*), 117.5 (*p*) (O*Ar*), 133.6 (d, $^2J_{PC}$ = 11.4 Hz, *o*), 130.0 (overlapped with solvent, *p*), 128.5 (*m*) n.o. (*i*), (*Ph*$_2$P), 72.8 (d, $^2J_{PC}$ = 7.3 Hz, O*C*(CH$_3$)$_2$), n. o. (=*C*H^{nbd}), 63.0 (*C*H$_2^{nbd}$), 51.1 (*C*H^{nbd}), 47.4 (P*C*H$_2$)[1], 35.4 (*C*(CH$_3$)$_3$), 35.0 (d, $^3J_{PC}$ = 4.8 Hz, OC(*C*H$_3$)$_2$), 32.0 (C(*C*H$_3$)$_3$) [[1]from the GHSQC experiment] [n.o.: not observed].

^{31}P {^{1}H} NMR (162 MHz, C_6D_5Br, 298 K): δ = 20.5 (d, $^1J_{RhP}$ = 164.7 Hz).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_5Br, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.43 / 7.18 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.22 / 6.71 (*m*-O*Ar* / *p*-O*Ar*), 3.99 / 3.27 (=C*H*^{nbd} / C*H*^{nbd}), 3.27 / 0.78 (C*H*^{nbd} / CH_2^{nbd}).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_5Br, 298 K): δ ^{1}H / δ ^{13}C = 7.43 / 133.6 (*o*-*Ph*$_2$P), 7.22 / 125.0 (*m*-O*Ar*), 7.18 / 128.5 (*m*-*Ph*$_2$P), 7.17 / 130.0 (*p*-*Ph*$_2$P), 6.71 /

117.5 (*p*-O*Ar*), 3.27 / 51.1 (CH^{nbd}), 2.63 / 47.4 (PCH_2), 1.58 / 32.0 ($C(CH_3)_3$), 1.41 / 35.0 ($OC(CH_3)_2$), 0.78 / 63.0 (CH_2^{nbd}).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_5Br, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.43 / 130.0 (*o*-Ph_2P / *p*-Ph_2P), 7.22 / 162.3, 35.4 (*m*-O*Ar* / *i*-O*Ar*, $C(CH_3)_3$), 6.71 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 1.58 / 138.5 ($C(CH_3)_3$ / *o*-O*Ar*), 1.41 / 72.8 ($OC(CH_3)_2$ / $OC(CH_3)_2$).

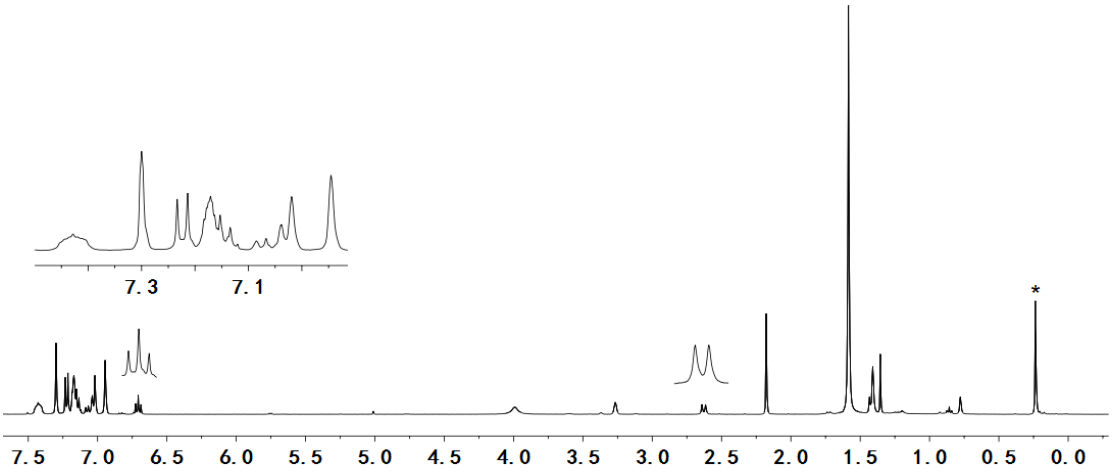


Fig S17. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K) [*: Silicone grease]

