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Selective carbon-carbon bond cleavage of 2,2’-dibromotolane via photolysis of its appropriate (disphosphine)Pt^0 complex in solid state

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1. Experimental

1.1 General methods

Melting points were determined with an AXIOLAB microscope with a TMHS 600 heating plate and are uncorrected. ^{1}H, ^{31}P, ^{13}C and ^{195}Pt NMR spectra were determined with BRUKER DRX 400 or BRUKER DRX 200 spectrometers at 25°C. In the case of ^{1}H and ^{13}C NMR chemical shifts are referred to the protons and carbon atoms of the solvent, respectively. Due to the complexity of the ^{1}H and ^{13}C NMR spectra of the compounds **4** and **6**, it was not possible to assign every signal and the appropriate coupling constants exactly. For ^{31}P NMR a 85 % H_3PO_4 and for ^{195}Pt NMR a 1.0 M solution of K_2PtCl_4 in D_2O was used as the external reference. ^{31}P and ^{13}C NMR spectra were measured proton decoupled. The ^{195}Pt NMR spectra were measured by ^{1}H-^{195}Pt-HMBC experiments. Solid state NMR ^{31}P spectra were obtained with a BRUKER AVANCE 400 II^{+} spectrometer at 9 T and with a BRUKER AMX 400 spectrometer at 7 T employing a BRUKER double resonance 4 mm MAS probe. Spinning speed was set to 10 kHz controlled within a range of ± 1 Hz. Data were obtained utilizing a 90° single pulse sequence with proton decoupling during data acquisition. For technical reasons, proton decoupling was omitted for measurements at 7 T. IR spectra were taken with a PERKIN ELMER System 2000 FT-IR spectrometer. Mass spectra were taken with a FINNIGAN MAT SSQ 710 mass spectrometer. Elemental analyses were performed with a LECO CHNS-932. All reactions were carried out in air unless otherwise stated. Solvents were of analytical grade and used without further purification. Starting materials [(dppbe)$PtCl_2$] (**2**),[1] 2,2'-dibromotolane (**1**)[2] and complex [(dppbe)(η^2-2,2'-dibromotolane)Pt^0] (**5**)[3] were prepared according to the literature procedure.

1.2 Crystal structure determination

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects and for absorption effects[4-6].

The structures were solved by direct methods (SHELXS[7]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97[8]). All hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically[8]. Ortep-3 for Windows[9] was used for structure representations.

Crystal Data for **3**[10]: $C_{44}H_{32}Br_2P_2Pt$, $M = 977.55$ g·mol^{-1}, colourless prism, size 0.04 × 0.04 × 0.03 mm^3, monoclinic, space group $P2_1/n$, $a = 11.1456(4)$, $b = 22.1637(7)$, $c = 15.3986(4)$ Å, $\beta = 106.710(2)°$, $V = 3643.3(2)$ Å^3, $T = -90°$C, $Z = 4$, $\rho_{calcd.} = 1.782$ g·cm^{-3}, μ(Mo-K_α) = 61.64 cm^{-1}, multi-scan, trans$_{min}$: 0.2908, trans$_{max}$: 0.6101, F(000) = 1896, 23208 reflections in h(-13/14), k(-28/26), l(-19/18), measured in the range 2.30° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 98.3 %, 8185 independent reflections, $R_{\text{int}} = 0.0899$, 6160 reflections with $F_o > 4\sigma(F_o)$, 442 parameters, 0 restraints, $R1_{\text{obs}} = 0.0544$, $wR^2_{\text{obs}} = 0.1328$, $R1_{\text{all}} = 0.0800$, $wR^2_{\text{all}} = 0.1463$, GOOF = 1.024, largest difference peak and hole: 3.193 / -2.345 e Å^{-3}.

Crystal Data for **4**[10]: $C_{44}H_{32}Br_2P_2Pt$, $M = 977.55$ g·mol^{-1}, colourless prism, size 0.05 × 0.05 × 0.04 mm^3, triclinic, space group $P\bar{1}$, $a = 8.8929(3)$, $b = 10.7362(4)$, $c = 21.0258(7)$ Å, $\alpha = 80.862(2)°$, $\beta = 88.179(2)°$, $\gamma = 68.483(2)°$, $V = 1843.09(11)$ Å^3, $T = -90$°C, $Z = 2$, $\rho_{\text{calcd.}} = 1.761$ g·cm^{-3}, μ (Mo-K$_\alpha$) = 60.93 cm^{-1}, multi-scan, trans$_{\text{min}}$: 0.3949, trans$_{\text{max}}$: 0.4449, F(000) = 948, 13314 reflections in h(-11/11), k(-13/13), l(-26/27), measured in the range $2.57° \leq \Theta \leq 27.49°$, completeness $\Theta_{\text{max}} = 98.9$ %, 8374 independent reflections, $R_{\text{int}} = 0.0376$, 6723 reflections with $F_o > 4\sigma(F_o)$, 442 parameters, 0 restraints, $R1_{\text{obs}} = 0.0560$, $wR^2_{\text{obs}} = 0.1408$, $R1_{\text{all}} = 0.0762$, $wR^2_{\text{all}} = 0.1501$, GOOF = 1.188, largest difference peak and hole: 5.363 / -2.102 e Å^{-3}.

Crystal Data for **6**[10]: $C_{44}H_{32}Br_2P_2Pt$, · 1.5 (C_4H_8O), $M = 1085.70$ g·mol^{-1}, colourless prism, size 0.04 × 0.04 × 0.01 mm^3, monoclinic, space group $P2_1/c$, $a = 21.3703(6)$, $b = 13.6258(3)$, $c = 15.6040(3)$ Å, $\beta = 93.290(1)°$, $V = 4536.20(18)$ Å^3, T = – 90°C, $Z = 4$, $\rho_{\text{calcd.}} = 1.590$ g·cm^{-3}, μ (Mo-K$_\alpha$) = 49.62 cm^{-1}, multi-scan, trans$_{\text{min}}$: 0.810, trans$_{\text{max}}$: 0.932, F(000) = 2136, 31809 reflections in h(-23/27), k(-17/17), l(-20/20), measured in the range $1.77° \leq \Theta \leq 27.48°$, completeness $\Theta_{\text{max}} = 99.9$ %, 10383 independent reflections, $R_{\text{int}} = 0.0757$, 7479 reflections with $F_o > 4\sigma(F_o)$, 506 parameters, 0 restraints, $R1_{\text{obs}} = 0.0488$, $wR^2_{\text{obs}} = 0.1059$, $R1_{\text{all}} = 0.0819$, $wR^2_{\text{all}} = 0.1194$, GOOF = 1.015, largest difference peak and hole: 1.561 / -1.758 e Å^{-3}.

