Supporting information

Mechanistic features of the copper-free Sonogashira reaction from ESI-MS

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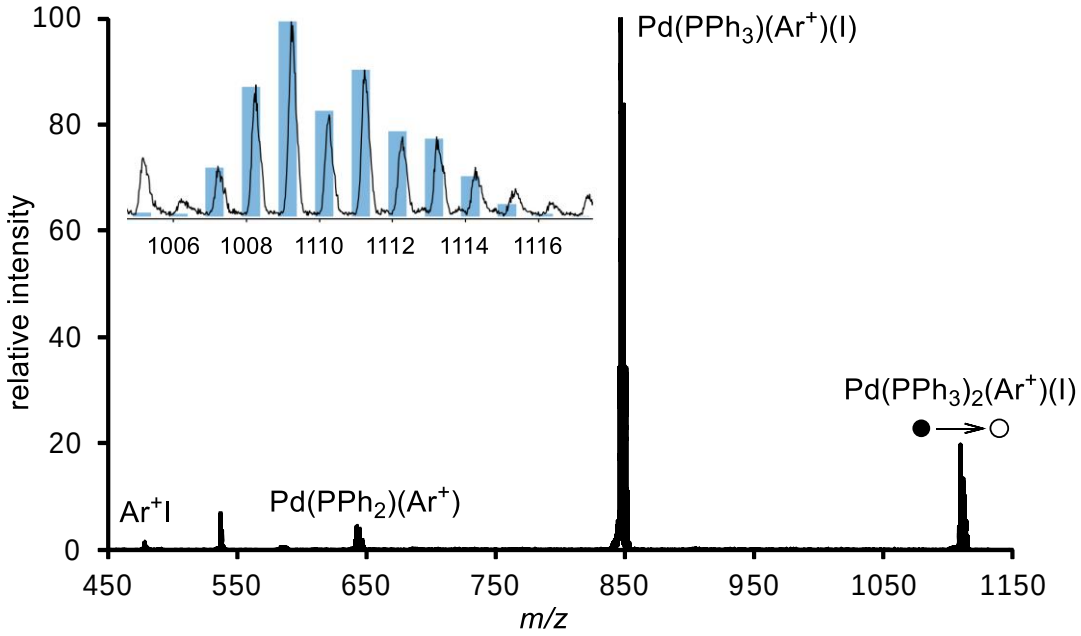

Figure SI1: ESI(+)-MS/MS of $Pd(PPh_3)_2(Ar^+)(I)$ (*m/z* 1109.4). Fragmentation occurs via loss of triphenylphosphine not loss of ArI indicating that elimination of ArI is not facile. Inset: actual spectrum (black) and predicted isotope pattern (blue bars) for $Pd(PPh_3)_2(Ar^+)(I)$.

A product ion MS/MS experiment on $Pd(PPh_3)_2(Ar^+)(I)$ (*m/z* 1109.4) is shown in Figure. The most abundant fragment is the result of the loss of one PPh_3, a small peak of Ar^+I was also observed at *m/z* 479.1. A singly charged palladium containing fragment was also observed at *m/z* 603.2 which is assigned to $Pd(Ar^+)(PPh_2)$ (loss of PhI). These results fully support the composition of the $Pd(PPh_3)_2(Ar^+)(I)$ (though do not help us resolve the question of whether the complex is *cis* or *trans*).

MS/MS experiments on $Pd(PPh_3)_2(Ar^+)(C_2Ph)$ (*m/z* 1083.4) also confirmed its composition. The most abundant fragment as opposed to previous study, is the product of RE of ArC_2Ph at *m/z* 453.2. Loss of one and two PPh_3 was also observed respectively at *m/z* 821.1 and 559.1

