Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Heterolytic carbon–iodine bond cleavage by a palladium(I) metalloradical

Table of contents

1. General experimental methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C *in vacuo* overnight. 1,2-Difluorobenzene (DFB) was stirred over neutral aluminium oxide, filtered, dried over CaH_2, vacuum distilled, freeze-pump-thaw degassed, and then stored over activated 3 Å molecular sieves.[1] Commercial anhydrous CH_2Cl_2, pentane, and hexane were freeze-pump-thaw degassed and stored over activated 3 Å molecular sieves. Phenyl iodide, 2-methoxyphenyl iodide and *tert*-butyl iodide were freeze-pump-thaw degassed and stored over activated 3 Å molecular sieves. $[Pd(P\mathit{t}Bu_3)_2][PF_6]$ **1**[2] and $[Pd(P\mathit{t}Bu_3)(\mu\text{-}I)]_2$ **2**[3] were prepared using literature procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. Coupling constants for virtual triplets are reported as the separation between the first and third lines.[4] NMR spectra in DFB were recorded using an internal capillary of C_6D_6.[1] ^{31}P NMR spectra are referenced to a solution of $O{=}P(OMe)_3$ in C_6D_6 (0.025 mol·L^{-1}, δ 3.80 relative to 85% H_3PO_4). UV-vis spectra were recorded on an Agilent Cary 3500 UV-vis Spectrometer Compact Peltier System. HR ESI-MS were recorded on a Bruker MaXis mass spectrometer.

2. Reactions of [Pd(P*t*Bu₃)₂][PF₆] 1

2.1. General procedure

To a solution of **1** (6.6 mg, 10 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was added the substrate at RT. The resulting solution was monitored using ^1H and ^{31}P NMR spectroscopy, with constant mixing when not in the spectrometer. The concentration of **1** can be monitored by a broad paramagnetically shifted ^1H resonance at δ 19 in DFB.

Table S1. ^{31}P NMR data in DFB solution (excluding anion).

Compound	$\boldsymbol{\delta_{31P}}$	**Comment**
$[Pd(P\mathit{t}Bu_3)_2]$	84.8	Isolated (commercial)
$[Pd(P\mathit{t}Bu_3)_2][PF_6]$ **1**	No signal	Isolated (literature)
$[Pd(P\mathit{t}Bu_3)(\mu\text{-}I)]_2$ **2**	103.5	Isolated (literature)
$[Pd(P\mathit{t}Bu_3)_2(Ph)][PF_6]$ **4a**	61.0	Observed *in situ* (new)
$[Pd(P\mathit{t}Bu_3)_2(2\text{-}(MeO)C_6H_4)][PF_6]$ **4b**	62.0	Isolated (new)
$[Pd(P\mathit{t}Bu_3)_2(2,6\text{-}(MeO)_2C_6H_3)][PF_6]$ **4c**	65.3	Isolated (new)
$P\mathit{t}Bu_3$	62.9	Isolated (commercial)
$[P\mathit{t}Bu_3H][PF_6]$	56.0	Isolated (literature)
$[P\mathit{t}Bu_3I]I$	114.7	Generated *in situ* (literature)
$[P\mathit{t}Bu_3Ph][PF_6]$ **3a**	49.7	Isolated (literature)
$[P\mathit{t}Bu_3(2\text{-}(MeO)C_6H_4)][PF_6]$ **3b**	64.2	Generated *in situ* (literature)
$[P\mathit{t}Bu_3Ad][PF_6]$ **3d**	49.9	Generated *in situ* (literature)

2.2. Phenyl iodide

2.2.1. 1.1 equivalents monitored by NMR spectroscopy

Following the general procedure using PhI (1.2 µL, 11 µmol). Complete consumption of **1** was observed by ^{1}H NMR spectroscopy within 24 h at RT. At this point, formation of [Pd(P*t*Bu$_3$)(*µ*-I)]$_2$ **2** and [P*t*Bu$_3$Ph]$^+$ **3a** in a 1:2 mixture (>97% selectivity) was observed by ^{31}P NMR spectroscopy. Phenyl phosphonium **3a** was subsequently isolated as a white solid by successive recrystallisation from DFB/hexane, pyridine/hexane and finally CH$_2$Cl$_2$/hexane at RT. Yield: 1.3 mg (3.1 µmol, 30%/Pd). Spectroscopic data is consistent with that reported for the corresponding triflate salt and the assignment is supported by determination of the solid-state structure and ESI-MS.[5]

^{31}P{^{1}H} NMR (162 MHz, DFB/C$_6$D$_6$): δ 49.7 (s, 1P, P*t*Bu$_3$Ph), -142.5 (sept, $^{1}J_{PF}$ = 710, 1P, PF$_6$).
HR ESI-MS (positive ion, 4 kV): 279.2238 ([*M*]$^+$, calcd 279.2236) *m/z*.

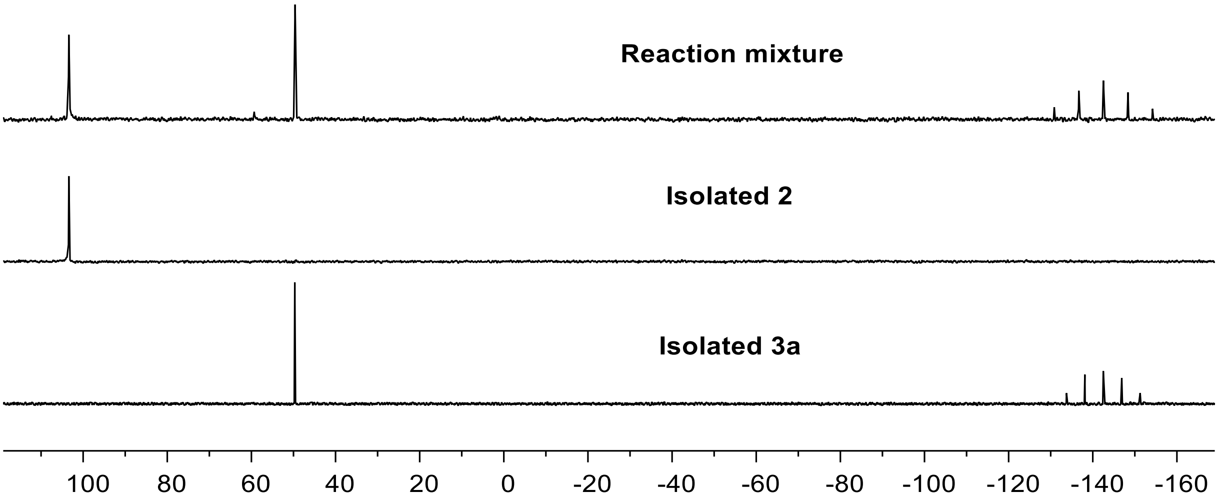

Figure S1. ^{31}P{^{1}H} NMR spectra of the products resulting from addition of 1.1 equivalents of PhI to **1** (DFB/C$_6$D$_6$, 162 MHz).

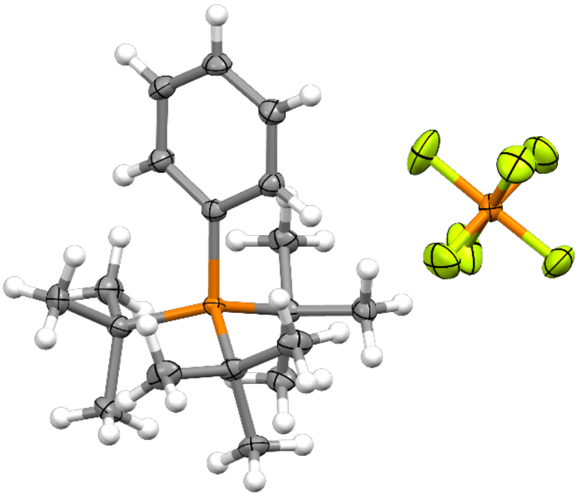

Figure S2. Solid-state structure of **3a**. Thermal ellipsoids at 50% probability.

2.2.2. 1.5 equivalents monitored by NMR spectroscopy

Following the general procedure using PhI (1.7 µL, 15 µmol). Complete consumption of **1** was observed by ^{1}H NMR spectroscopy within 3 h at RT. At this point, a 1:3:1 mixture of [Pd(P*t*Bu$_3$)(μ-I)]$_2$ **2**, [P*t*Bu$_3$Ph]$^+$ **3a**, and a species assigned to [Pd(P*t*Bu$_3$)$_2$(Ph)]$^+$ **4a** was observed by ^{31}P NMR spectroscopy, along with a trace amount of [P*t*Bu$_3$I]$^+$. After a further 2 h, decomposition of **4a** into **3a** gave a 1:4 mixture of **2** and **3a**, with trace amounts of [P*t*Bu$_3$H]$^+$.

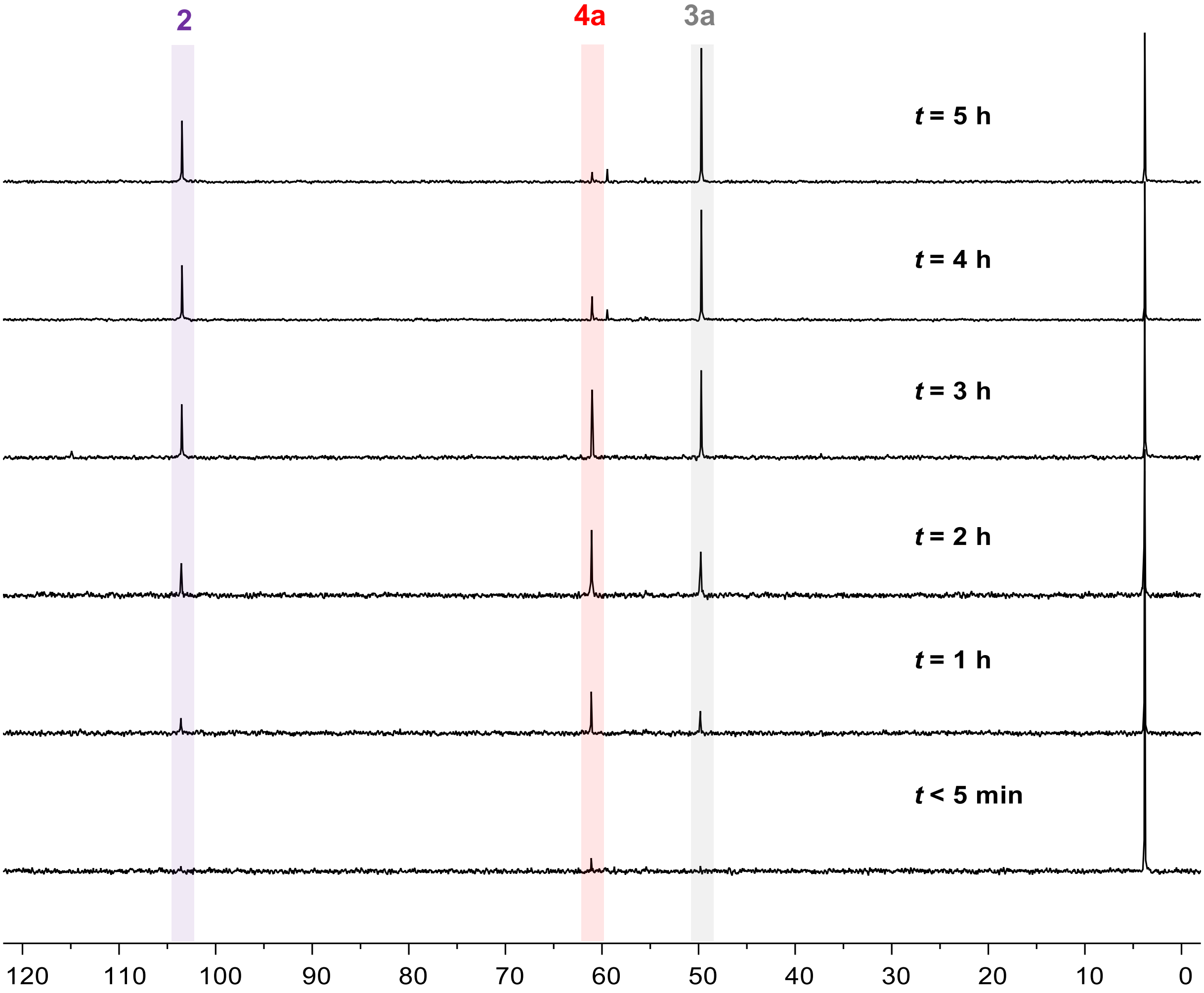

Figure S3. ^{31}P{^{1}H} NMR spectra collected following addition of 1.5 equivalents of PhI to **1** (DFB/C$_6$D$_6$, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