1.3 Synthesis of [(dppbe)(η^2-(1))Pt^0] 3

Under an atmosphere of argon, to a suspension of [(dppbe)PtCl$_2$] (**2**) (70 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) and ethanol (2 mL) was added $NaBH_4$ (5 mg, 0.13 mmol). After 10 min the suspension became yellow and the [(dppbe)PtCl$_2$] (**2**) dissolved. The mixture was stirred at RT for additional 2 h, and water (2 mL) was added. After the vigorous evaluation of hydrogen was almost completed the organic layer was separated using a pipette and to this phase 2,2'-dibromotolane (**1**) (30 mg, 0.09 mmol) was added (For any reason this sequence is crucial). After stirring this solution over night the solvent was reduced to dryness using a rotary evaporator without exclusion of air. The crude product was washed with diethyl ether, dissolved in THF (10 mL) and filtrated over silica gel. The solvent was evaporated again and the crude product was crystallized from toluene. Yellow crystals; yield: 56 mg (0.056 mmol) (56 %) m. p. 239-241°C dec.

δ_H (400 MHz, [D_2]dichloromethane) 7.81 (2H, m), 7.55 (8H, m), 7.48 (4H, m), 7.36 (4H, m), 7.29 (8H, m), 7.17 (2H, dd, ${}^3J$(H,H) = 7.6 Hz, ${}^4J$(H,H) = 1.6 Hz), 7.00 (2H, dt, ${}^3J$(H,H) = 7.6 Hz, ${}^4J$(H,H) = 0.8 Hz), 6.92 (2H, dt, ${}^3J$(H,H) = 7.6 Hz, ${}^4J$(H,H) = 1.6 Hz).

δ_C (100 MHz, [D_2]dichloromethane) 146.30 (t, ${}^1J$(P,C) = 44.0 Hz), 139.48 (t, ${}^3J$(P,C) = 9.0 Hz), 135.58 (t, ${}^1J$(P,C) = 24.0 Hz), 134.84 (s), 133.96 (t, ${}^2J$(P,C) = 7.4 Hz), 133.24 (t, ${}^3J$(P,C) = 6.8 Hz), 132.83 (s), 132.27 (s), 131.12 (s), 130.12 (s), 128.66 (t, ${}^2J$(P,C) = 5.1 Hz), 127.10 (s), 126.55 (s), 123.59 (s).

δ_P (81 MHz, [D_2]dichloromethane) 51.1 (s, ${}^1J$(P,Pt) = 3161 Hz).

δ_{Pt} (85.6 MHz, [D_6]benzene) – 4747 (t, ${}^1J$(Pt,P) = 3175 Hz).

IR (KBr) ν_{max}/cm^{-1} 3053 (m), 1780 (m) (C≡C), 1625 (m), 1480 (s), 1434 (vs), 1097 (s), 1025 (s), 755 (vs), 694 (vs), 548 (vs), 527 (vs), 505 (s).

MS (FAB in nba) m/z (%) 977 (7, [M]$^+$), 897 (18, [M-Br]$^+$), 821 (4, [M-(*o*-BrC_6H_4)]$^+$), 797 (18, [M-(C≡C-(*o*-BrC_6H_4))]$^+$), 721 (40, [Pt(dppbe)(Br)]$^+$), 307 (100).

UV-Vis λ_{max}(CH_2Cl_2)/nm 263 (ε/dm^3·mol^{-1}·cm^{-1} 10800), 302 (21000).

Elemental analysis (%) calcd. for $C_{42}H_{32}Br_2P_2Pt$ (977.56): C 54.06, H 3.30, Br 16.35; found: C 54.09 H 3.55, Br 16.77.

1.4 Synthesis of [(dppbe)Pt(C≡C-(o-Br-C_6H_4))(o-Br-C_6H_4)] 4

Crystals of **3** (15 mg, 0.015 mmol) were placed in a sample vial and irradiated with sunlight for 3 h. From time to time the vial is turned for steady irradiation conditions of the sample. The yellow crystals became colourless and weathered to give white powder of **4**; yield: 14 mg (93 %) m. p. 140-141°C.

δ_H (400 MHz, [D_2]dichloromethane) (2H, dd, J(H,H) = 11.5 Hz, J(H,H) = 7.5 Hz), 7.79 (1H, t, J(H,H) = 6.5 Hz), 7.73-7.65 (3H, m), 7.61 (1H, dd, J(H,H) = 11.7 Hz, J(H,H) = 8.0 Hz), 7.50-7.39 (1H, m), 7.56-7.51 (2H, m), 7.50-7.40 (8H, m), 7.39-7.34 (3H, m), 7.25 (2H, dt, J(H,H) = 2.4 Hz, J(H,H) = 8.0 Hz), 7.16-6.98 (5H, m), 6.95

(1H, dt, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.5 Hz), 6.86 (1H, dt, ^4J(H,H) = 2.0 Hz, ^3J(H,H) = 8.0 Hz), 6.77 (1H, t, ^3J(H,H) = 7.5 Hz), 6.69 (1H, t, ^3J(H,H) = 7.5 Hz).

δ_C (50 MHz, [D$_2$]dichloromethane) 143.42 (s), 139.63 (d, ^3J(P,C) = 2.9 Hz, ^2J(Pt,C) = 22.0 Hz), 134.90 (d, J(P,C) = 12.3 Hz), 134.43 (s), 134.19 (s), 134.00 (s), 133.55 (d, J(P,C) = 5.0 Hz), 133.39 (s), 132.69 (s), 132.39 (s), 132.01 (s), 131.18 (d, J(P,C) = 23.4 Hz), 130.35 (s) 129.06 (s), 128.87 (s), 128.57 (d, J(P,C) = 10.6 Hz), 127.60 (s), 126.68 (s), 126.34 (s), 125.44 (d, J(P,C) = 9.3 Hz), 125.72 (s), 124.97 (s, ^3J(Pt,C) = 6.5 Hz), 124.34 (s), 107.76 (d, ^2J(P,C) = 33.0 Hz), 92.52 (s).

δ_P (81 MHz, [D$_2$]dichloromethane) 50.1 (d, ^2J(P,P) = 5.5 Hz, ^1J(P,Pt) = 2473 Hz), 46.7 (d, ^2J(P,P) = 5.5 Hz, ^1J(P,Pt) = 1767 Hz).