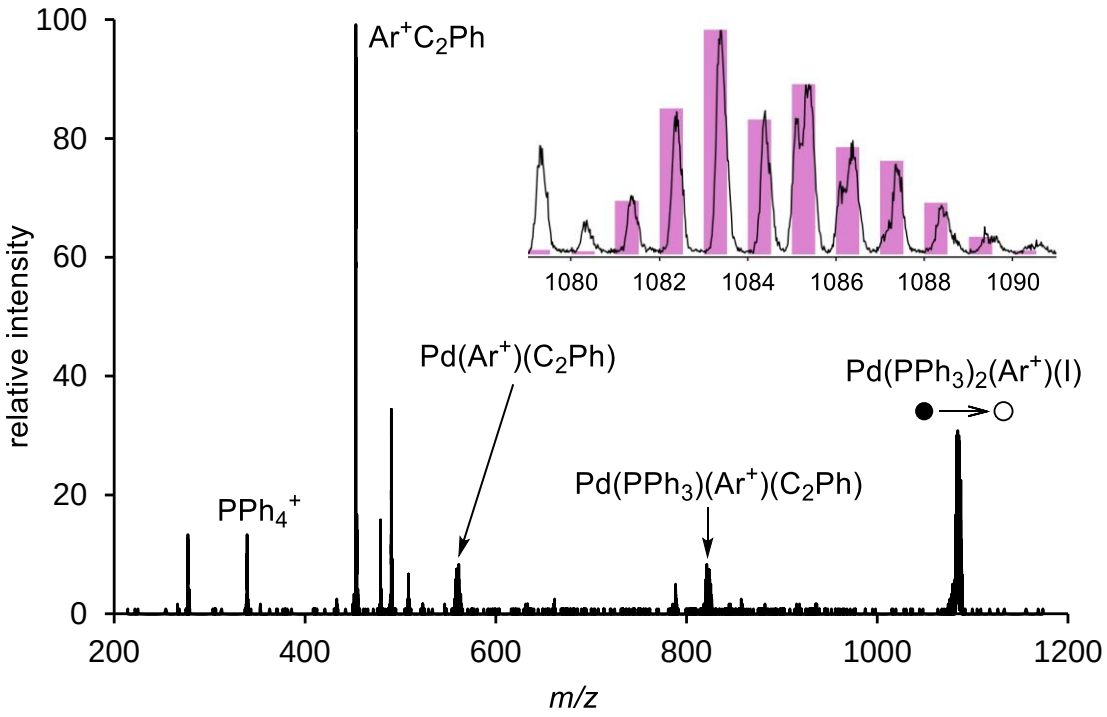

Figure SI2: ESI(+)-MS/MS of $Pd(PPh_3)_2(Ar^+)(C_2Ph)$ (*m/z* 1083.4). Inset: actual spectrum (black) and predicted isotope pattern (pink bars) for $Pd(PPh_3)_2(Ar^+)(C_2Ph)$. ArC_2Ph is the most abundant fragment which denotes that reductive elimination of the product is favourable. Loss of one and two triphenylphoshpine is observed. Some peaks were not assigned.