2.2.3. 1.5 equivalents in presence of excess phosphine monitored by NMR spectroscopy

Following the general procedure using PhI (1.7 µL, 15 µmol) and P*t*Bu$_3$ (70 µL of a 0.72 M solution in hexane, 50 µmol). Complete consumption of **1** was observed by ^{1}H NMR spectroscopy within 6 h at RT. At this point, a 1:3:3 mixture of [Pd(P*t*Bu$_3$)(*µ*-I)]$_2$ **2**, [P*t*Bu$_3$Ph]$^+$ **3a**, and [Pd(P*t*Bu$_3$)$_2$(Ph)]$^+$ **4a** was observed by ^{31}P NMR spectroscopy, with the signal for P*t*Bu$_3$ shifted to higher frequency and broadened. After a further 3 h, decomposition of **4a** into **3a** gave a 1:5 mixture of **2** and **3a**, with trace amounts of [P*t*Bu$_3$H]$^+$.

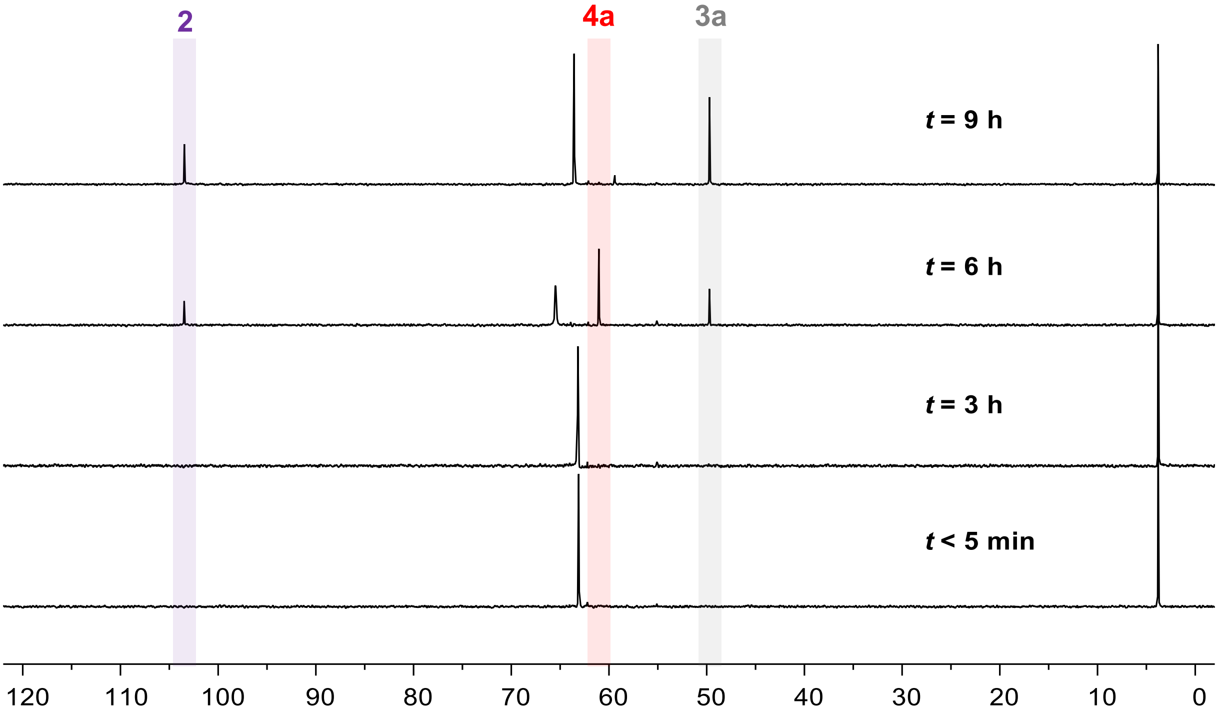

Figure S4. ^{31}P{^{1}H} NMR spectra collected following addition of 1.5 equivalents of PhI to **1** in the presence of excess P*t*Bu$_3$ (DFB/C$_6$D$_6$, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

2.2.4. 1.5 equivalents monitored by UV/vis spectroscopy

To a 6 mL glass screw top vial charged with **1** (26.2 mg, 40 µmol) and a magnetic stirrer bar in an inert atmosphere glove box was added a solution of PhI (2 mL, 0.03 mol L^{-1}, 60 µmol) in DFB. The vial was sealed and the solution stirred at RT for 6 h. The reaction was monitored every 30 minutes by taking 40 µL aliquots, which were diluted to 3 mL and analysed immediately by UV/vis spectroscopy. Concentrations of **1** and **2** were determined by least squares fitting of spectra recorded of isolated samples between 475 and 800 nm, whilst the concentration of **4a** was estimated using the background corrected absorption at 305 nm (maximum from residue, *cf.* **4b**/**4c**) and ε = 7000 L^{-1} mol^{-1} cm^{-1}. After 6 h, 0.5 mL of the solution was transferred into a J. Young valve NMR tube and analysed by ^{31}P NMR spectroscopy, which indicated formation of a 1:3 mixture of **2** and **3a**, with trace amounts of $[PtBu_3H]^+$.

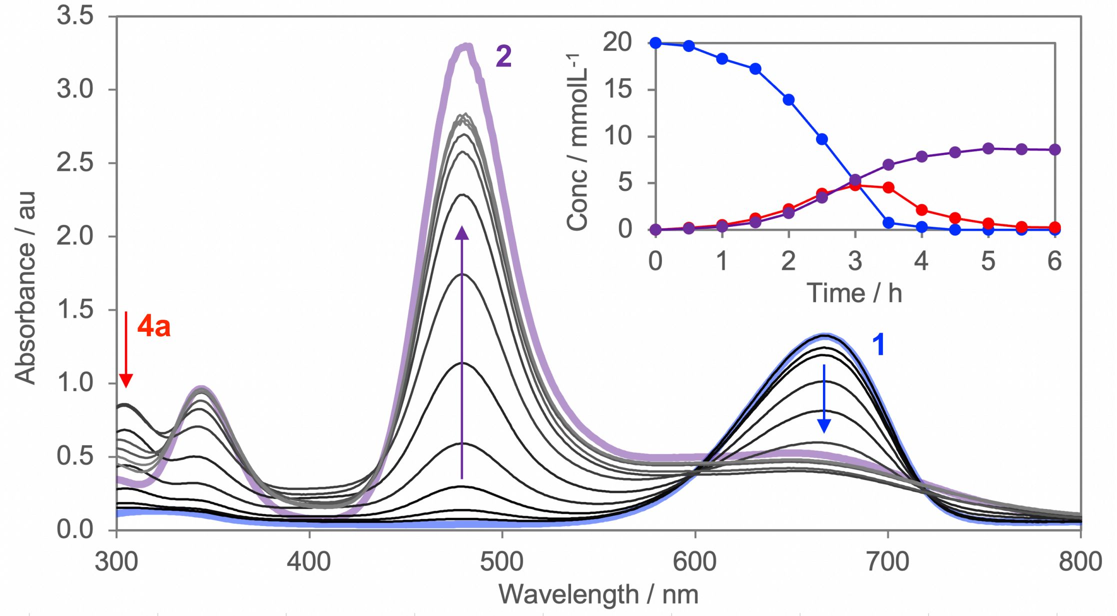

Figure S5. UV/vis spectra collected following addition of 1.5 equivalents of PhI to **1**, reference spectra of **1** (blue) and **2** (purple), and time course data for **1** (blue), **2** (purple) and **4a** (red).

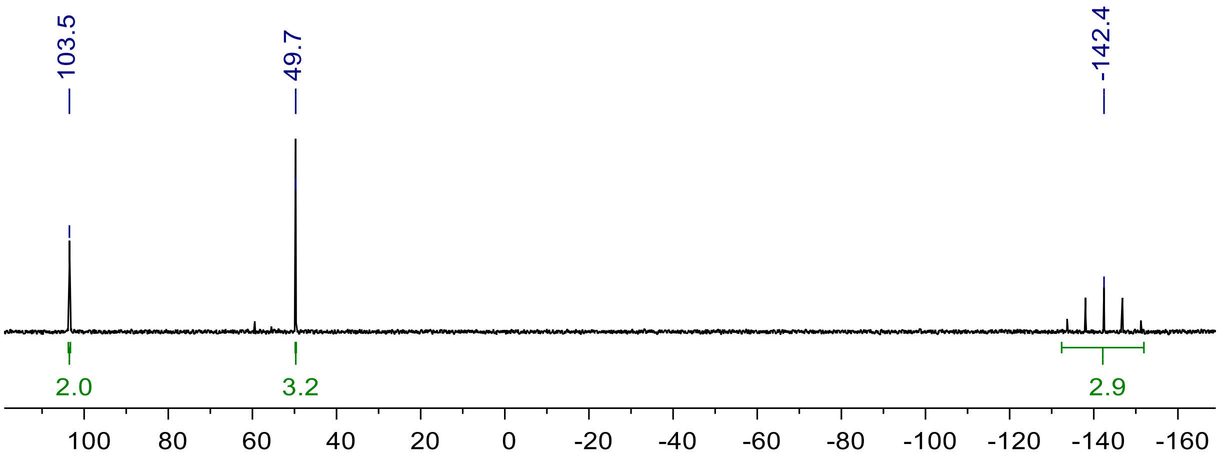

Figure S6. $^{31}P\{^1H\}$ NMR spectra of the products resulting from addition of 1.5 equivalents of PhI to **1** (DFB/C_6D_6, 162 MHz).

