Supporting Information

Functionalization of 1,3-diphosphacyclobutadiene cobalt complexes via Si–P bond insertion

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The supporting information contains:

(S1) $^{31}P\{^{1}H\}$ NMR spectra of 6–8

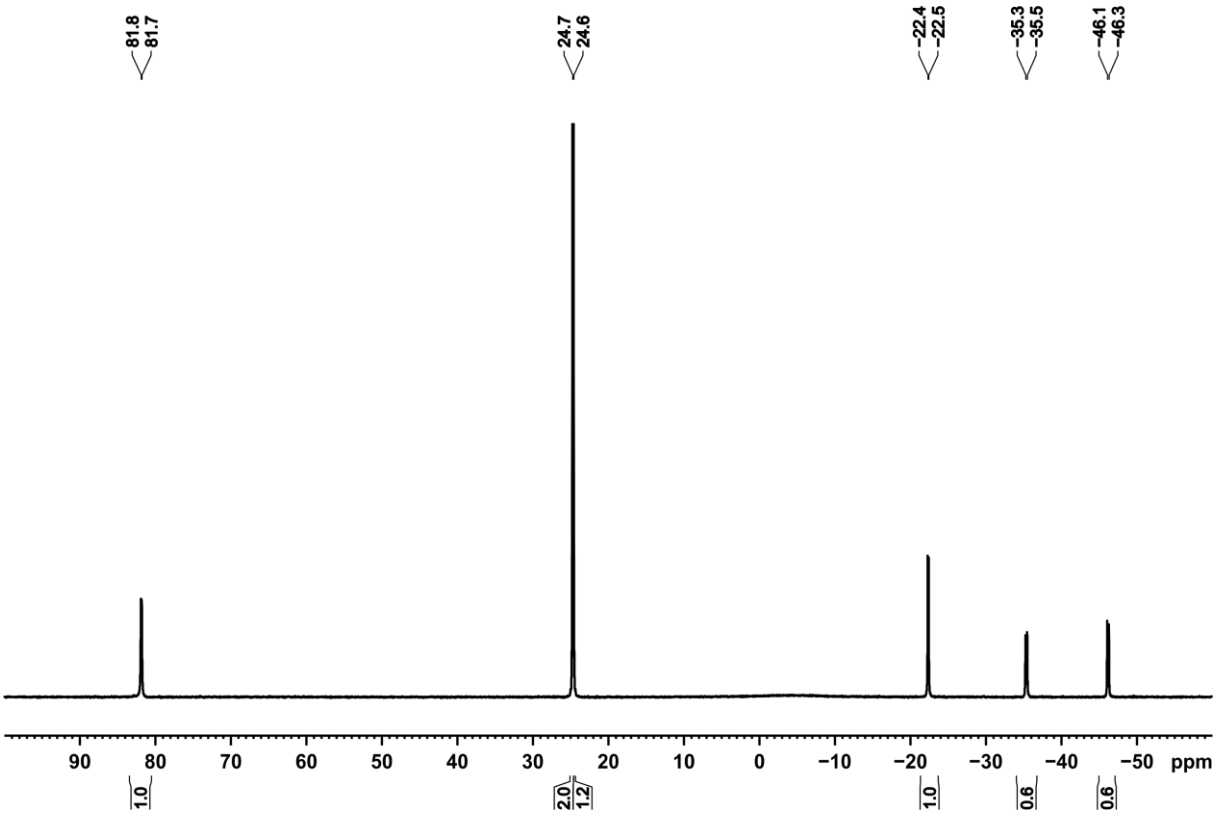

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (161.49 Mhz, C_6D_6, 300 K) of **6/6'**.