δ_{Pt} (85.6 MHz, [D$_2$]dichloromethane) – 4703 (dd, ^1J(Pt,P) = 2454 Hz, ^1J(Pt,P) = 1778 Hz).

IR (KBr) ν_{max}/cm^{-1} 3053 (s), 2115 (s) (C≡C), 1625 (m), 1482 (m), 1461 (s), 1435 (vs), 1101 (s), 1025 (s), 999 (s), 744 (vs), 693 (vs), 550 (vs), 533 (vs), 506 (s).

MS (FAB in nba) m/z (%): 977 (7, [M]$^+$), 897 (20, [M-Br]$^+$), 821 (6, [M-(*o*-BrC$_6$H$_4$)]$^+$), 797 (15, [M-(C≡C-(*o*-BrC$_6$H$_4$))]$^+$), 721 (70, [Pt(dppbe)(Br)]$^+$), 563 (40, [Pt(dppbe)-Ph]$^+$), 485 (100, [Pt(dppbe)-2Ph]$^+$).

Elemental analysis (%) calcd. for $C_{42}H_{32}Br_2P_2Pt$ (977.56): C 54.06, H 3.30, Br 16.35; found: C 54.00 H 3.30, Br 16.12.

1.5 Synthesis of [(dppbe)Pt((o-C$_6$H$_4$)-C≡C-(o-Br-C$_6$H$_4$))(Br)] 6

Complex **3** (204 mg, 0.21 mmol) was dissolved in toluene (100 mL). This solution was irradiated with sunlight for five days. The solvent was removed under reduced pressure to give a yellow residue. The $^{31}P\{^1H\}$ NMR spectrum of the crude product showed complete conversion of **3** to **4** and **6** as a 1:1 mixture. Column chromatography (SiO$_2$, CH$_2$Cl$_2$) of the crude product afforded **6** as a yellow solid, yield: 95 mg (48 %) m. p. 153-155°C.

δ_H (400 MHz, [D$_2$]dichloromethane) 7.83 (2H, m), 7.72-7.57 (6H, m), 7.54-7.47 (6H, m), 7.22 (3H, m), 7.12 (2H, m), 7.08 (2H, dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.0 Hz), 6.98 (1H, dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 2.0 Hz), 6.94 (1H, m), 6.78 (2H, m).

δ_C (50 MHz, [D$_2$]dichloromethane) 144.39 (t, J(P,C) = 39.5 Hz), 137.51 (s, ^1J(Pt,C) = 21.3 Hz), 134.57 (d, J(P,C) = 11.5 Hz), 134.36 (s), 134.10 (d, J(P,C) = 11.2 Hz), 133.81 (s), 133.70 (s), 133.38 (s), 132.51 (s, br), 132.39 (s), 131.96 (s), 131.69 (s), 131.59 (s), 131.25 (d, *J*(P,C) = 6.7 Hz), 130.39 (s), 129.91 (s), 129.58 (s), 129.35 (s), 128.98 (s), 128.86 (s), 128.59 (s), 128.47 (s), 127.38 (d, *J*(P,C) = 7.1 Hz), 127.24 (s), 127.17 (s), 125.16 (s), 123.06 (s), 100.23 (s), 87.44 (s).

δ_P (81 MHz, [D$_2$]dichloromethane) 48.85 (d, ^2J(P,P) = 4.7 Hz, ^1J(P,Pt) = 1749 Hz), 42.87 (d, ^2J(P,P) = 4.7 Hz, ^1J(P,Pt) = 4064 Hz).

δ_{Pt} (85.6 MHz, [D$_2$]dichloromethane) – 4567 (dd, ^1J(Pt,P) = 1703 Hz, ^1J(Pt,P) = 3961 Hz).

IR (KBr) ν_{max}/cm^{-1} (s), 2210 (w) (C≡C), 1629 (m), 1474 (m), 1435 (s), 1100 (s), 1025 (m), 752 (s), 693 (vs), 561 (vs), 534 (vs), 506 (vs).

MS (FAB in nba) m/z (%): 977 (2, [M]$^+$), 897 (25, [M-Br]$^+$), 817 (10, [M-2Br]$^+$), 721 (100, [(Pt(dppbe)(Br)]$^+$), 641 (25, [Pt(dppbe)]$^+$), 561 (25, [Pt(dppbe)-Ph]$^+$), 485 (70, [Pt(dppbe)-2Ph]$^+$).

Elemental analysis (%) calcd. for $C_{42}H_{32}Br_2P_2Pt$ (977.56): C 54.06, H 3.30, Br 16.35; found: C 54.35 H 3.60, Br 16.82.

1.6 Thermal induced back reaction of 4 to 3 and thermal stability of 3

A sample of **4** (11 mg, 0.011 mmol) was dissolved in [D$_8$]toluene. The solution was heated in a sealed ampoule for 40 h at 105ºC. The $^{31}P\{^1H\}$ NMR spectrum showed 30 % conversion of **4** to **3**, after 100 h 40 % respectively. Heating for additional 8 d gave a conversion of 60 %, as well as, small amounts of side products. During a further experiment a sample of **3** (8 mg, 0.008 mmol) was heated similarly for 8 d at 105°C, though, no reaction was observed in the $^{31}P\{^1H\}$ NMR spectrum.

1.7 Data processing and simulation of ^{31}P solid state NMR spectra

Data were processed by apodization with line broadening of 10 Hz. Simulation of the ^{31}P solid state NMR spectra of **3** at 7 T and 9 T was done by using two Gaussian singlet signals according to the parameters determined from solution state NMR i.e. *J*-coupling constant of ^1J(P,Pt) = 3184 Hz and intensity ratio of the satellites of 1:4 with respect to the central main line. The intensities of both signals were of equal height according to the assumption that both ^{31}P positions became magnetically non-equivalent in the solid state. Deviations of the simulations and measurements are mainly due to omitting the line broadening of 10 Hz during the simulation procedure.

Simulation of the solid state NMR spectrum of **4** was done using the assumption that the signals **A**, **B**, and **E** (see Fig. S2) are present in the solid state. The presence of **C** and **D** could be excluded since no satellite was found below 20 ppm outside the main spectrum. Furthermore, the possibility of magnetically non-equivalent ^{31}P positions, as experimentally found in the initial state **3**, was taken into account.