2.3. 2-methoxyphenyl iodide

Following the general procedure using 2-(MeO)C_6H_4I (2.0 µL, 15 µmol). Complete consumption of **1** was observed by ^{1}H NMR spectroscopy within 24 h at RT. At this point, a 1:2:2 mixture of [Pd(P*t*Bu_3)(*µ*-I)]$_2$ **2**, [Pd(P*t*Bu_3)$_2$(2-(MeO)C_6H_4)]$^+$ **4b**, and [P*t*Bu_3I]$^+$ was observed by ^{31}P NMR spectroscopy, along with a trace amount of [P*t*Bu_3(2-(MeO)C_6H_4)]$^+$ **3b**. After a further 7 days, decomposition of **4b** into **3b** and [P*t*Bu_3H]$^+$ was observed. Spectroscopic data of **3b** is consistent with that reported for the corresponding [B{3,5-$(CF_3)_2C_6H_3$}$_4$]$^-$ salt in this solvent and the assignment is supported by determination of the solid-state structure.[6]

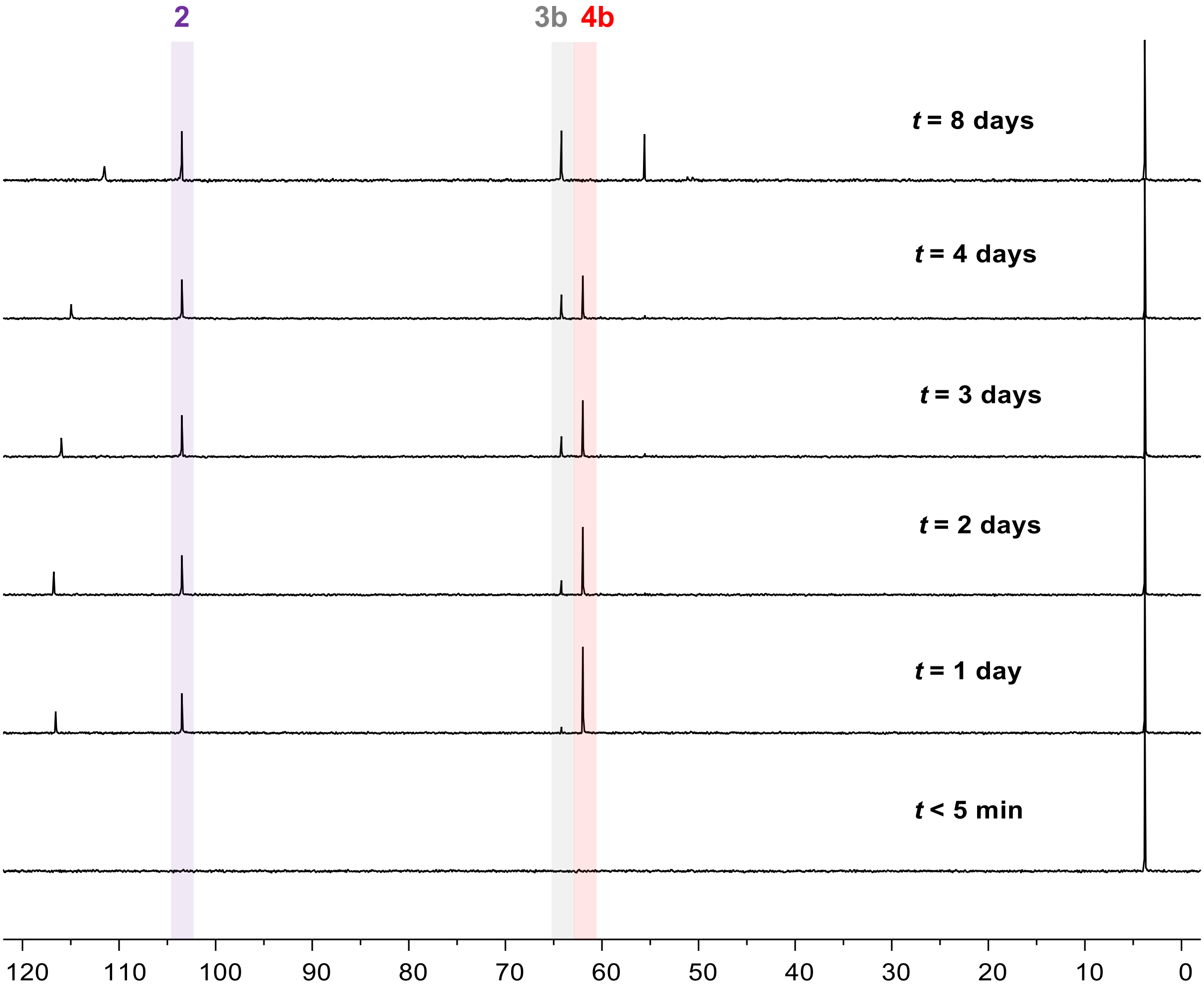

Figure S7. ^{31}P{^{1}H} NMR spectra collected following addition of 1.5 equivalents of 2-(MeO)C_6H_4I to **1** (DFB/C_6D_6, 162 MHz; O=P$(OMe)_3$ internal reference at δ 3.8).

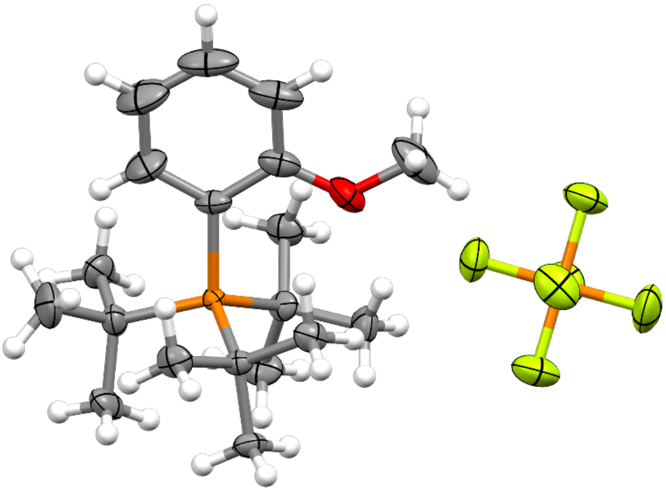

Figure S8. Solid-state structure of **3b**. Thermal ellipsoids at 50% probability.

2.4. 2,6-dimethoxyophenyl iodide

Following the general procedure using 2,6-$(MeO)C_6H_3I$ (4.1 mg, 16 μmol). Complete consumption of **1** was observed by ^1H NMR spectroscopy within 24 h at RT. At this point a 1:3:2 mixture of $[Pd(PtBu_3)(\mu\text{-}I)]_2$ **2**, $[Pd(PtBu_3)_2(2,6\text{-}(MeO)_2C_6H_4)]^+$ **4c**, and $[PtBu_3I]^+$ was observed by ^{31}P NMR spectroscopy.

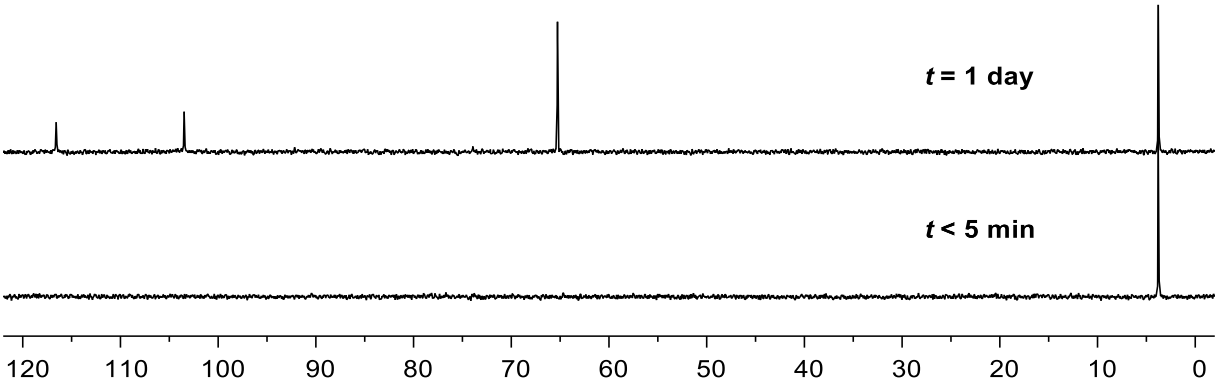

Figure S9. $^{31}P\{^1H\}$ NMR spectra collected following addition of 1.5 equivalents of 2,6-$(MeO)C_6H_3I$ to **1** (DFB/C_6D_6, 162 MHz; $O{=}P(OMe)_3$ internal reference at δ 3.8).

2.5. Adamantyl iodide

Following the general procedure using AdI (3.9 mg, 15 μmol). Complete consumption of **1** was observed by ^1H NMR spectroscopy within 8 days at RT. At this point a mixture containing $[Pd(PtBu_3)(\mu\text{-}I)]_2$ **2** and $[PtBu_3Ad]^+$ **3d** in a 1:2 ratio was observed by ^{31}P NMR spectroscopy along with trace amounts of $[PtBu_3H]^+$ and an unknown species at δ 77.3. Spectroscopic data of **3d** is consistent with that reported for the corresponding $[B(C_6F_5)_3F]^-$ salt and the assignment is supported by ESI-MS (observed, 337.3025; calcd 337.3019 *m*/*z*).[7]

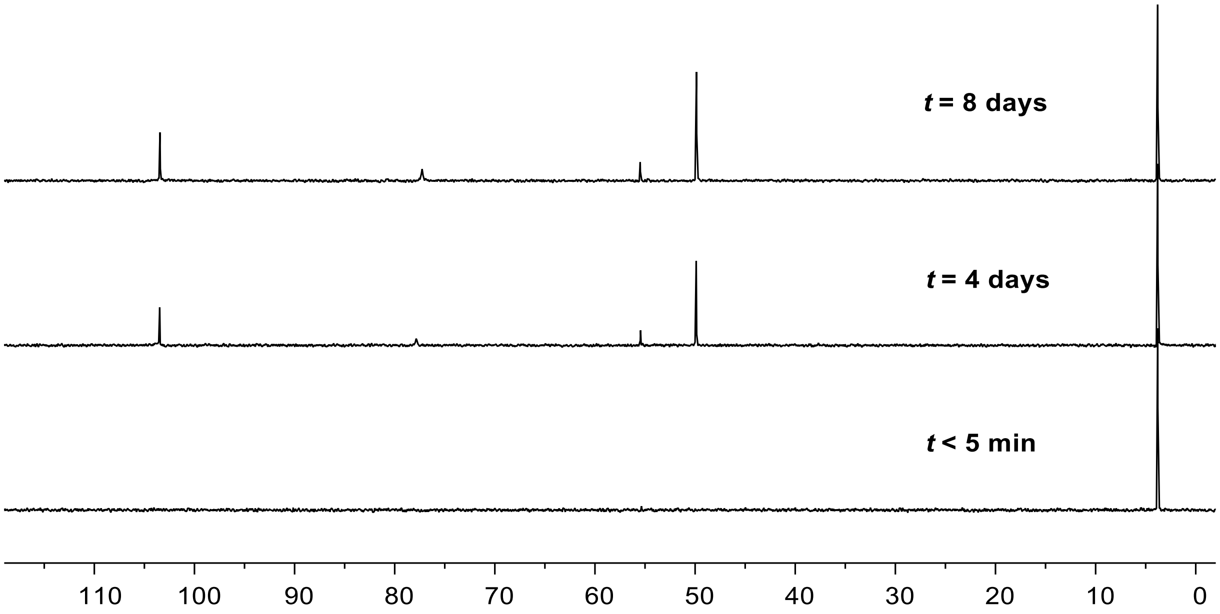

Figure S10. $^{31}P\{^1H\}$ NMR spectra collected following addition of 1.5 equivalents of AdI to **1** (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