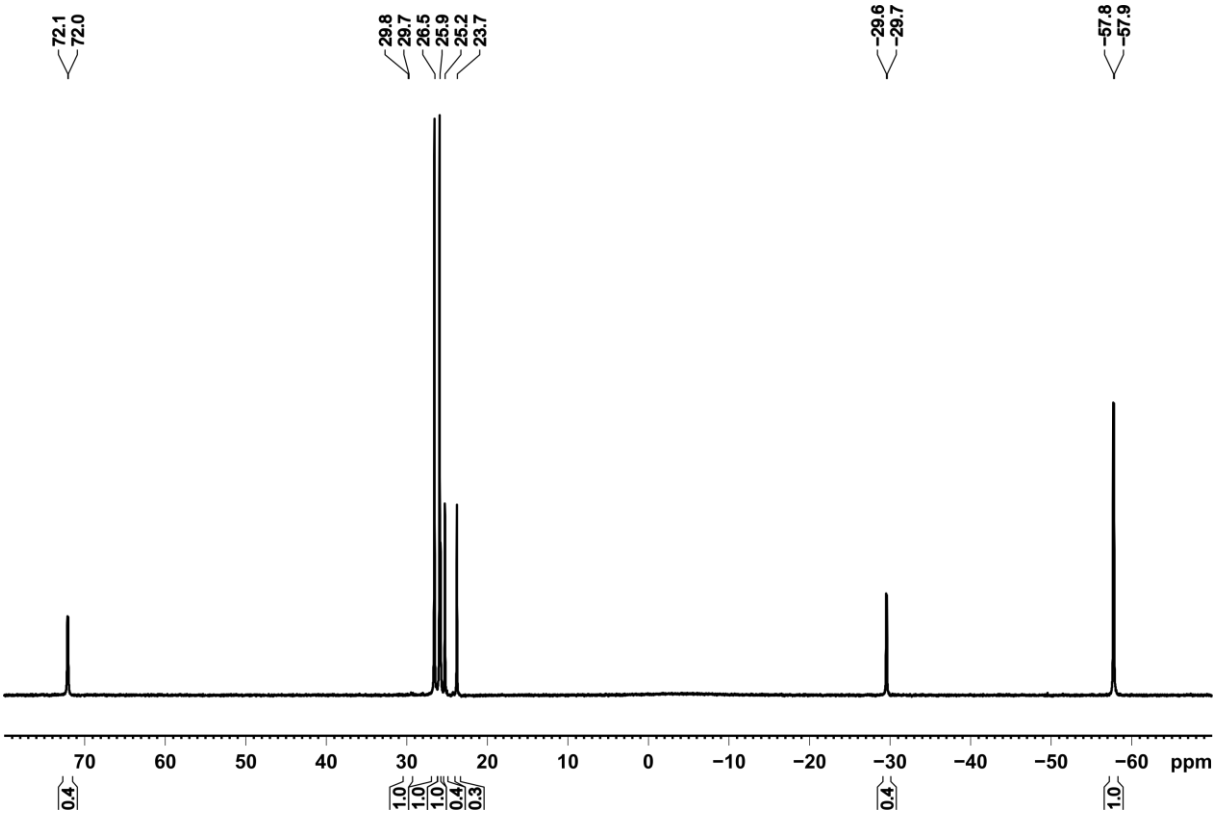

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (161.49 Mhz, C_6D_6, 300 K) of **7/7'**.

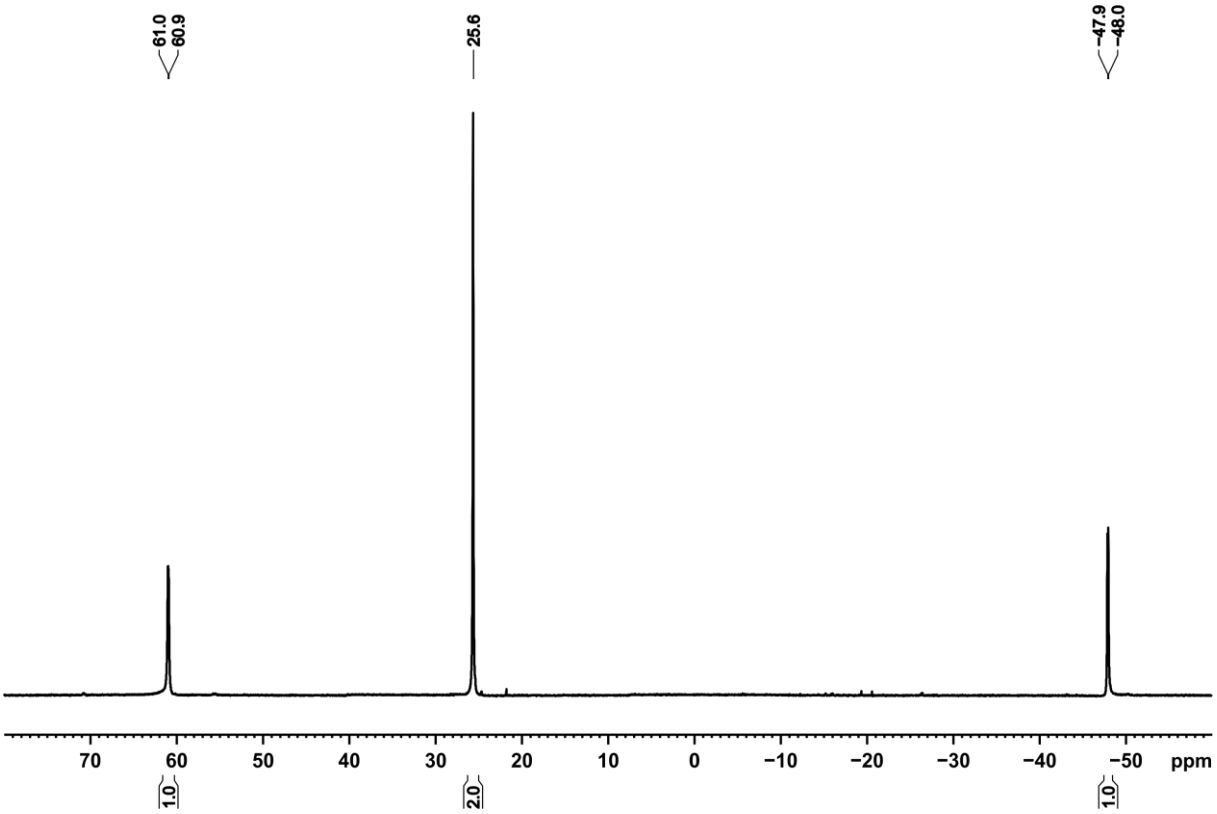

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (161.49 Mhz, C_6D_6, 300 K) of **8**.