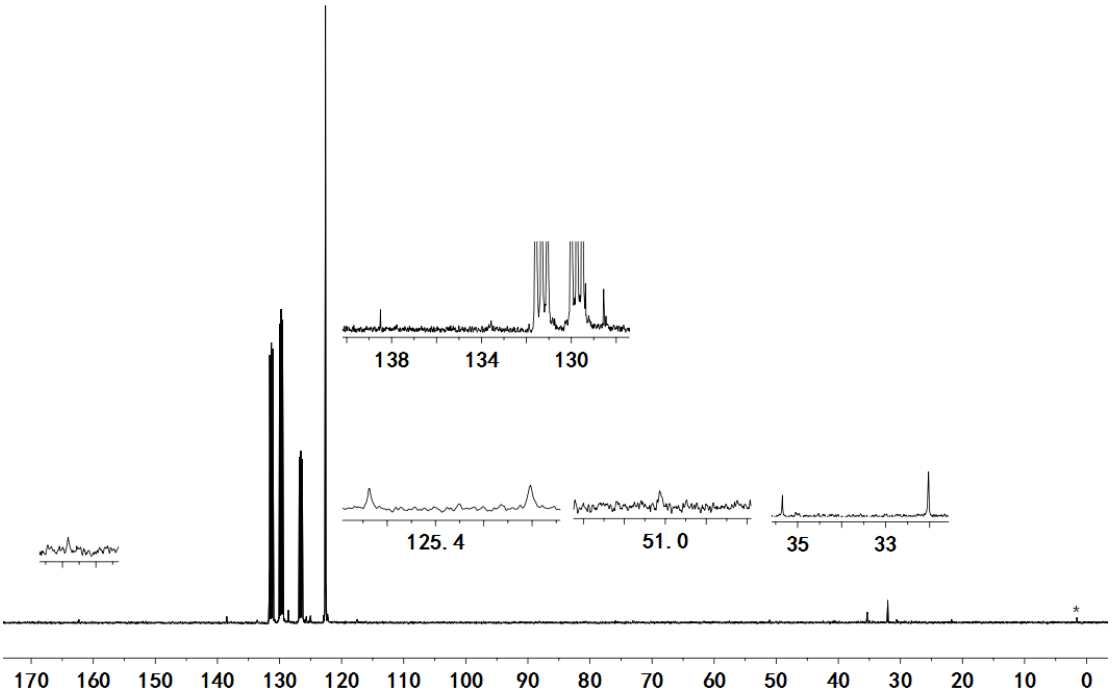


Fig S18. ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, 298 K) [*: Silicone grease]

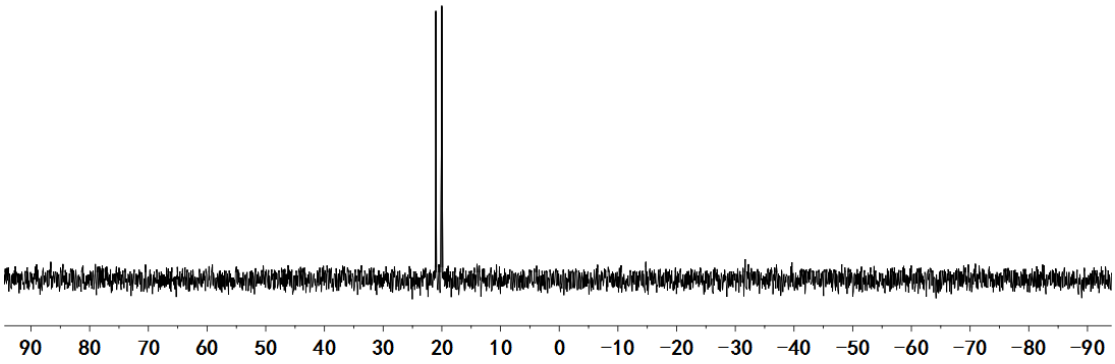


Fig S19. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_5Br, 298 K)