2.6. *tert*-Butyl iodide

Following the general procedure using *t*BuI (1.7 µL, 14 µmol). Complete consumption of **1** was observed by ^{1}H NMR spectroscopy within 24 h at RT. At this point a 1:2 mixture of [Pd(P*t*Bu$_3$)(μ-I)]$_2$ **2** and [P*t*Bu$_3$H]$^+$ was observed by ^{31}P NMR spectroscopy. Generation of 2-methylpropene was apparent from the ^{1}H NMR spectrum, with resonances at δ 4.56 (2H) and 1.54 (6H).[8]

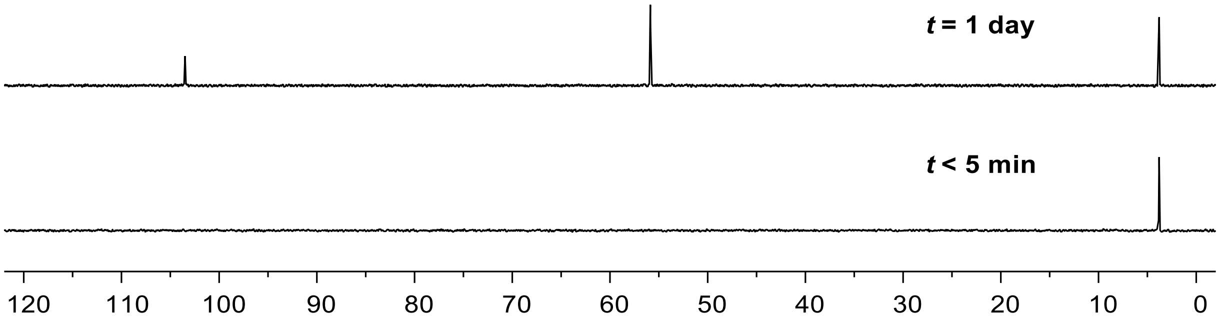

Figure S11. $^{31}P\{^1H\}$ NMR spectra collected following addition of 1.4 equivalents of *t*BuI to **1** (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

2.7. Potassium iodide / 18-crown-6

Following the general procedure using KI (16.8 mg, 101 µmol) and 18-crown-6 (26.3 mg, 99.5 µmol). Complete consumption of **1** and conversion to [Pd(P*t*Bu$_3$)(μ-I)]$_2$ **2** and P*t*Bu$_3$ was observed within 5 min at RT.

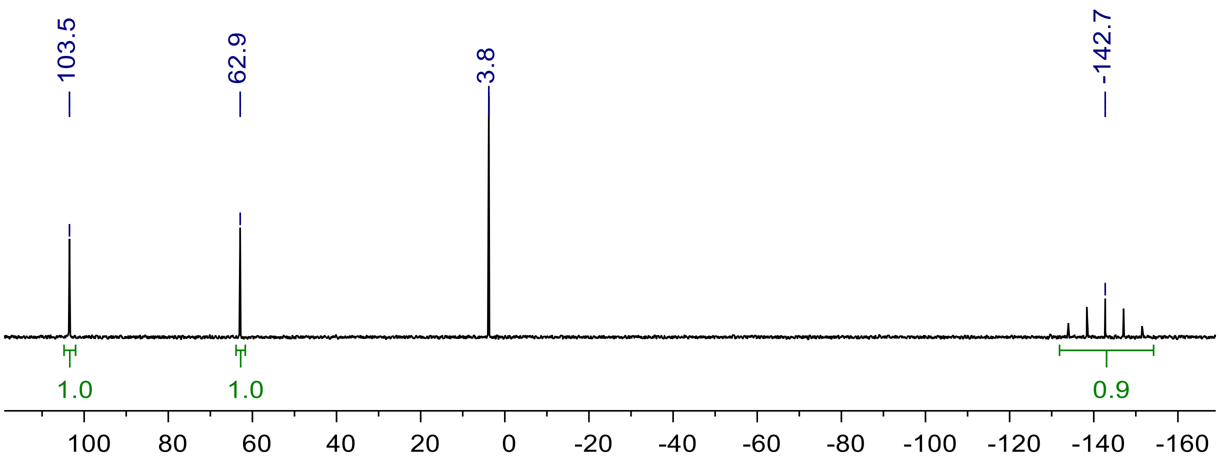

Figure S12. $^{31}P\{^1H\}$ NMR spectra of the products resulting from addition of 10 equivalents of KI and 18-crown-6 to **1** (DFB/C_6D_6, 162 MHz, O=P(OMe)$_3$ internal reference at δ 3.8).

3. Control reactions with tri-*tert*-butylphosphine

3.1. General procedure

To a solution of P*t*Bu$_3$ (10 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was added 10 equivalents of substrate at RT. The resulting solution was monitored using ^1H and ^{31}P NMR spectroscopy, with constant mixing when not in the spectrometer.

3.2. Phenyl iodide

Following the general procedure using PhI (11.2 µL, 100 µmol). No reaction was apparent after 24 h at RT, nor after subsequent heating at 50 °C for 24 h.

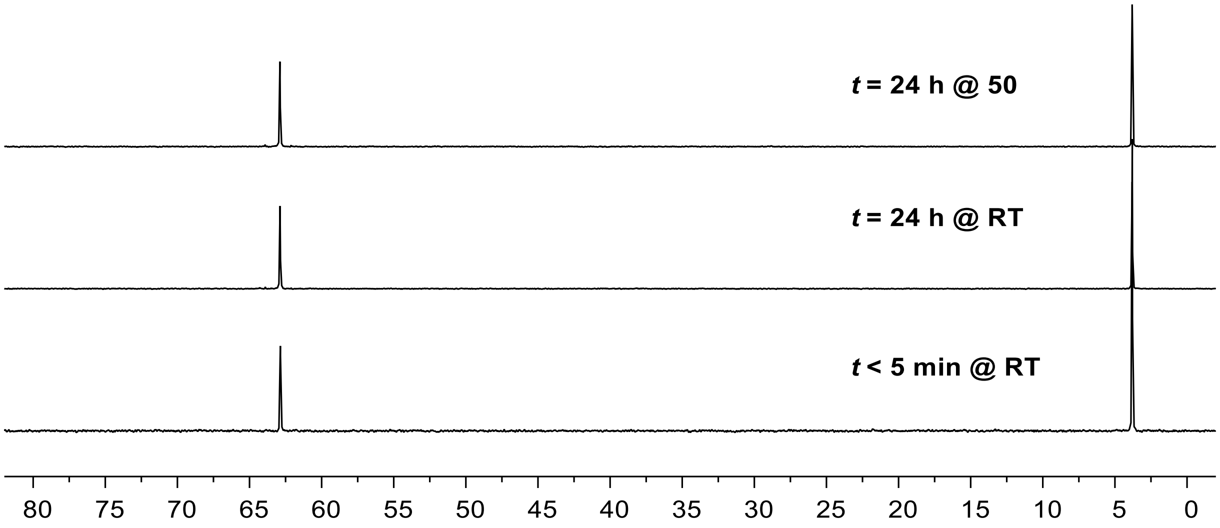

Figure S13. $^{31}P\{^1H\}$ NMR spectra collected following addition of PhI to P*t*Bu$_3$ (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

3.3. Adamantyl iodide

Following the general procedure using AdI (26.2 mg, 100 µmol). No reaction was apparent after 24 h at RT, nor after subsequent heating at 50 °C for 24 h.

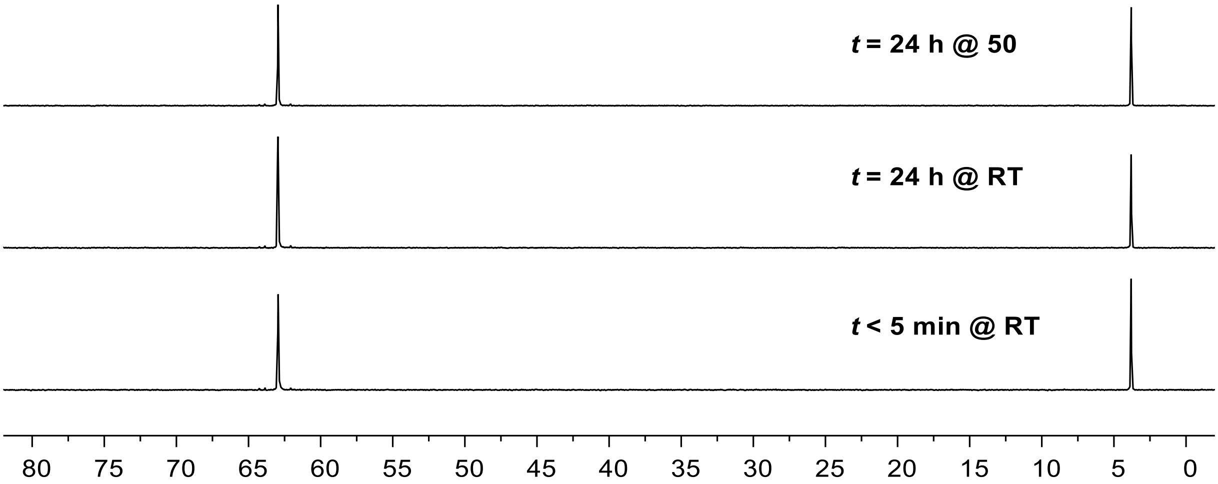

Figure S14. $^{31}P\{^1H\}$ NMR spectra collected following addition of AdI to P*t*Bu$_3$ (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at *δ* 3.8).

3.4. *tert*-Butyl iodide

Following the general procedure using *t*BuI (11.9 µL, 100 µmol). No reaction was apparent after 24 hours at RT, nor after subsequent heating at 50 °C for 24 h.