(S2) UV/Vis spectra

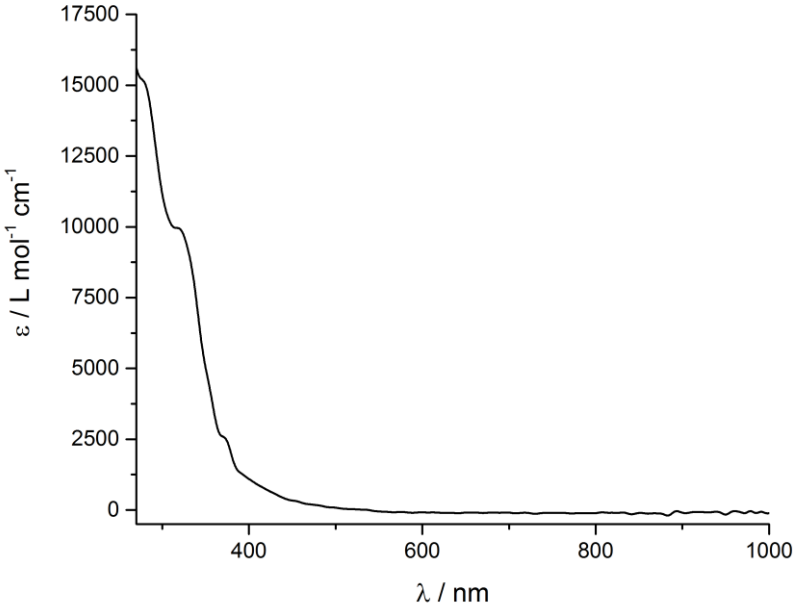

Figure S4. UV/Vis spectrum of **2a** in *n*-hexane.

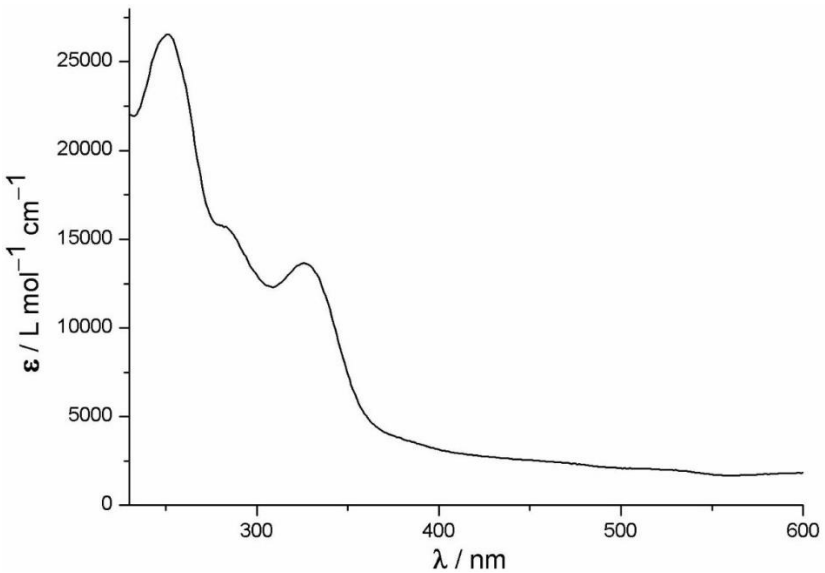

Figure S5. UV/Vis spectrum of **2b** in *n*-hexane.

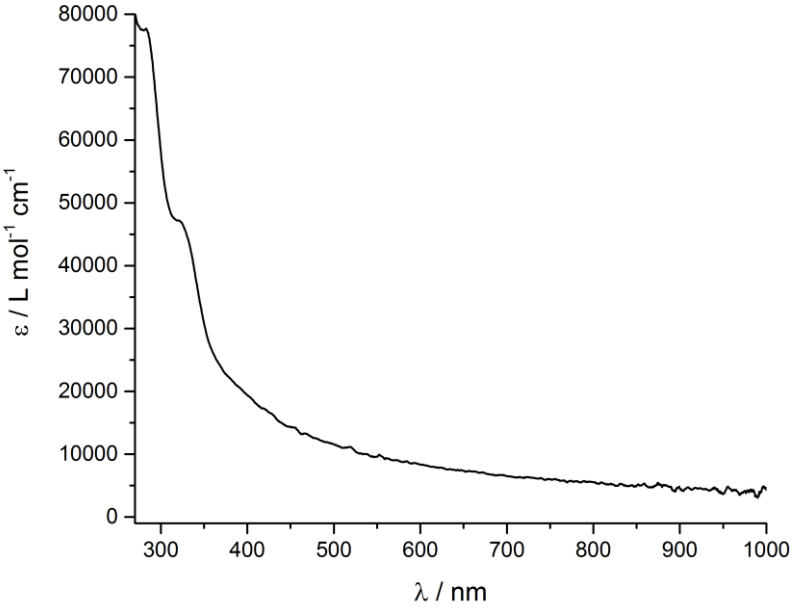

Figure S6. UV/Vis spectrum of **4** in THF.