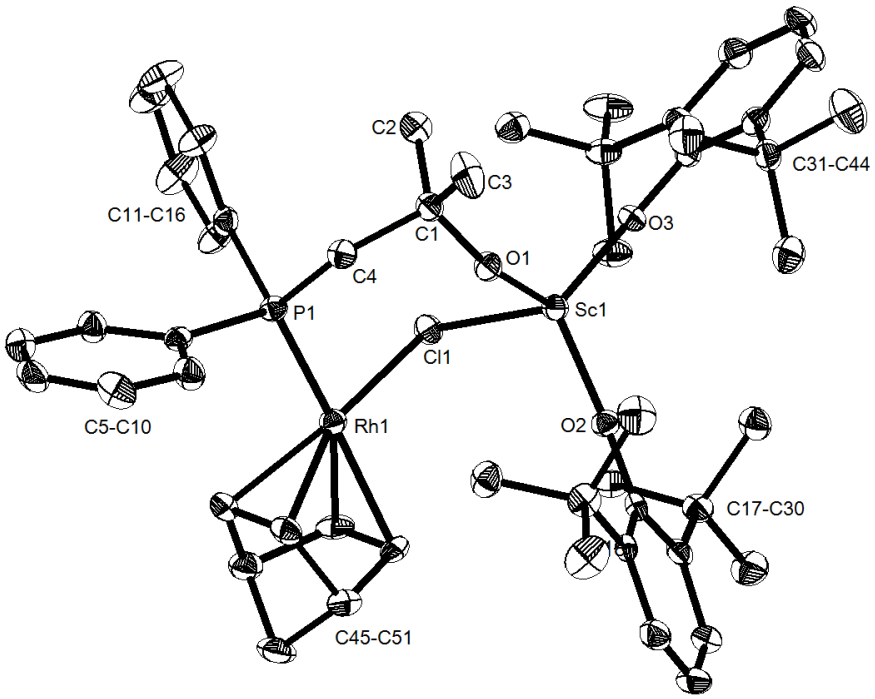
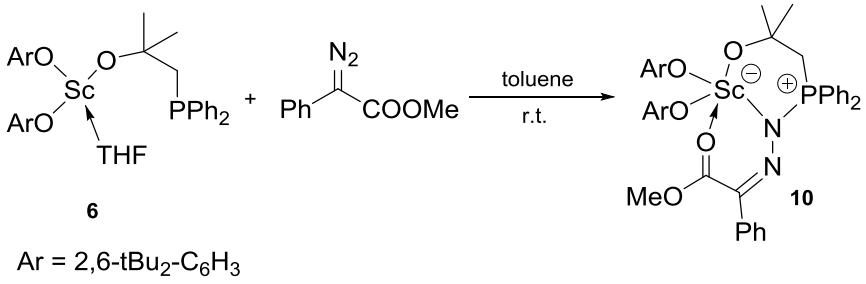


Fig S20. Crystal structure of complex **9**.

Preparation of complex 10:



Scheme S6.

Following the procedure described for **7**, reaction of complex **6** (100 mg, 0.13 mmol) and methyl diazophenylacetate (23 mg, 0.13 mmol) gave complex **10** as a yellow solid (105 mg, 93%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -35°C.

Elemental Analysis: calcd. for $C_{53}H_{68}N_2O_5PSc$: C, 71.60; H, 7.71; N, 3.15. Found: C, 71.40; H, 8.42; N, 2.76.