The spectrum could be reasonable simulated by applying 5 Gaussian signals. A pair attributed to **B** at 42 ppm and 40 ppm (red) as well as a pair attributed to **A** at 36 ppm and 34 ppm (blue), respectively. A fifth singlet signal (green) was located at 39 ppm assigned to **E** by virtue of its *J*-coupling. The remaining gap at 45 ppm maybe attributed to the second signal of **E**, however, no clear satellites could be resolved and adding a sixth signal was omitted.

Please note, despite the high number of lines, the degree of freedom of the simulation is strongly reduced by coupling every 3 lines to pseudo triplets of fixed frequency spacing and intensity ratios.

2. Selected solution state NMR spectra

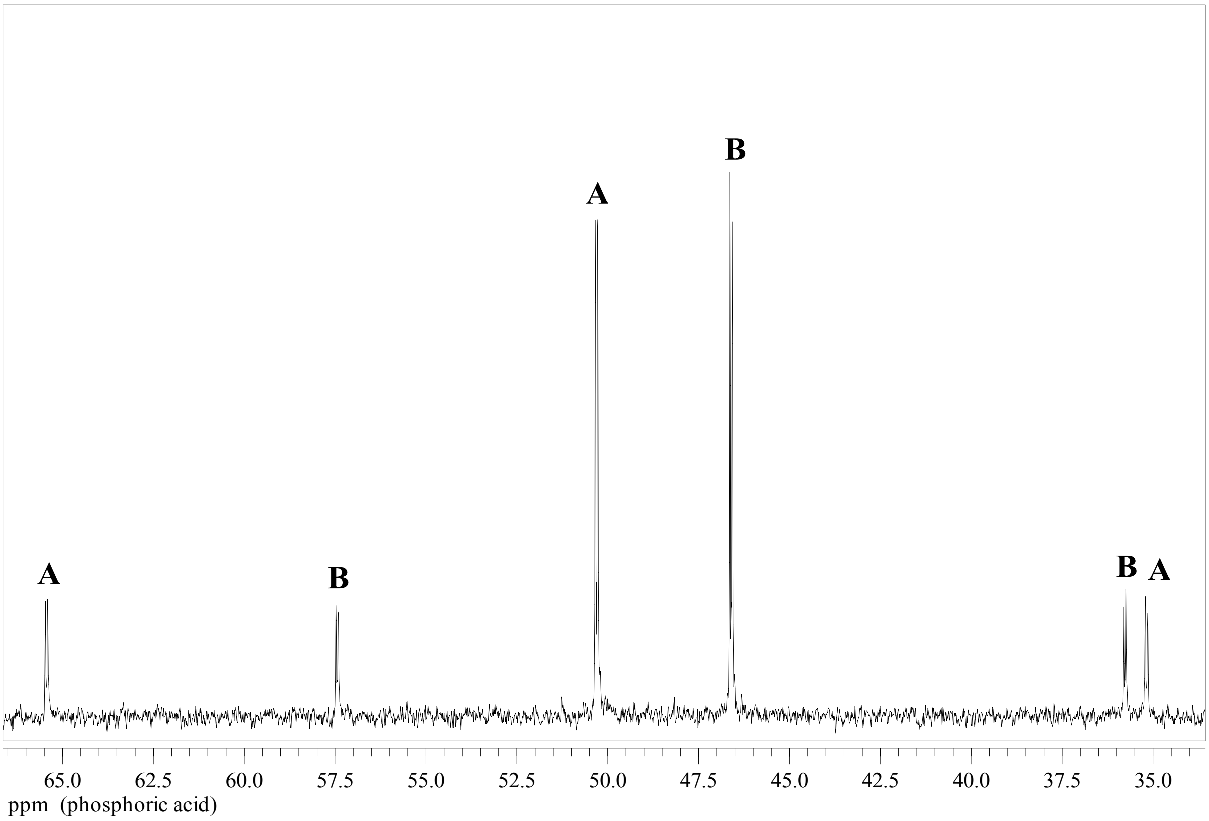

Figure S1: $^{31}P\{^{1}H\}$ NMR spectrum of **4** (**A**/**B**), obtained after irradiation of crystals of **3** with sunlight.