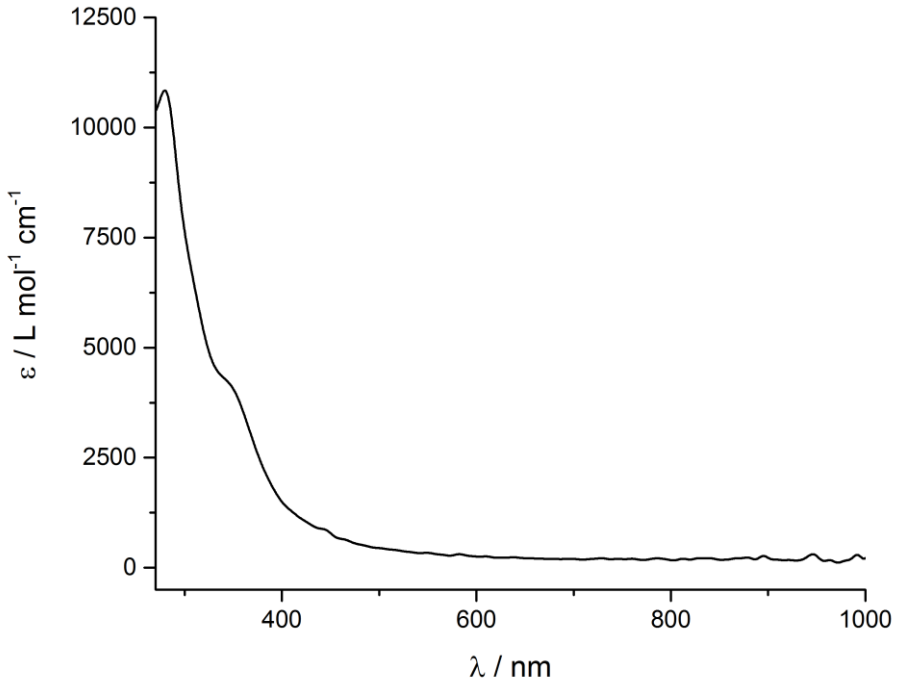

Figure S7. UV/Vis spectrum of **5** in *n*-hexane.

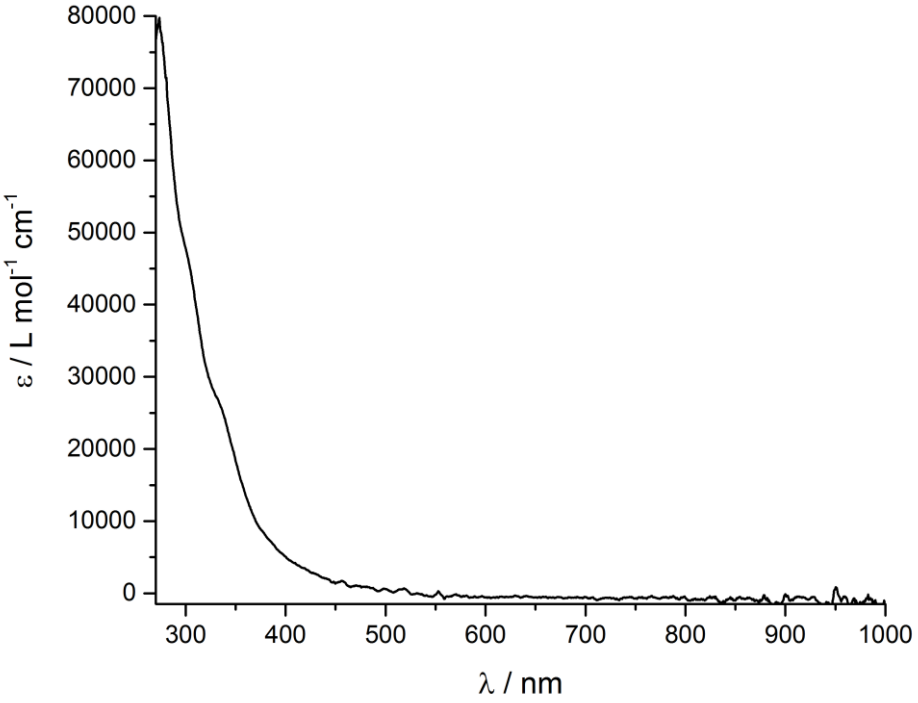

Figure S8. UV/Vis spectrum of **9** in *n*-hexane.