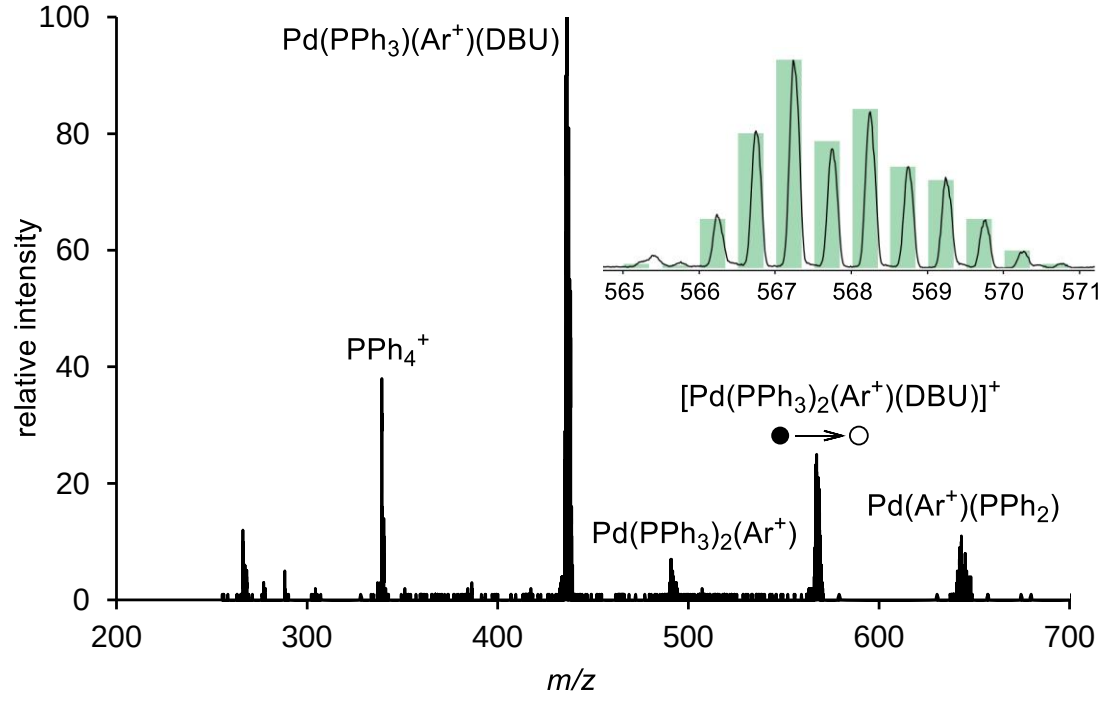

Figure SI3: ESI(+)-MS/MS of $[Pd(PPh_3)_2(Ar^+)(DBU)]^+$ (doubly charged, *m/z* 567.1). Inset: actual spectrum (black) and predicted isotope pattern (green bars) for $[Pd(PPh_3)_2(Ar^+)(DBU)]^+$. The most abundant fragment is obtained by the loss of one triphenylphoshpine (doubly charged, *m/z* 436.2). Also the loss of DBU is observed (doubly charged, *m/z* 491.5). The $Pd(Ar^+)(PPh_2)$ fragment is likely a result of the high energy fragmentation, and PPh_4^+ is a common fragment in CID experiments involving PPh_3.