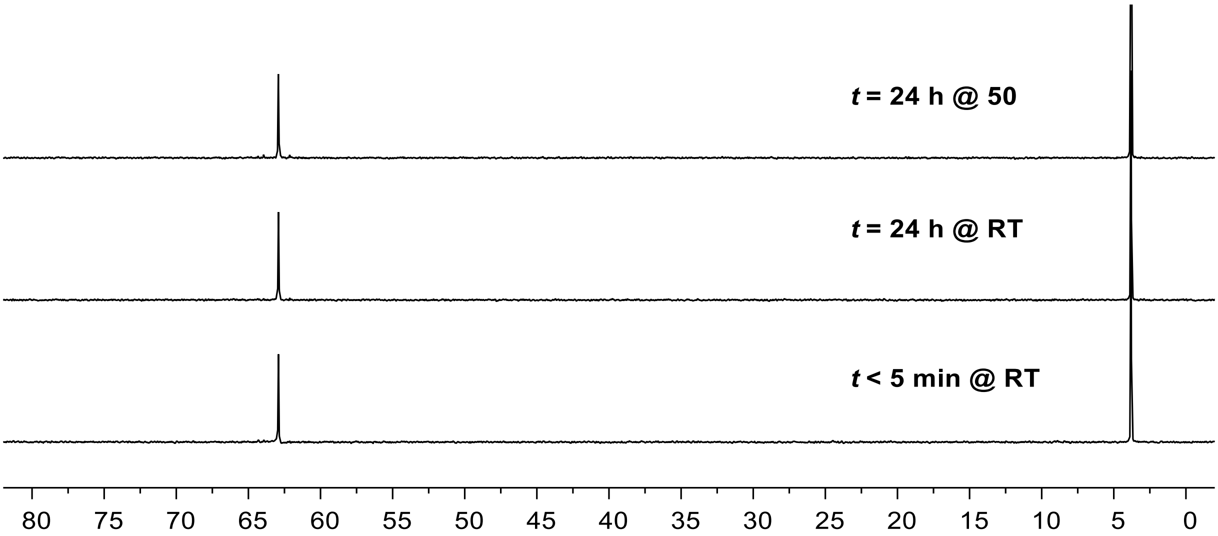

Figure S15. $^{31}P\{^1H\}$ NMR spectra collected following addition of *t*BuI to P*t*Bu$_3$ (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at *δ* 3.8).

3.5. Iodine

To a solution of I_2 (13.0 mg, 51 μmol) in DFB (0.5 mL) within a J. Young valve NMR tube was added a solution of P*t*Bu$_3$ in hexane (15 μL, 0.69 M, 10 μmol) at RT. Analysis within 5 min using ^{1}H and ^{31}P NMR spectroscopy indicated complete conversion to [P*t*Bu$_3$I]I. Spectroscopic data of **3d** is consistent with that reported for the corresponding $[B(C_6F_5)_3F]^-$ salt.[9]

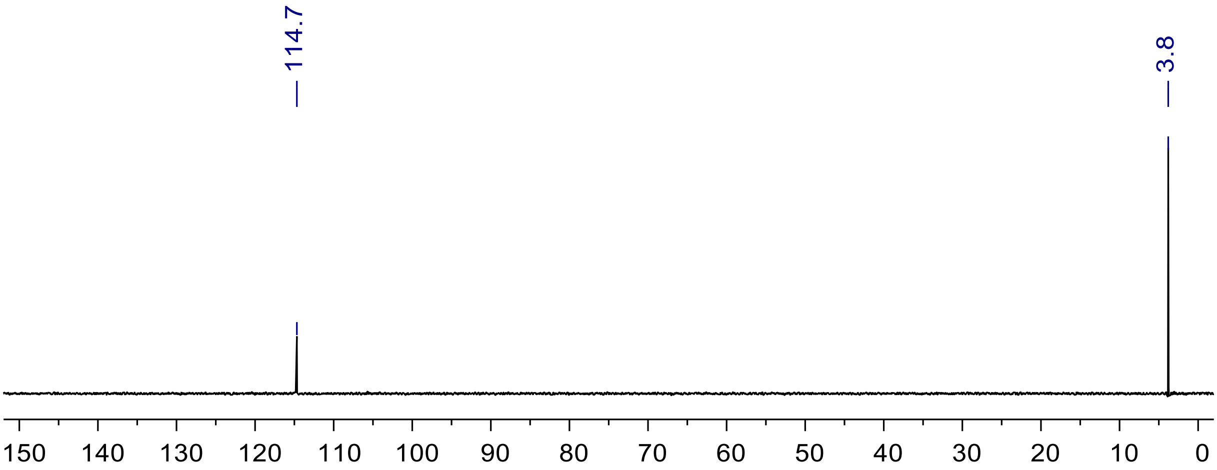

Figure S16. $^{31}P\{^1H\}$ NMR spectra collected following addition of I_2 to P*t*Bu$_3$ (DFB/C_6D_6, 162 MHz; O=P(OMe)$_3$ internal reference at δ 3.8).

3.6. Preparation of [P*t*Bu$_3$H][PF$_6$]

To a solution of P*t*Bu$_3$ in pentane (1.25 mL, 0.87 M, 1.1 mmol) was added a solution of HCl in diethyl ether (1.44 mL, 1 M, 1.4 mmol) dropwise at RT. The resulting solution was stirred at RT for 30 min and volatiles removed *in vacuo*. The white residue was extracted with degassed acetone (10 mL) and a solution of Na[PF$_6$] (241.0 mg, 1.4 mmol) in degassed acetone (10 mL) was added to the filtrate. The resulting solution was stirred for 30 min and volatiles removed *in vacuo*. The product was thereafter extracted from the residual salts using CH_2Cl_2 (3×5 mL) and dried in *in vacuo*. Yield: 280.1 mg (804 μmol, 73%). Spectroscopic data are in agreement with the literature and the assignment is supported by determination of the solid-state structure.[6]

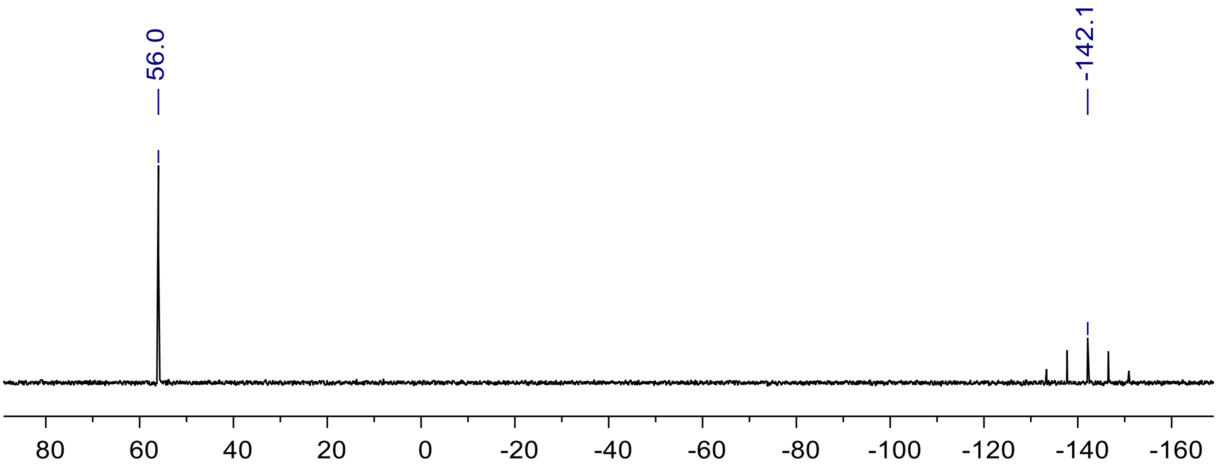

Figure S17. $^{31}P\{^1H\}$ NMR spectrum of [P*t*Bu$_3$H][PF$_6$] (DFB/C$_6$D$_6$, 162 MHz).

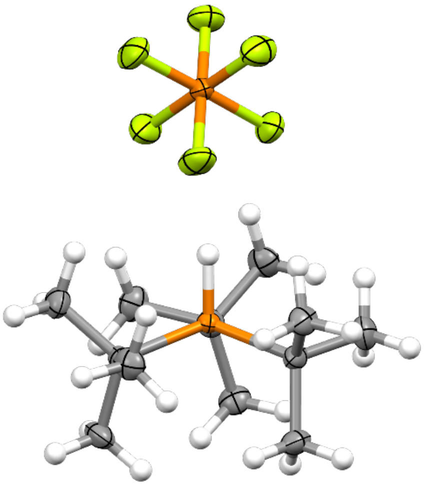

Figure S18. Solid-state structure of [P*t*Bu$_3$H][PF$_6$]. Thermal ellipsoids at 50% probability.

4. Isolation, characterisation, and stability of [Pd(P*t*Bu$_3$)$_2$(2-(MeO)C$_6$H$_4$)][PF$_6$] 4b

4.1. Preparation of 4b

To a solution of [Pd(P*t*Bu$_3$)$_2$][PF$_6$] **1** (75.1 mg, 114 μmol) in DFB (5 mL) was added 2-methoxyphenyl iodide (14.9 μL, 115 μmol) and the resulting solution stirred for 18 h at RT. The solvent was removed *in vacuo* and the residue purified by column chromatography (silica, CH$_2$Cl$_2$) to afford the product, which was subsequently recrystallised from DFB/hexane at –40 °C and obtained as red blocks. Yield: 28.0 mg (36.7 μmol, 32%).

^{1}H NMR (500 MHz, DFB/C$_6$D$_6$, selected data): *δ* 6.64 (t, $^3J_{HH}$ = 7.9, 5-Ar), 6.17 (d, $^3J_{HH}$ = 6.2, 3-Ar), 3.63 (s, 3H, OMe), 1.19 (vt, J_{PH} = 12.7, 54H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, DFB/C$_6$D$_6$): *δ* 159.0 (vt, J_{PC} = 11, 1-Ar), 157.5 (s, 2-Ar), 135.9 (s, 6-Ar), 127.0 (s, 4-Ar), 120.6 (s, 5-Ar), 110.5 (s, 3-Ar), 53.6 (s, OMe), 40.2 (vt, J_{PC} = 7, *t*Bu{C}), 31.9 (vt, J_{PC} = 4, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (162 MHz, DFB/C$_6$D$_6$): *δ* 62.0 (s, 2P, P*t*Bu$_3$), -142.3 (sept, $^1J_{PF}$ = 710, 1P, PF$_6$).

HR ESI-MS (positive ion, 4 kV): 617.3233 ([*M*]$^+$, calcd 617.3239) *m/z*.

UV/Vis (DFB): λ_{max}/nm = 310 (ε = 8300 L^{-1} mol^{-1} cm^{-1}), 435 (ε = 1900 L^{-1} mol^{-1} cm^{-1}).