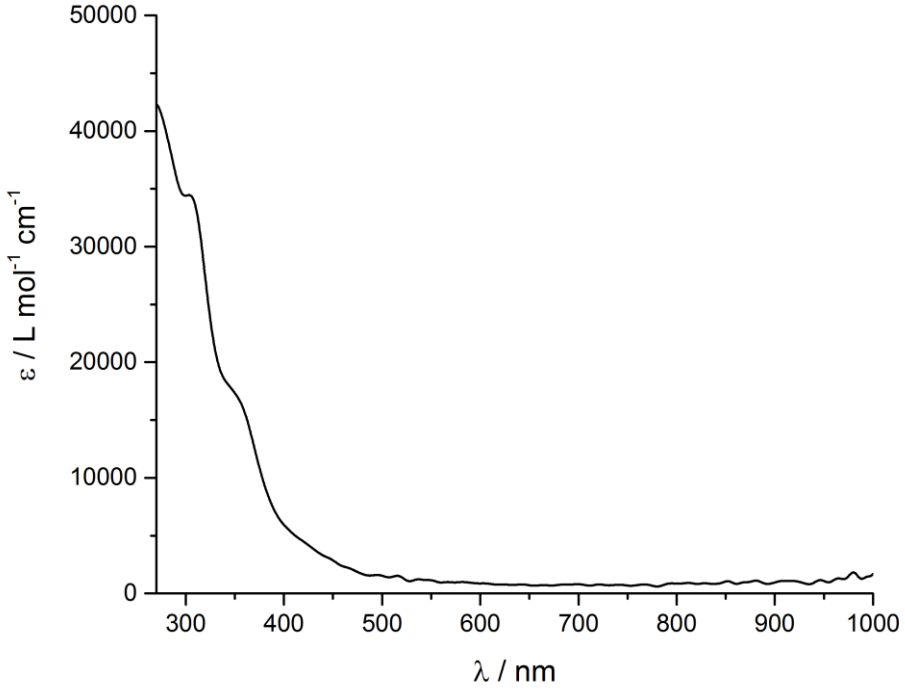

Figure S9. UV/Vis spectrum of **10** in *n*-hexane.

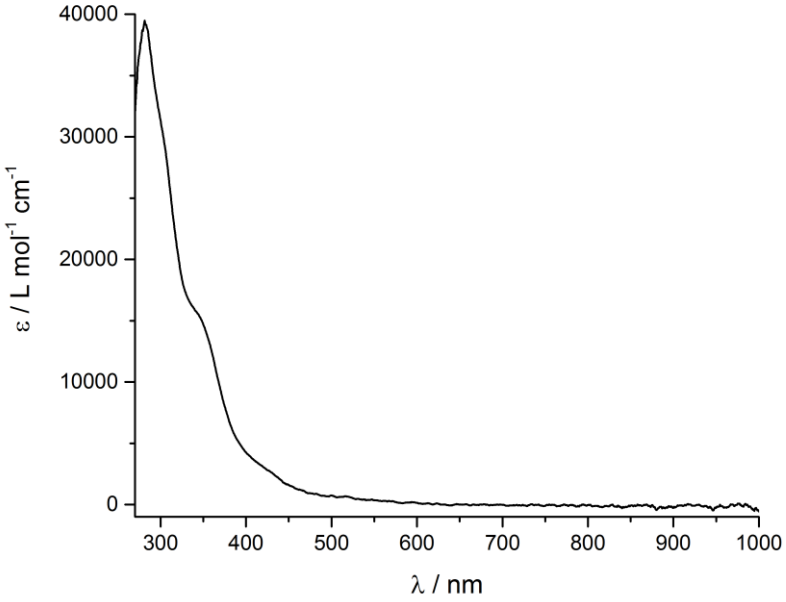

Figure S10. UV/Vis spectrum of **11** in *n*-hexane.

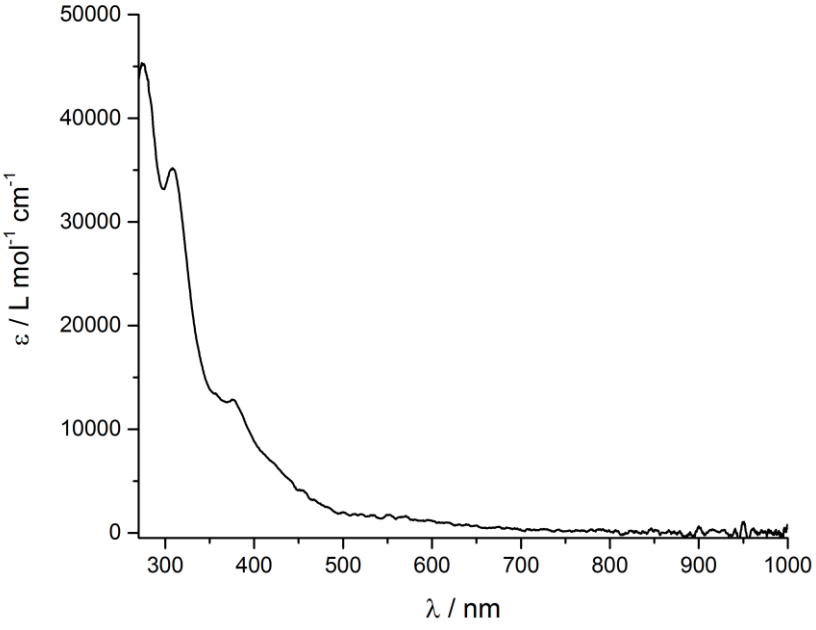

Figure S11. UV/Vis spectrum of **12** in *n*-hexane.