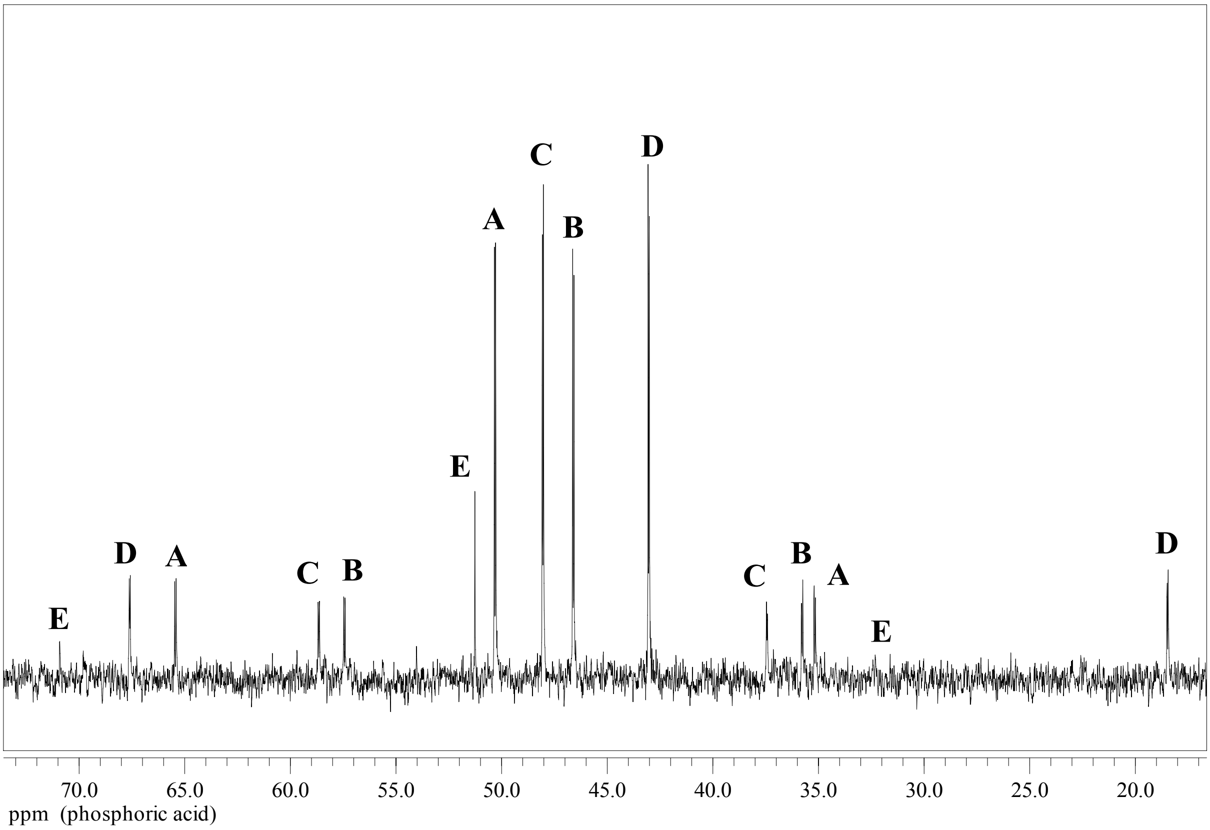

Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum after irradiation of **3** (**E**) in solution with sunlight, yielding **4** (**A**/**B**) and **6** (**C**/**D**).

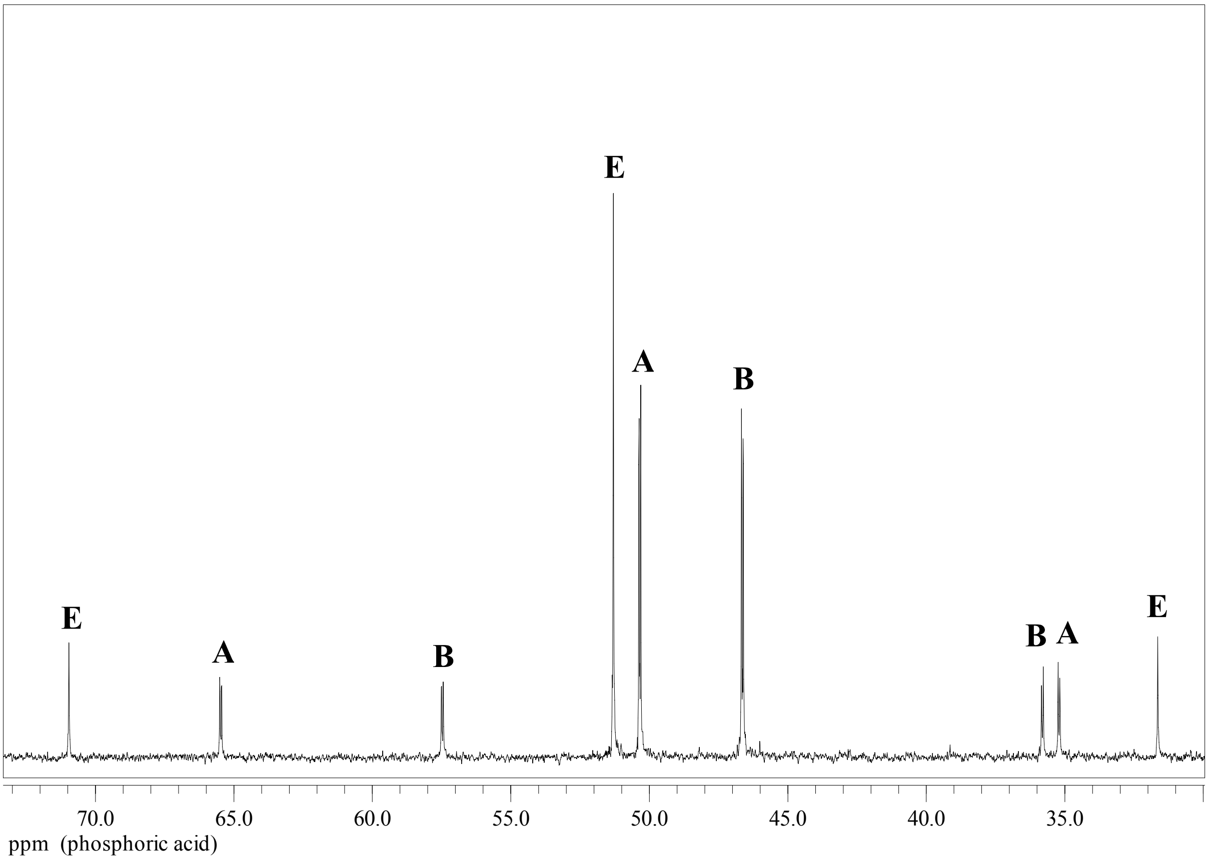

Figure S3: $^{31}P\{^1H\}$ NMR spectrum after heating of **4** (**A**/**B**) for 40 h at 105ºC.