^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 7.37 (m, 4H, *m*), 6.83 (*m*, 2H, *p*) (O*Ar*), 7.33 (2H, *o*), 7.31 (1H, *p*), 6.77 (2H, *m*) (each m, N=C*Ph*), 6.95 (4H, *m*), 6.94 (2H, *p*), 6.80 (4H, *o*) (each m, *Ph*$_2$P), 3.12 (d, $^2J_{PH}$ = 8.8 Hz, 2H, PC*H*$_2$), 3.02 (s, 3H, COOC*H*$_3$), 1.67 (s, 36H, C(C*H*$_3$)$_3$), 1.44 (s, 6H, OC(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 174.0 (*C*OOCH$_3$), 164.0 (*i*), 138.5 (*o*), 125.3 (*m*), 116.3 (*p*) (O*Ar*), 145.3 (d, $^3J_{PC}$ = 40.0 Hz, N=*C*), 132.1 (d, $^3J_{PC}$ = 9.7 Hz, *m*), 130.4 (d, $^1J_{PC}$ = 106.6 Hz, *i*)^t, 130.1 (*p*), 129.0 (d, $^2J_{PC}$ = 12.1 Hz, *o*) (*Ph*$_2$P), 132.2 (*o*), 131.9 (d, $^4J_{PC}$ = 2.3 Hz, *i*), 129.8 (*p*)^t, 128.7 (*m*), (N=C*Ph*), 74.9 (d, $^2J_{PC}$ = 4.9 Hz, O*C*(CH$_3$)$_2$), 54.9 (COO*C*H$_3$), 46.2 (d, $^1J_{PC}$ = 37.4 Hz, P*C*H$_2$), 35.7 (*C*(CH$_3$)$_3$), 33.5 (d, $^3J_{PC}$ = 9.3 Hz, OC(*C*H$_3$)$_2$), 32.7 (C(*C*H$_3$)$_3$). [^{t} tentative assignment]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ = 15.5 ($\nu_{1/2}$ ~ 8 Hz)

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.37 / 6.83 (*m*-O*Ar* / *p*-O*Ar*), 6.80 /6.95 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 6.77 /7.33 (*m*-N=C*Ph* / *o*-N=C*Ph*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.37 / 125.3 (*m*-O*Ar*), 7.33 / 132.2 (*o*-N=C*Ph*), 6.95 / 132.1 (*m*-*Ph*$_2$P), 6.83 / 116.3

(*p*-O*Ar*), 6.80 / 129.0 (*o*-*Ph*$_2$P), 3.02 / 54.9 (N=COO*CH*$_3$), 3.12 / 46.2 (P*CH*$_2$), 1.67 / 32.7 (C(*CH*$_3$)$_3$), 1.44 / 33.5 (OC(*CH*$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.37 / 164.0, 125.3, 35.7 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.94 / 129.0 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P). 6.83 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 3.12 / 130.4, 74.9, 33.5 (P*CH*$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 3.02 / 174.0, 145.3 (N=COOC*H*$_3$ / N=C*C*OOCH$_3$, N=*C*COOCH$_3$), 1.67 / 138.5, 125.3, 35.7 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 1.44 / 74.9, 46.2 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