(S3) IR(ATR) spectra

Infrared spectra were recorded with an Agilent Cary 670 FTIR spectrometer.

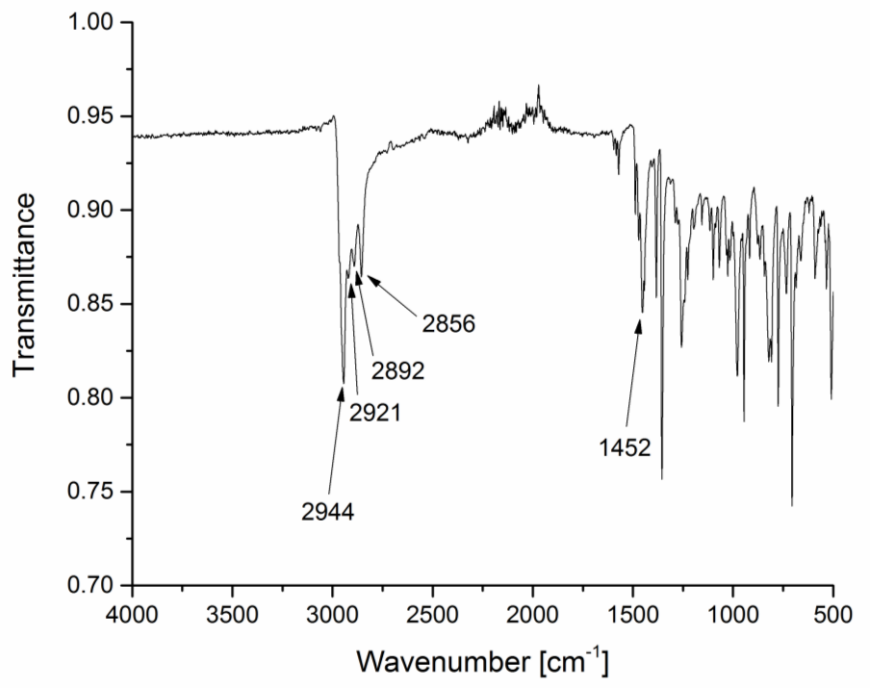

Figure S12. IR(ATR) spectrum of **5**.

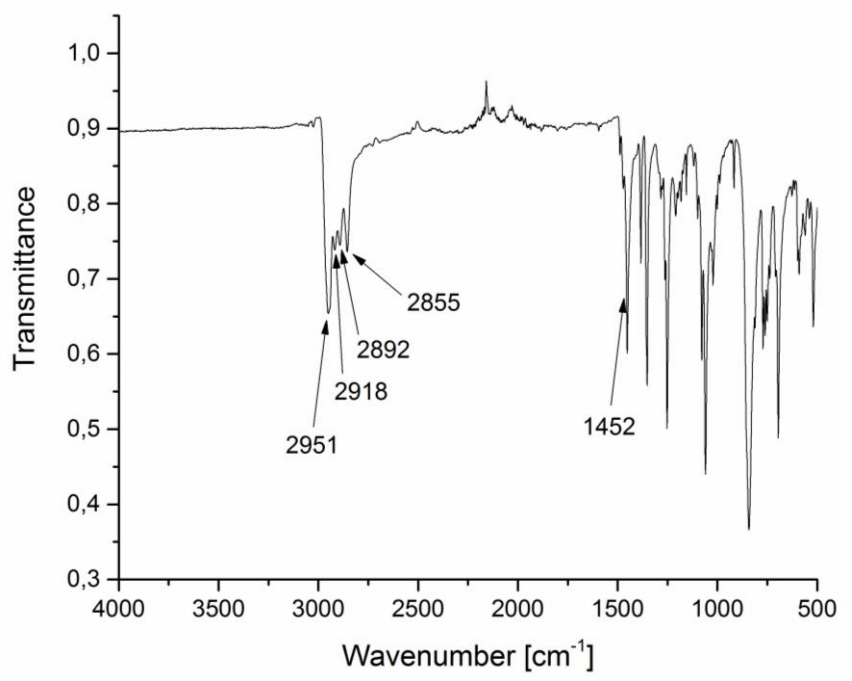

Figure S13. IR(ATR) spectrum of **10**.