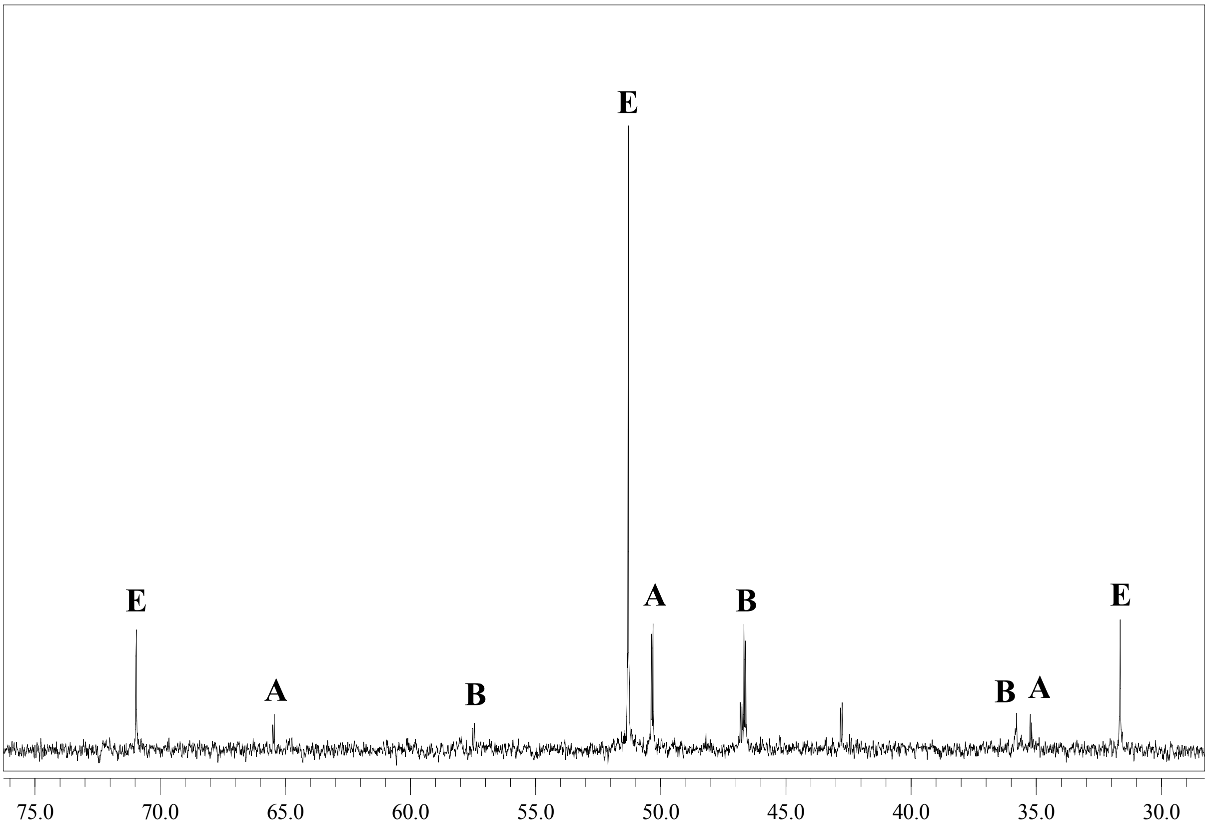

Figure S4: $^{31}P\{^1H\}$ NMR spectrum after heating of **4** (**A**/**B**) for 240 h at 105ºC.

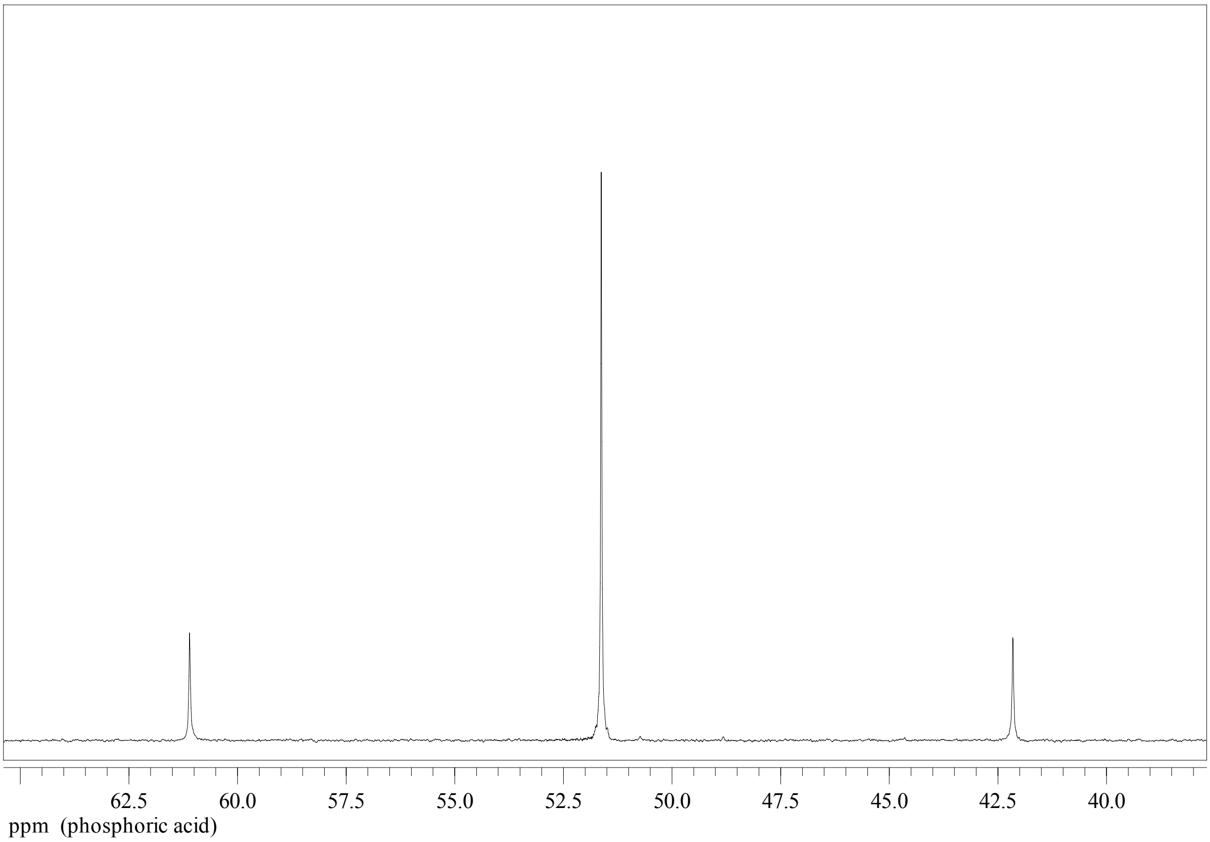

Figure S5: $^{31}P\{^{1}H\}$-NMR spectrum of complex **5** after irradiation with sunlight in the solid state.