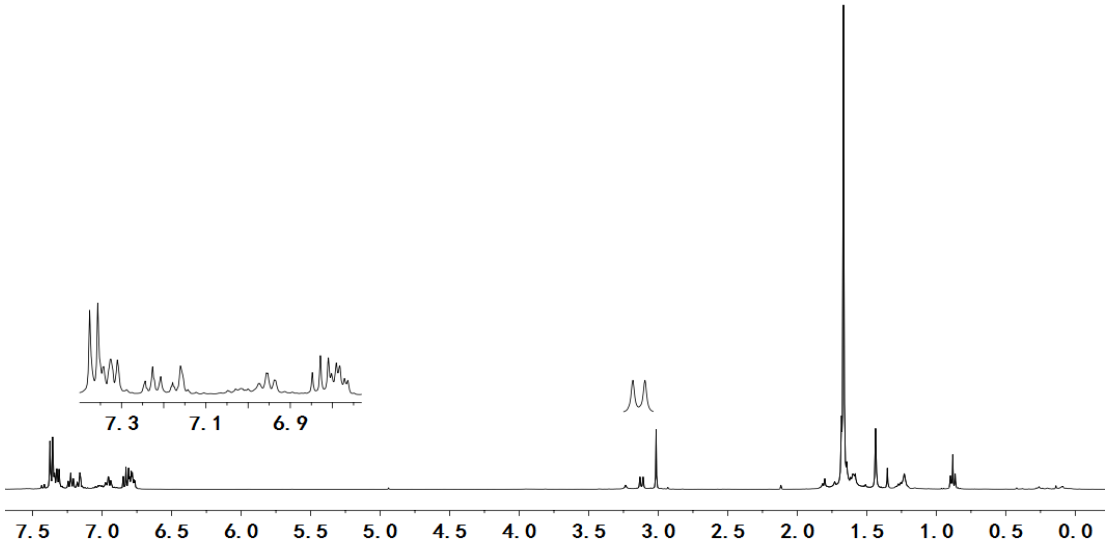


Fig S21. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

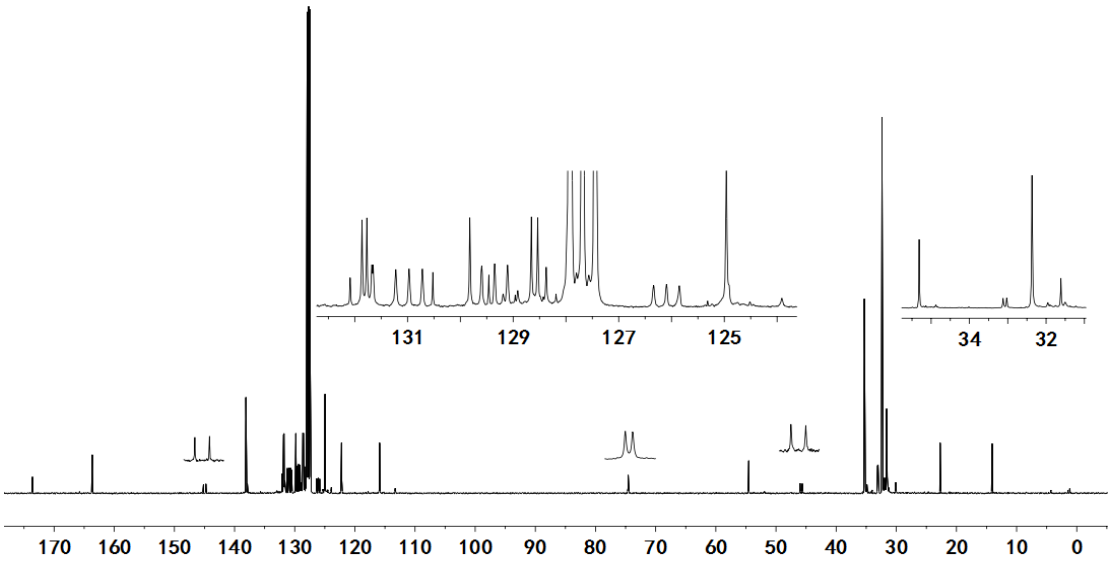


Fig S22. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