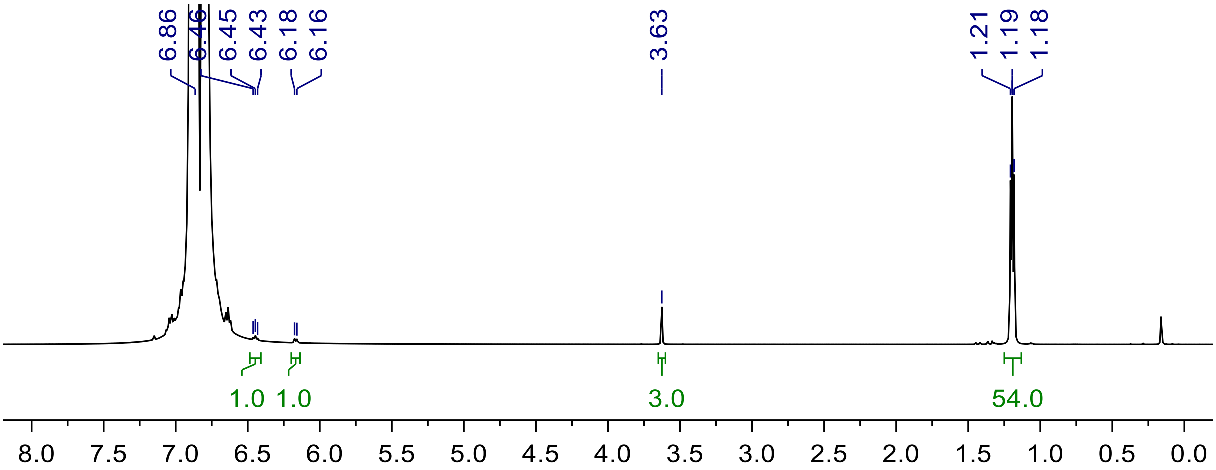

Figure S19. ^{1}H NMR spectrum of **4b** (DFB/C$_6$D$_6$, 500 MHz).

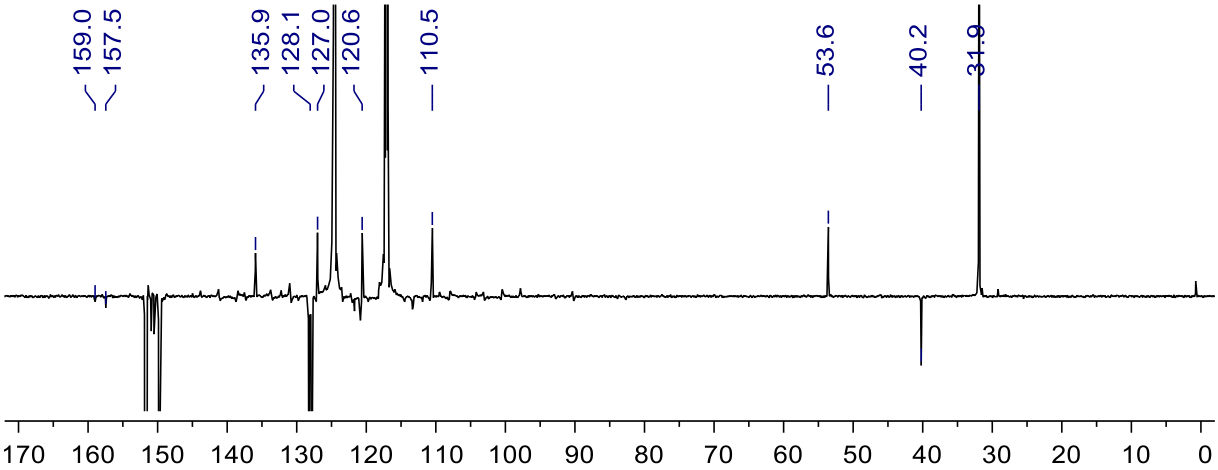

Figure S20. $^{13}C\{^{1}H\}$ APT NMR spectrum of **4b** (DFB/C_6D_6, 126 MHz).

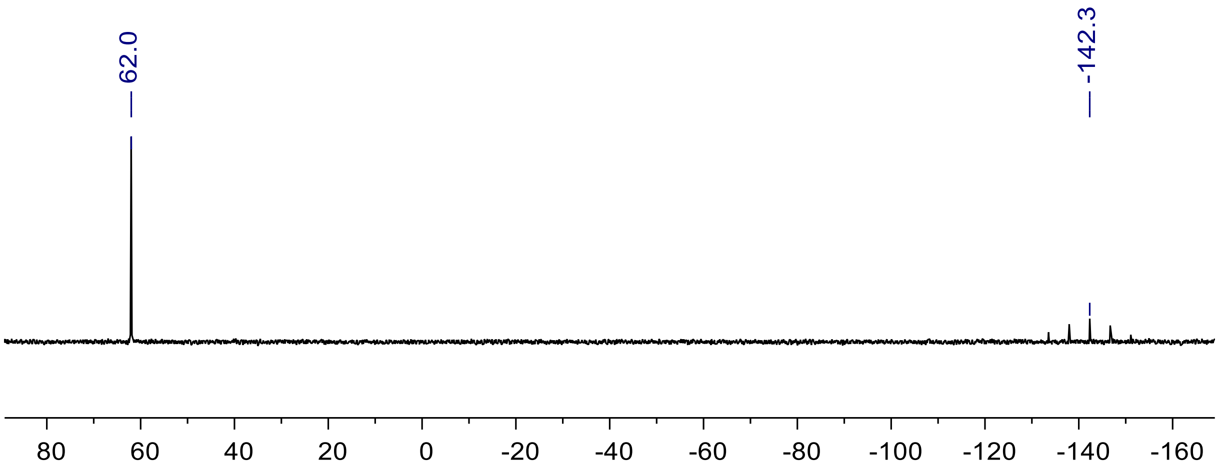

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **4b** (DFB/C_6D_6, 162 MHz).

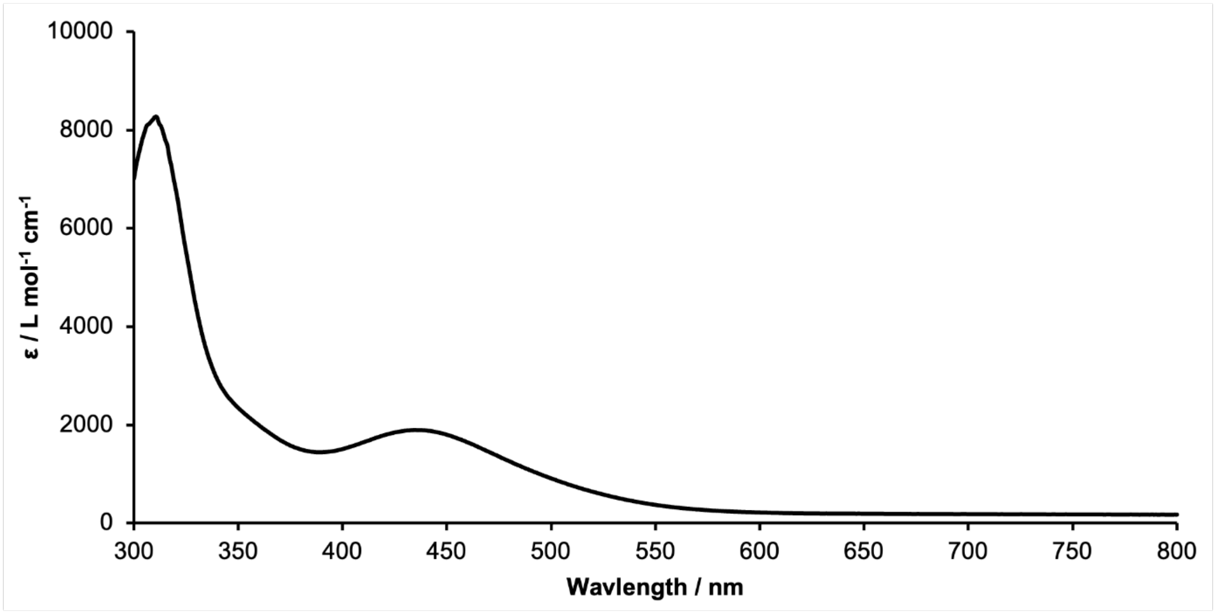

Figure S22. UV/vis spectrum of **4b** (DFB).

4.2. Stability of 4b

A solution of **4b** (7.4 mg, 9.7 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was monitored over 14 days at RT using ^{1}H and ^{31}P NMR spectroscopy, with constant mixing when not in the spectrometer. Onward reactivity of **4b** was observed with an approximate $t_{1/2}$ of 3 days, concomitant with formation of [P*t*Bu$_3$(2-(MeO)C$_6$H$_4$)]$^+$ **3b**, [P*t*Bu$_3$H]$^+$, and precipitation of palladium black.

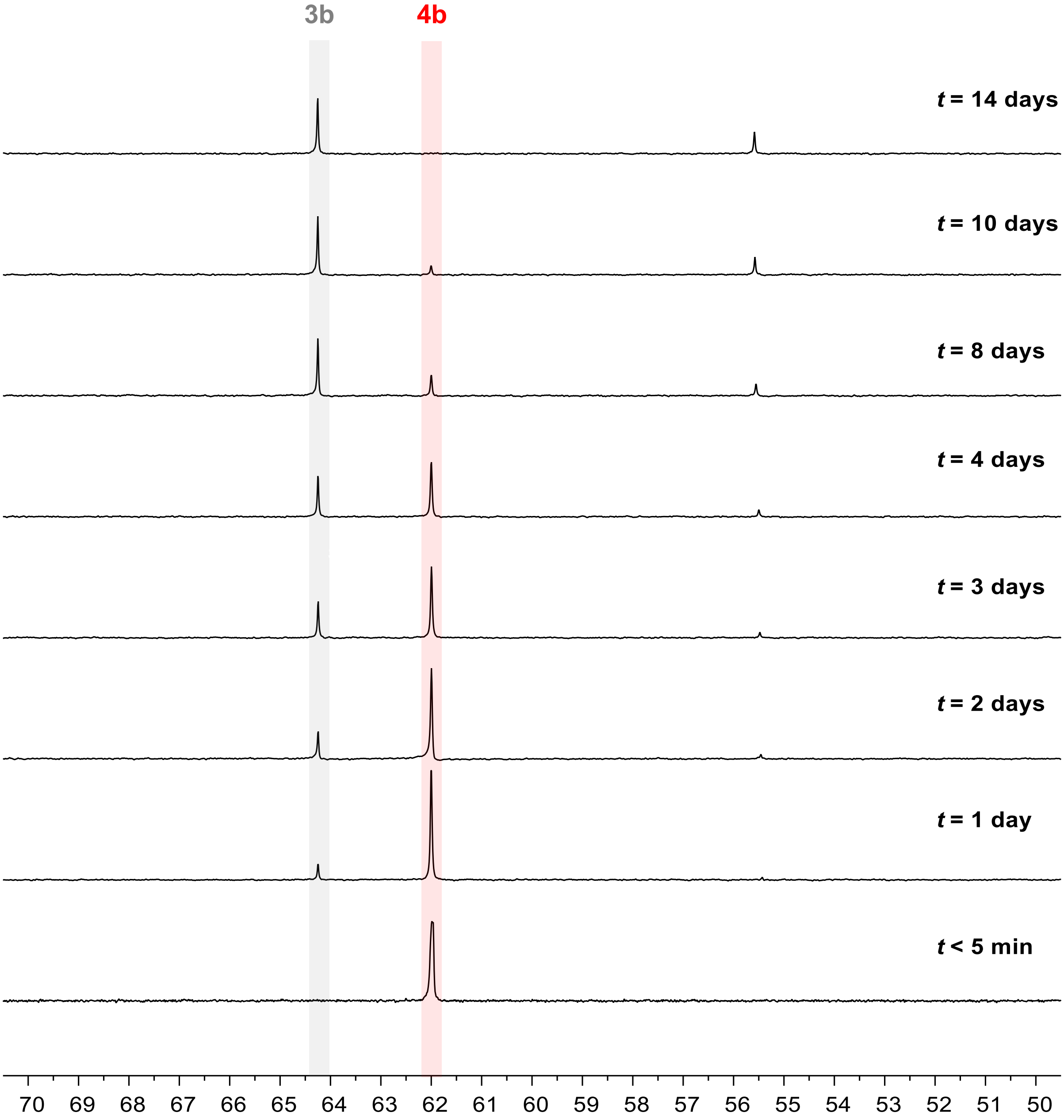

Figure S23. ^{31}P{^{1}H} NMR spectra collected following thermolysis of **4b** at RT (DFB/C$_6$D$_6$, 162 MHz).