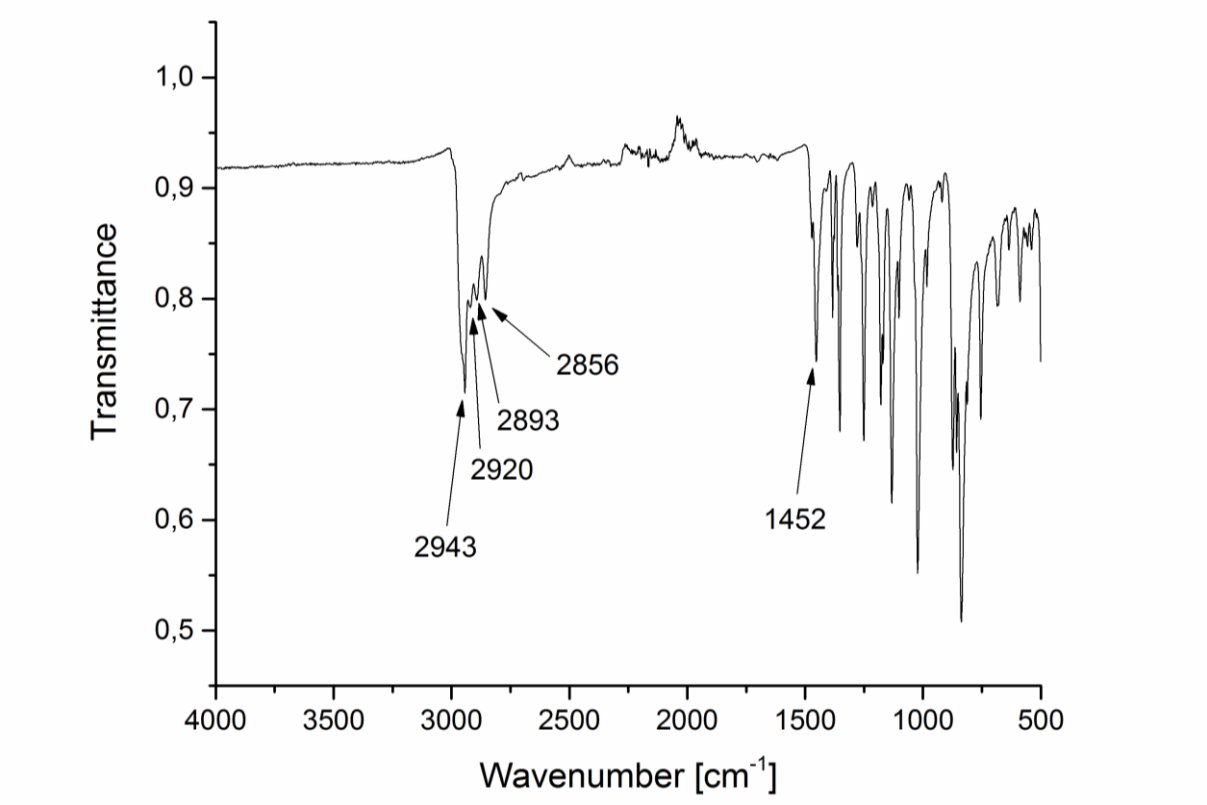

Figure S14. IR(ATR) spectrum of **11**.