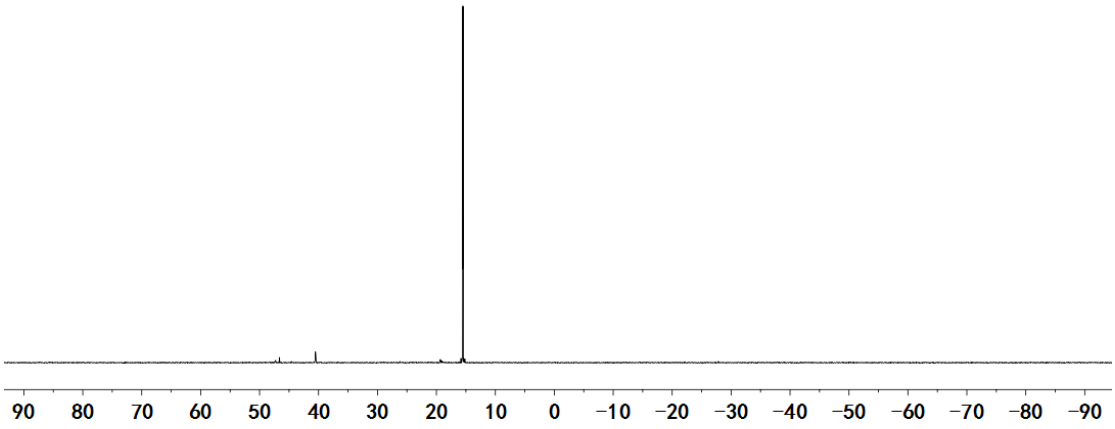


Fig S23. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K)

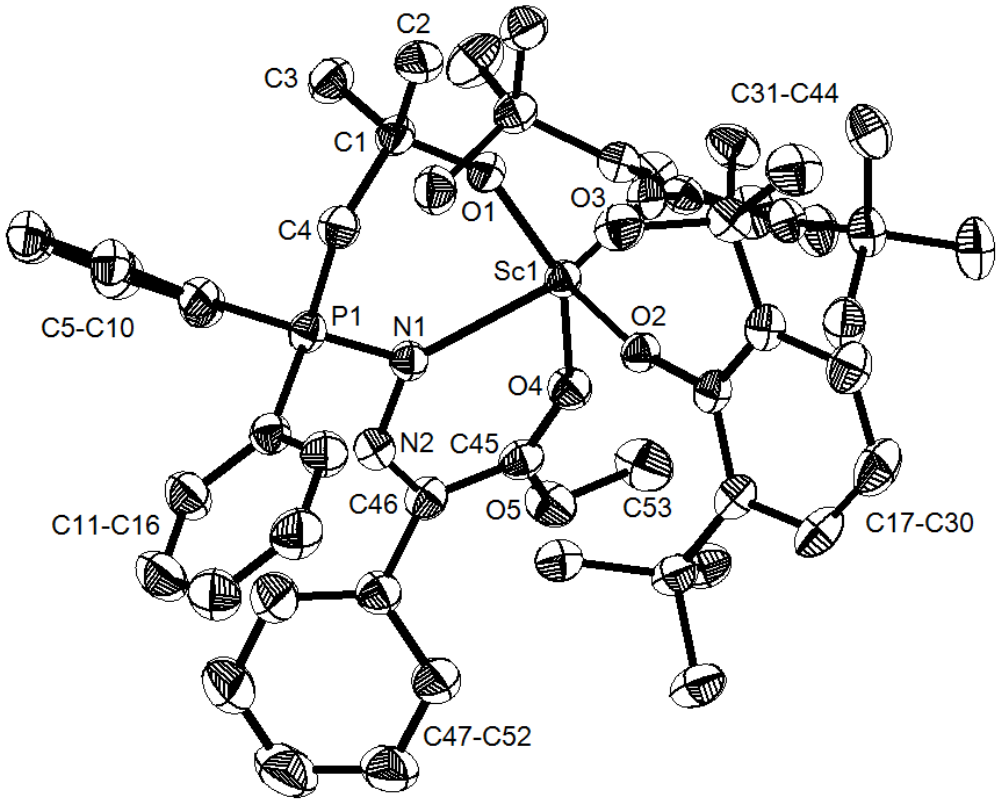


Fig S24. Crystal structure of complex **10**.