4.3. Stability of 4b in the presence of excess P*t*Bu$_3$

A solution of **4b** (7.6 mg, 10 µmol) and P*t*Bu$_3$ (64 µL of a 0.72 M solution in hexane, 46 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was monitored over 15 days at RT using ^{1}H and ^{31}P NMR spectroscopy, with constant mixing when not in the spectrometer. Onward reactivity of **4b** was observed with an approximate $t_{1/2}$ of 3 days, concomitant with formation of [Pd(P*t*Bu$_3$)$_2$] and [P*t*Bu$_3$(2-(MeO)C$_6$H$_4$)]$^+$ **3b**.

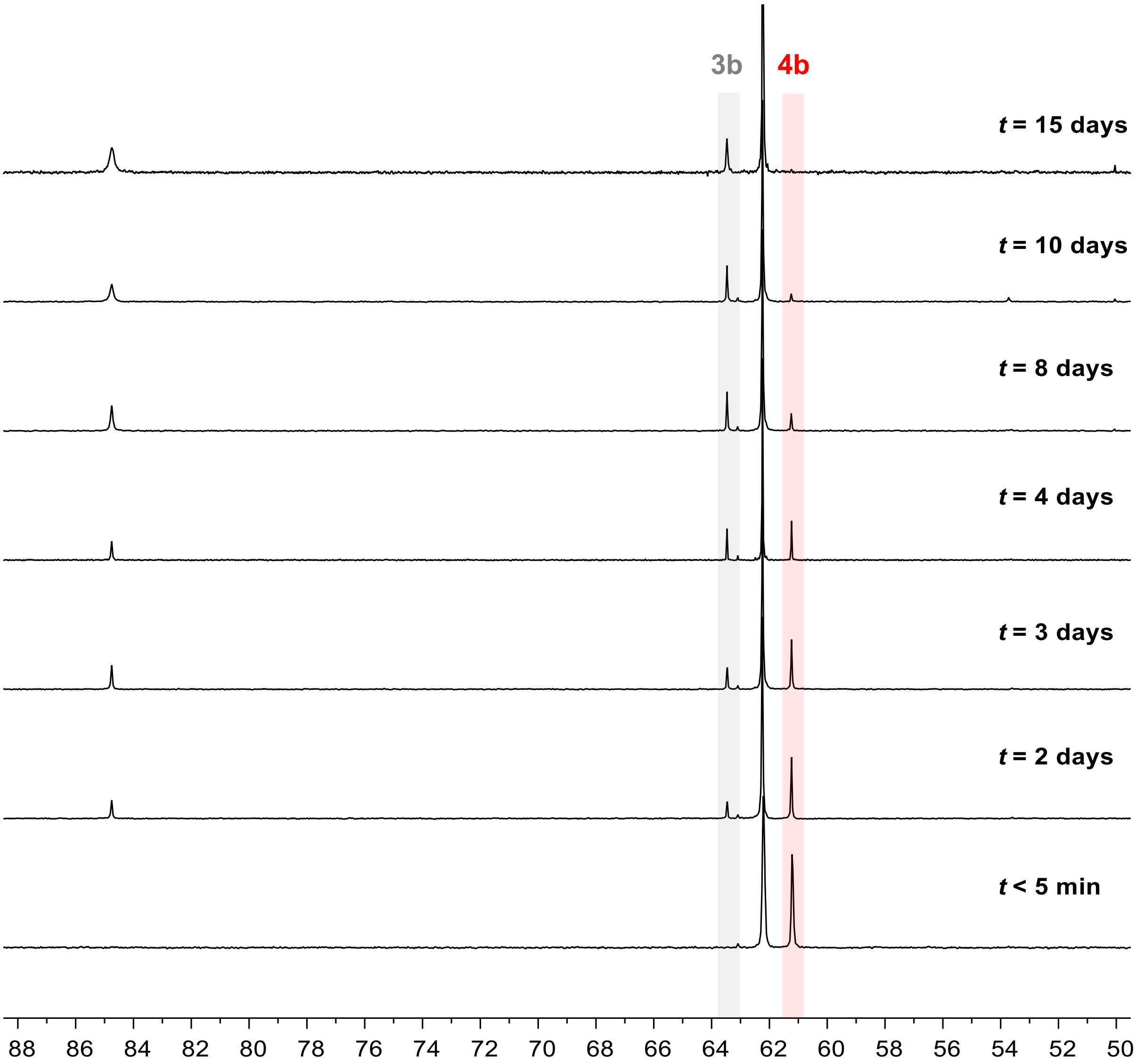

Figure S24. ^{31}P{^{1}H} NMR spectra collected following thermolysis of **4b** at RT in the presence of excess P*t*Bu$_3$ (DFB/C$_6$D$_6$, 162 MHz).

5. Isolation, characterisation, and stability of [Pd(P*t*Bu$_3$)$_2$(2,6-(MeO)$_2$C$_6$H$_3$)][PF$_6$] 4c

5.1. Preparation of 4c

A solution of [Pd(P*t*Bu$_3$)$_2$][PF$_6$] (100 mg, 152 µmol) and 2,6-bis(methoxy)phenyl iodide (40.3 mg, 153 µmol) in DFB (5 mL) was stirred at RT for 1 day. The solvent was removed *in vacuo* and the residue purified by column chromatography (silica, CH$_2$Cl$_2$) to afford the product, which was subsequently recrystallised from DFB/hexane at –40 °C and obtained as red blocks. Yield: 45.4 mg (57.2 µmol, 38%).

^{1}H NMR (500 MHz, DFB/C$_6$D$_6$, selected data): δ 5.93 (d, $^3J_{HH}$ = 6.4, 2H, Ar), 3.61 (s, 6H, OMe), 1.20 (vt, J_{PH} = 12.8, 54H, P*t*Bu$_3$).

^{13}C{^{1}H} NMR (126 MHz, DFB/C$_6$D$_6$): δ 158.8 (vt, J_{PC} = 3, 2-Ar), 128.0 (s, 4-Ar), 107.3 (s, 1-Ar), 103.7 (s, 3-Ar), 53.6 (s, OMe), 39.9 (vt, J_{PC} = 7, *t*Bu{C}), 31.9 (vt, J_{PC} = 5, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (162 MHz, DFB/C$_6$D$_6$): δ 65.3 (s, 2P, P*t*Bu$_3$), -142.4 (sept, $^1J_{PF}$ = 710, 1P, PF$_6$).

HR ESI-MS (positive ion, 4 kV): 647.3441 ([*M*]$^+$, calcd 647.3345) *m/z*.

UV/Vis (DFB): λ_{max}/nm = 321 (ε = 9900 L^{-1} mol^{-1} cm^{-1}), 463 (ε = 1700 L^{-1} mol^{-1} cm^{-1}).

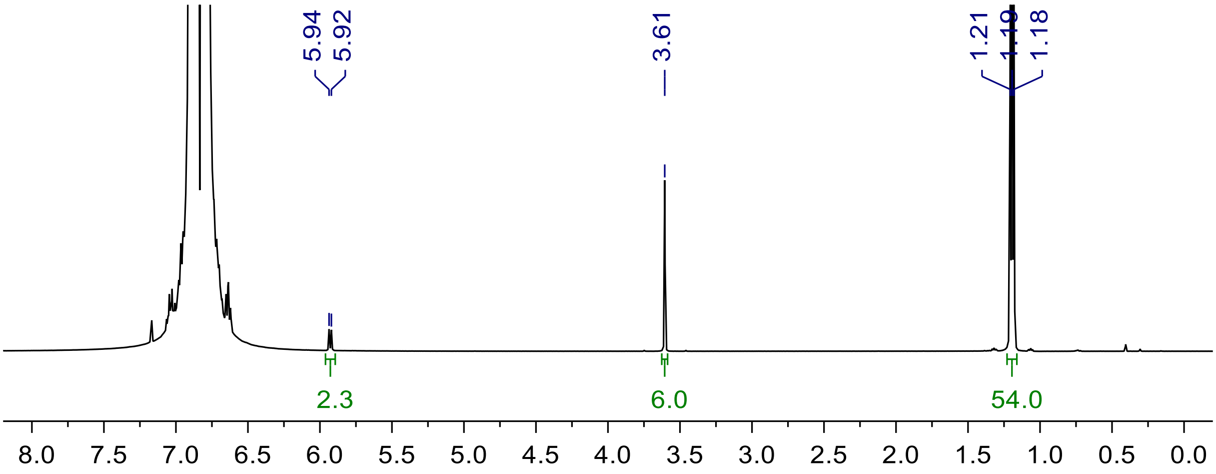

Figure S25. ^{1}H NMR spectrum of **4c** (DFB/C$_6$D$_6$, 500 MHz).

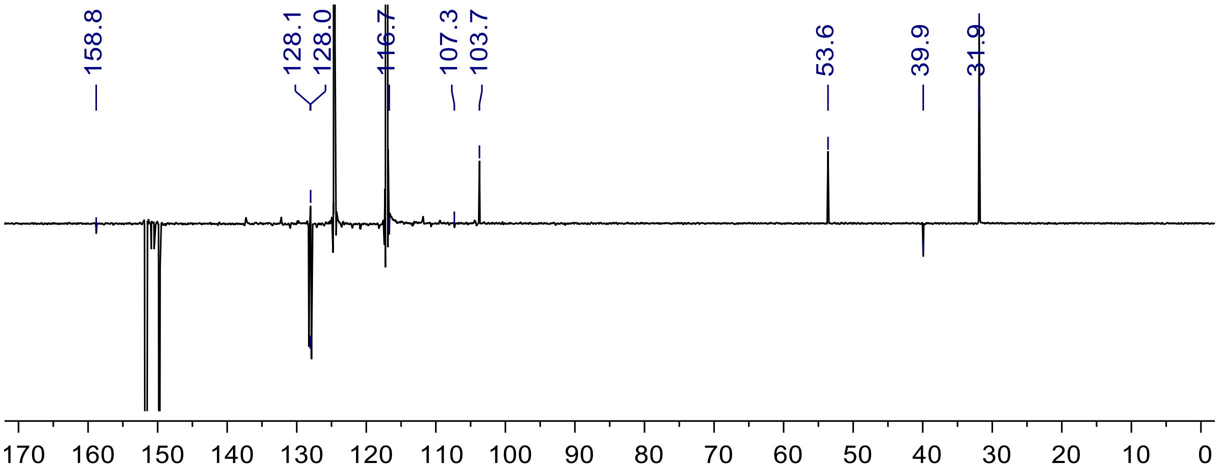

Figure S26. $^{13}C\{^{1}H\}$ APT NMR spectrum of **4c** (DFB/C_6D_6, 126 MHz).