3. Solid state NMR spectra

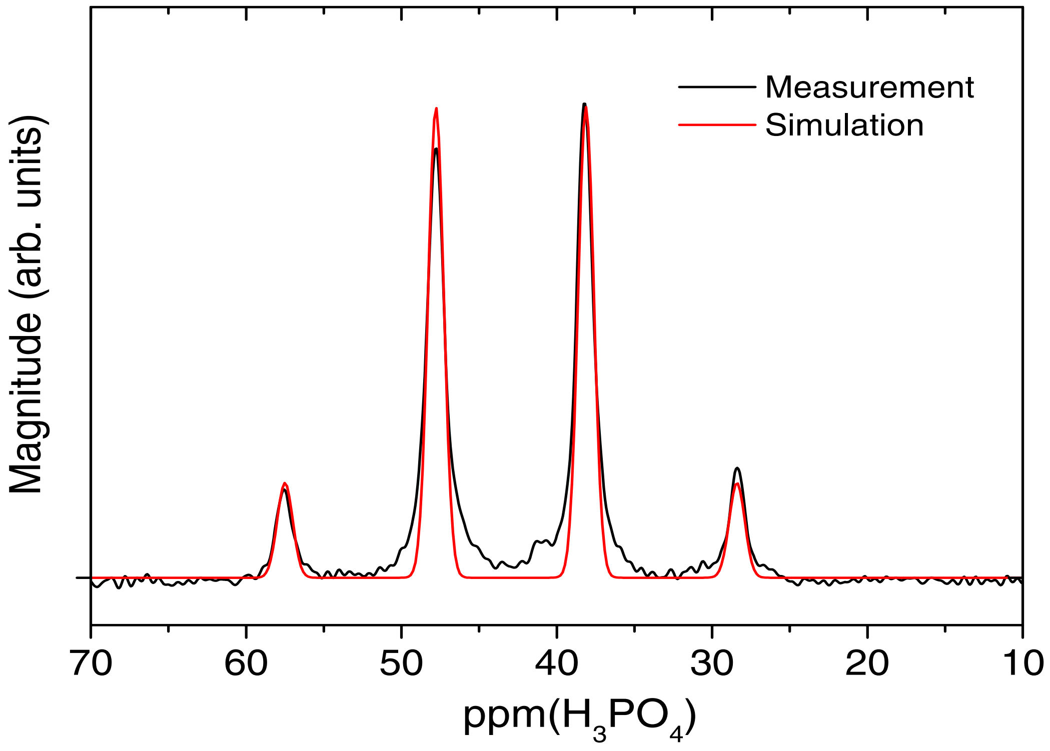

Figure S6: $^{31}P\{^1H\}$ Solid State NMR spectrum of **3** at 9 T together with simulations as discussed above.

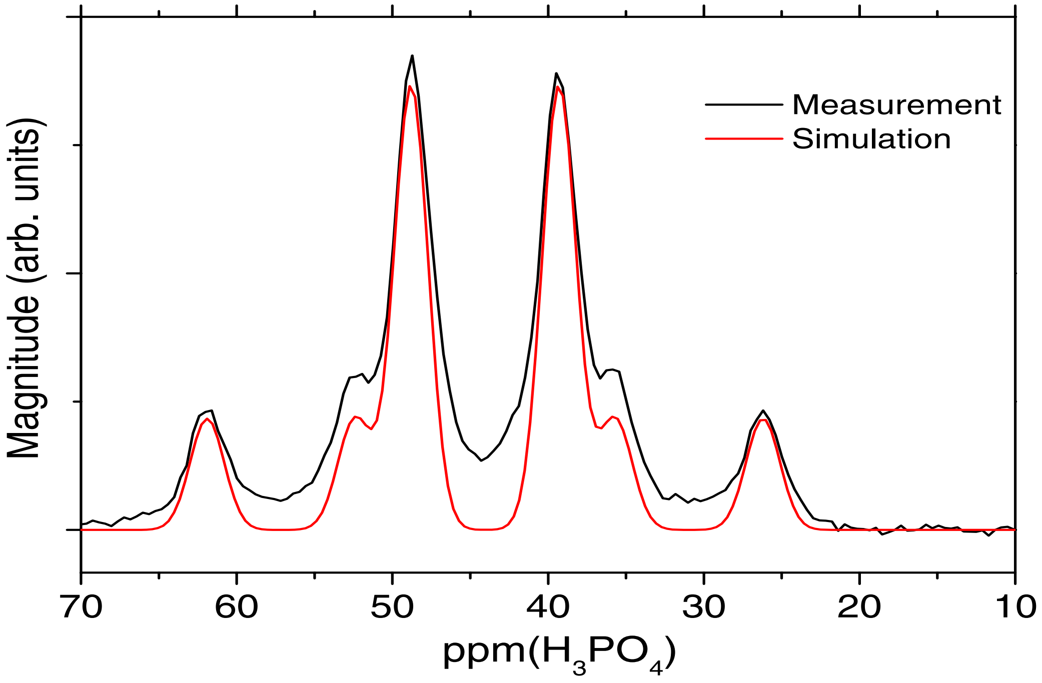

Figure S7: $^{31}P\{^1H\}$ Solid State NMR spectrum of **3** at 7 T together with simulations as discussed above.

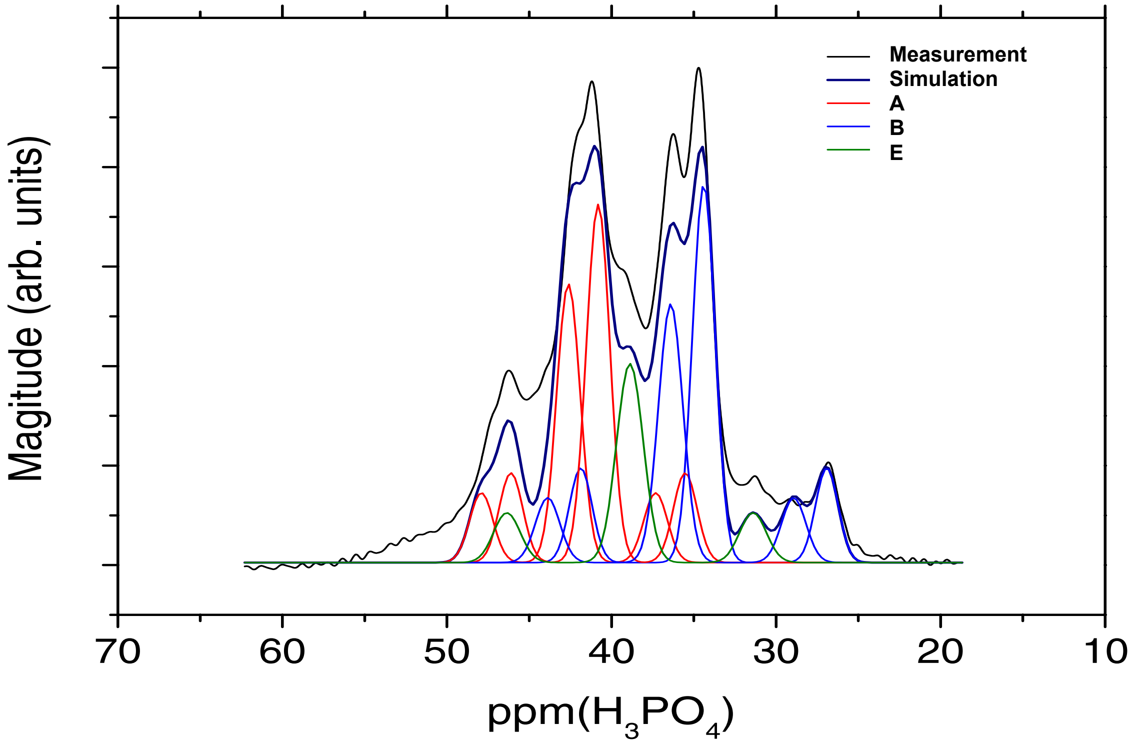

Figure S8: $^{31}P\{^1H\}$ Solid State NMR spectrum of **4** at 9 T, yielded by irradiation of crystals of **3** together with simulations as discussed above.