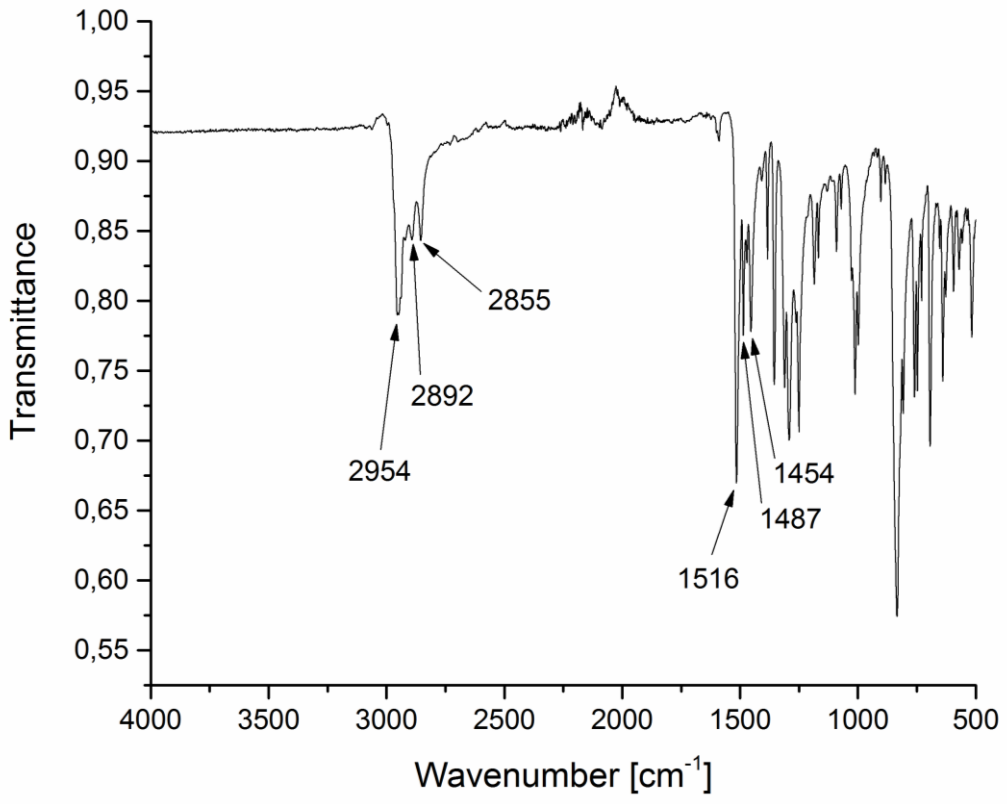

Figure S15. IR(ATR) spectrum of **12**.

(S4) Crystallographic data of 2b

The crystals were processed with an Agilent Technologies SuperNova device. Multi-scan absorption correction[1, 2] was applied to the data. The structure was solved by SHELXS[3] and least-square refinements on F^2 were carried out with SHELXL.[4] Crystallographic data are given in Table 1.

CCDC 1849351 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

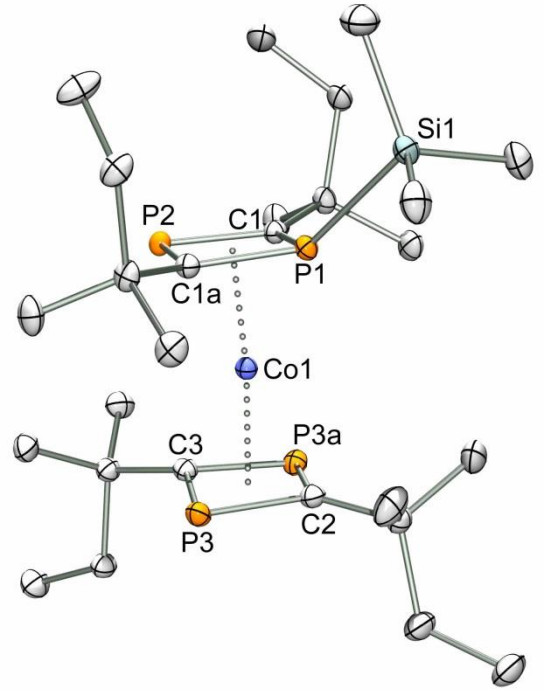

Figure S16. Solid-state molecular structure of [Co(η^4-P_2C_2tPent$_2$SiMe$_3$)(η^4-P_2C_2tPent$_2$)] (**2b**). Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C1–P1 1.784(2), C1–P2 1.794(2), C1a–P1 1.784(2), C1a–P2 1.794(2), C2–P3 1.796(2), C3–P3 1.801(2), Co1–P1 2.1866(6), Co1–P2 2.2651(6), Co1–P3 2.2570(6), Co1–P3a 2.2570(6); Co1–C1 2.118(2), Co1–C1a 2.118(2), Co1–C2 2.080(2), Co1–C3 2.073(2), Co1–C4 2.070(3), P1–Si1 2.2893(8), C1–P1–C1a 84.42(7), C1–P2–C1a 83.84(7), Si1–P1–C1 127.20(5), Si1–P1–C1a 127.20(5), P1–C1–P2 95.81(7), P1–C1a–P2 95.81(7), C2–P3–C3 80.71(8), C2–P3a–C3 80.71(8), P3–C2–P3a 99.3(1), P3–C3–P3a 98.9(1).

Table S1. Crystallographic data and structure refinement of **2b**.

	2b
Empirical formula	$C_{27}H_{53}CoP_4Si$
Crystal size [mm^3]	0.2067 x 0.1618 x 0.1027
Color and shape	yellow blocks
Formula weight [g mol^{-1}]	588.59
Crystal system	orthorhombic
Space group	*Pnma*
Absorption correction	multi-scan
Transmission min/max	1.000/0.359
a [Å]	16.9382(3)
b [Å]	11.0030(2)
c [Å]	17.2884(2)
V [$Å^3$]	3222.06(9)
Z	4
T [K]	123.0(2)
λ [Å]	1.54178
ρ_{calc} [g/cm^3]	1.21
μ (mm^{-1})	6.5
Theta range [°]	7.306–147.16
Reflections collected to θ_{max} [°]	17036
Unique reflections (R_{int})	3321 (0.033)
Refl. obs. [$I > 2\sigma(I)$]	3051
Parameters	176
Completeness to θ	0.992
R-values [$I > 2\sigma(I)$]	0.0641/0.0272
R-values (all data)	0.0660/0.0311
GOF on F^2	1.037
Residual density [$eÅ^{-3}$]	–0.25/0.28

(S5) References

[1] SCALE3ABS, CrysAlisPro, Aglient Technologies Inc., Oxford, GB, **2015**.

[2] G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, **2007**.

[3] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[4] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.