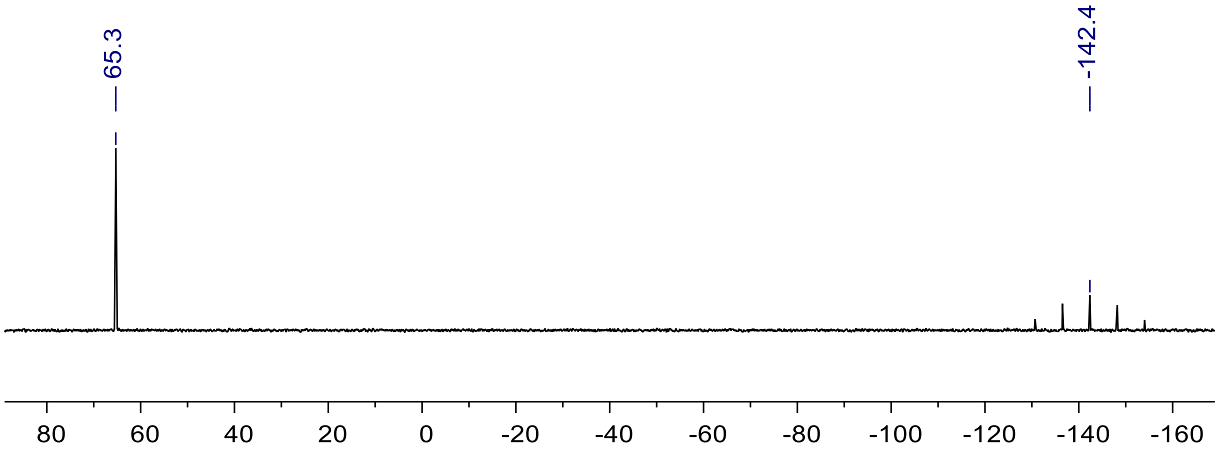

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **4c** (DFB/C_6D_6, 162 MHz).

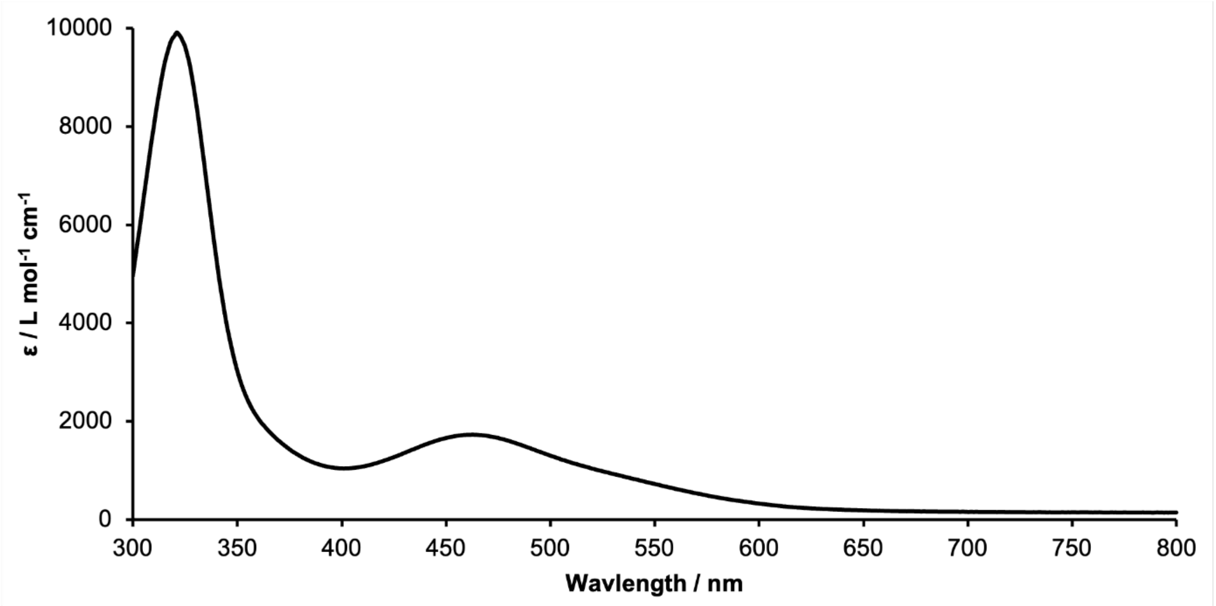

Figure S28. UV/vis spectrum of **4c** (DFB).

5.2. Stability of 4c

A solution of **4c** (7.8 mg, 9.8 μmol) in DFB (0.5 mL) within a J. Young valve NMR tube was monitored over 14 days at RT using ^{1}H and ^{31}P NMR spectroscopy, with constant mixing when not in the spectrometer. No onward reactivity was apparent.

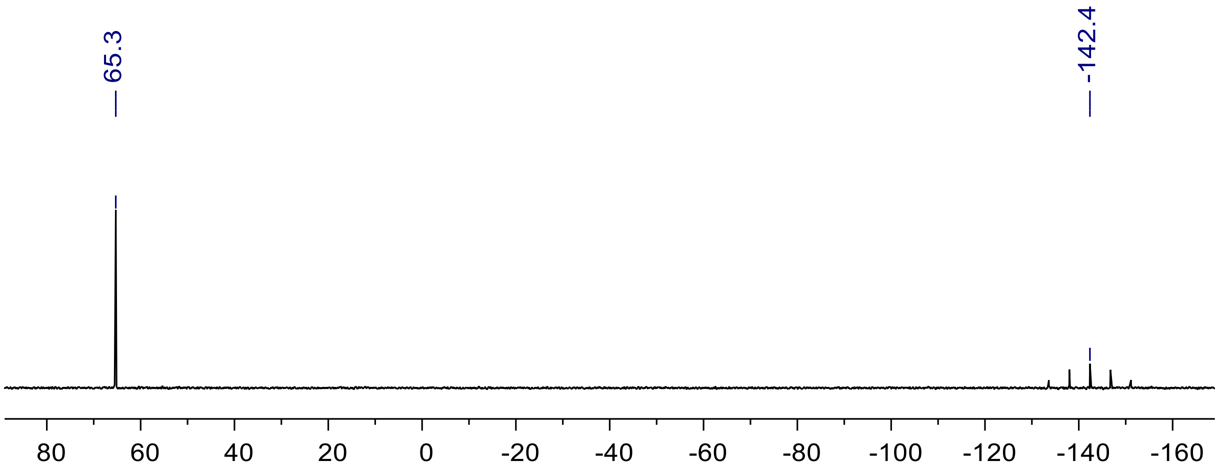

Figure S29. ^{31}P{^{1}H} NMR spectrum collected after thermolysis of **4b** at RT for 14 days (DFB/C_6D_6, 162 MHz).

6. Mechanistic sketch

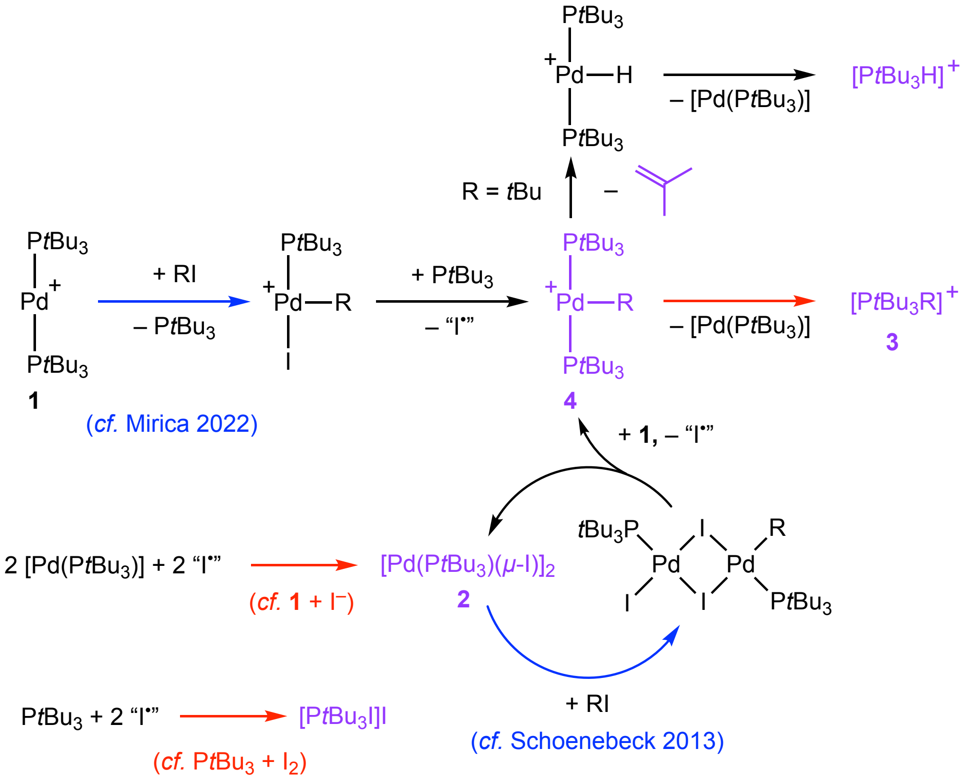

Figure S30. Overview of proposed mechanism: observed products in purple, reactions with experimental evidence in red, reactions with literature precedents in blue.

7. References

---

[1] S. D. Pike, M. R. Crimmin and A. B. Chaplin, *Chem. Commun.* 2017, **53**, 3615–3636.

[2] T. Troadec, S.-y. Tan, C. J. Wedge, J. P. Rourke, P. R. Unwin and A. B. Chaplin, *Angew. Chem. Int. Ed.* 2016, **55**, 3754–3757.

[3] M. Aufiero, T. Sperger, A. S. K. Tsang and F. Schoenebeck, *Angew. Chem. Int. Ed.*, 2015, **54**, 10322–10326.

[4] P. S. Pregosin, *NMR in Organometallic Chemistry*, Wiley-VCH, 2012, pp 251–254.

[5] E. Rémond, A. Tessier, F. R. Leroux, J. Bayardon and Sylvain Jugé, *Org. Lett.* 2010, **12**, 1568–1571.

[6] Q. Simpson, M. J. G. Sinclair, D. W. Lupton, A. B. Chaplin and J. F. Hooper. *Org. Lett.* 2018, **20**, 5537–5540.

[7] C. B. Caputo and D. W. Stephan, *Organometallics*, 2012, **31**, 27−30.

[8] A. Y. Jordan and T. Y. Meyer, *J. Organomet. Chem.*, 1999, **591**, 104–113

[9] I. Behrends, S. Bähr and C. Czekelius, *Chem.–Eur. J.*, 2016, **22**, 17177–17181