4. Theoretical studies

4.1 Optimized geometries

The geometries of complexes **3** and **5** in the electronic ground state were optimized using Density Functional Theory (DFT) in its Resolution of the Identity (RI) version,[11] i.e. RI-DFT. The Becke exchange[12] and Perdew correlation[13] functional (BP86) has been combined with a polarized valence triple-ζ basis set (TZVP) for all atoms. Relativistic effects have been considered for Pt atom using the ECP-60-mwb Stuttgart/Dresden pseudopotential[14]. All calculations were performed with the TURBOMOLE[15] program package. The optimized geometries along with selected geometrical parameters are given in Fig. S9.

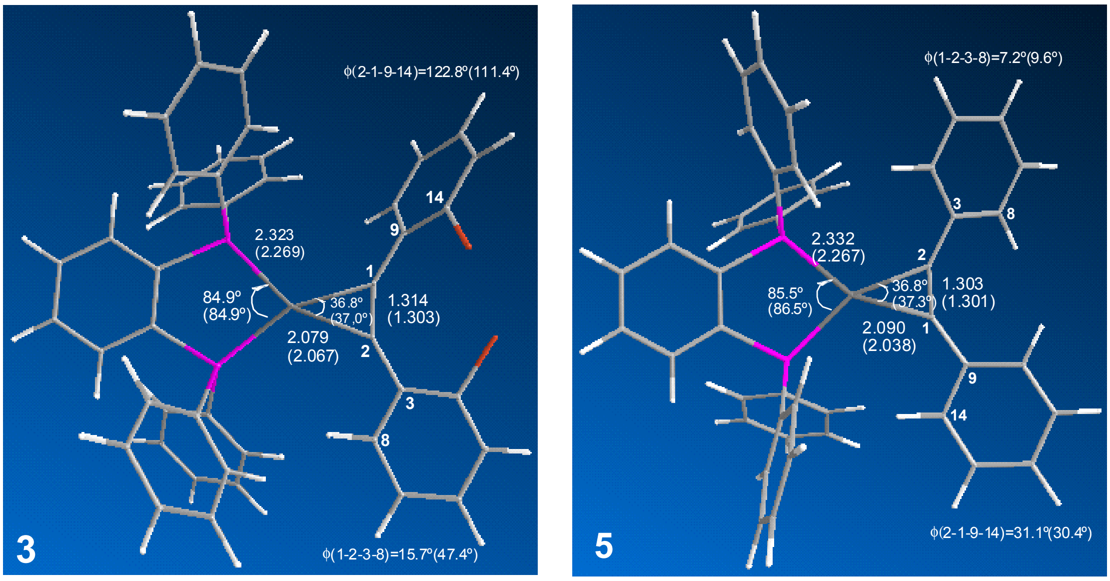

Figure S9: RI-BP86 optimized geometries of complexes **3** and **5**. Distances in Angstroms and angles in degrees. Experimental X-ray parameters in parenthesis.

4.2 Vertical transitions

The vertical transition energies have been obtained using time-dependent DFT (TD-DFT) with 56 roots. The most important transitions with associated oscillator strengths and corresponding excitations for complexes **3** and **5** are collected in Tables S1 and S2, respectively.

Wavelength (nm)	Oscillator strength	Assignment
402	0.0270	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (89.8 %)
392	0.0229	$d_{x2-y2}\rightarrow\pi^{*}_{alkyne}$ (65.4 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (16.6 %)
390	0.0230	$\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (64.1 %) $d_{x2-y2}\rightarrow\pi^{*}_{alkyne}$ (19.0 %)
383	0.0207	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (87.8 %)
376	0.0399	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (49.5 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (38.5 %)
363	0.0270	$d_{z2}\rightarrow\pi^{*}_{alkyne}$ (40.9 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (12.2 %) $d_{yz}\rightarrow\pi^{*}_{dppbe}$ (11.0 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (10.1 %)
357	0.1242	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (35.0 %) $d_{z2}\rightarrow\pi^{*}_{alkyne}$ (26.0 %) $d_{x2-y2}\rightarrow\pi^{*}_{alkyne}$ (11.0 %)
355	0.0245	$\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (33.3 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (30.6 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (10.4 %)
330	0.0688	$d_{xz}\rightarrow\pi^{*}_{alkyne}$ (68.6 %)
320	0.0158	$d_{xz}\rightarrow\pi^{*}_{alkyne}$ (51.3 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (28.3 %)
318	0.0631	$d_{xz}\rightarrow\pi^{*}_{Ph}$ (33.8 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (16.2 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (13.1 %) $d_{yz}\rightarrow\pi^{*}_{Ph}$ (10.5 %)

Table S1: Vertical transition energies of **3** in nm, with oscillator strengths and corresponding assignments.

Wavelength (nm)	Oscillator strength	Assignment
427	0.0126	$\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (32.6 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (30.4 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (22.2 %)
411	0.0821	$\pi_{alkyne}\rightarrow\pi^{*}_{alkyne}$ (33.5 %) $d_{x2-y2}\rightarrow\pi^{*}_{alkyne}$ (18.1 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (17.8 %)
395	0.0883	$\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (45.1 %) $\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (20.8 %)
390	0.0597	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (95.1 %)
388	0.0131	$\pi_{alkyne}\rightarrow\pi^{*}_{Ph}$ (96.7 %)
376	0.0351	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (95.5 %)
364	0.0427	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (92.0 %)
342	0.0345	$d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (61.1 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (29.9 %)
340	0.0178	$d_{xy}\rightarrow\pi^{*}_{dppbe}$ (58.4 %) $d_{x2-y2}\rightarrow\pi^{*}_{Ph}$ (20.7 %)

326	0.0233	$d_{xy}\rightarrow\pi^*_{dppbe}$ (94.5 %)
317	0.1155	$\pi_{alkyne}\rightarrow\pi^*_{Ph}$ (58.2 %) $\pi_{Ph}\rightarrow\pi^*_{dppbe}$ (12.9 %) $d_{yz}\rightarrow\pi^*_{alkyne}$ (12.4 %)

Table S2: Vertical transition energies of **5** in nm, with oscillator strengths and corresponding assignments.

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