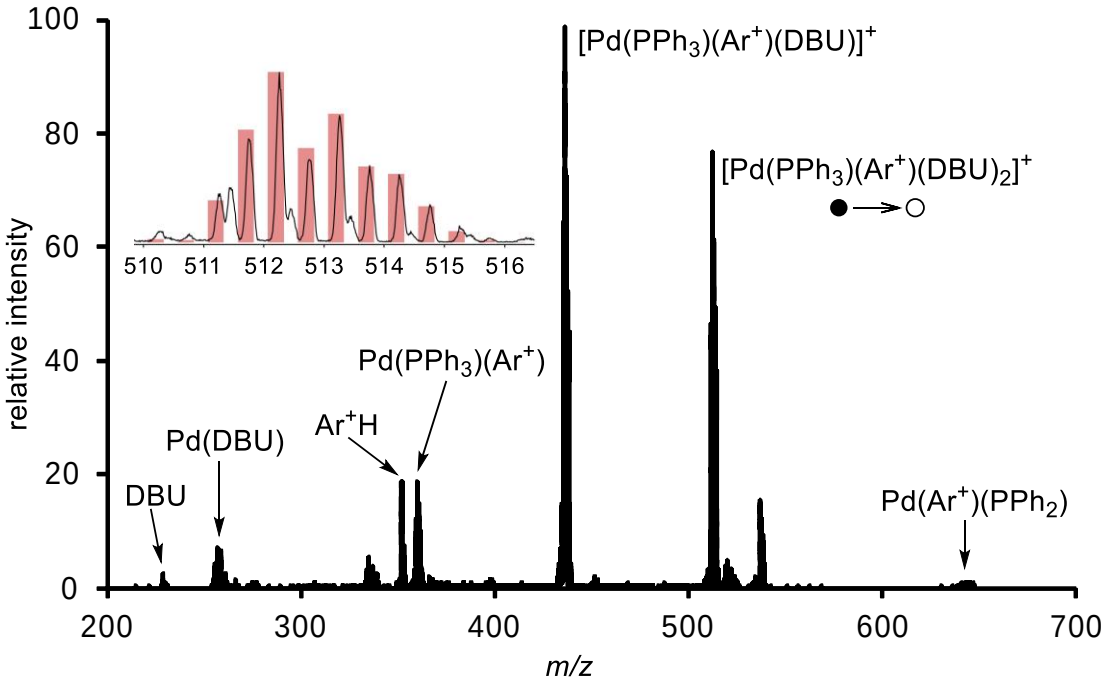

Figure SI4: ESI(+)-MS/MS of $[Pd(PPh_3)(Ar^+)(DBU)_2]^+$ (doubly charged, *m/z* 512.3). Inset: actual spectrum (black) and predicted isotope pattern (red bars) for $[Pd(PPh_3)(Ar^+)(DBU)_2]^+$. The most abundant fragment is obtained by the loss of one DBU (doubly charged, *m/z* 436.2). Also the loss of the second DBU (doubly charged, *m/z* 360.1)

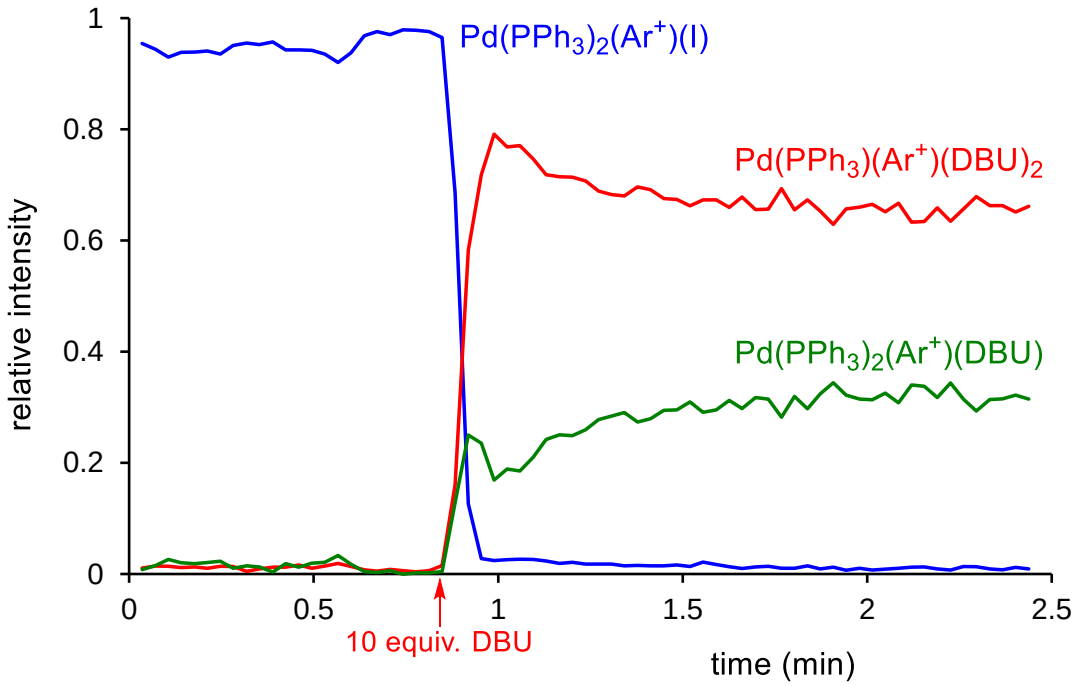

Figure SI5: Addition of ten equivalents of DBU at 0.8 minutes to the mixture of charged Ar^+I (0.5 mM) and catalyst (6 mol %) at reflux in MeOH (10 mL). Ar = $[p\text{-}C_6H_4CH_2PPh_3]^+$, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. Traces are ESI(+)-MS data normalized to the total ion current.

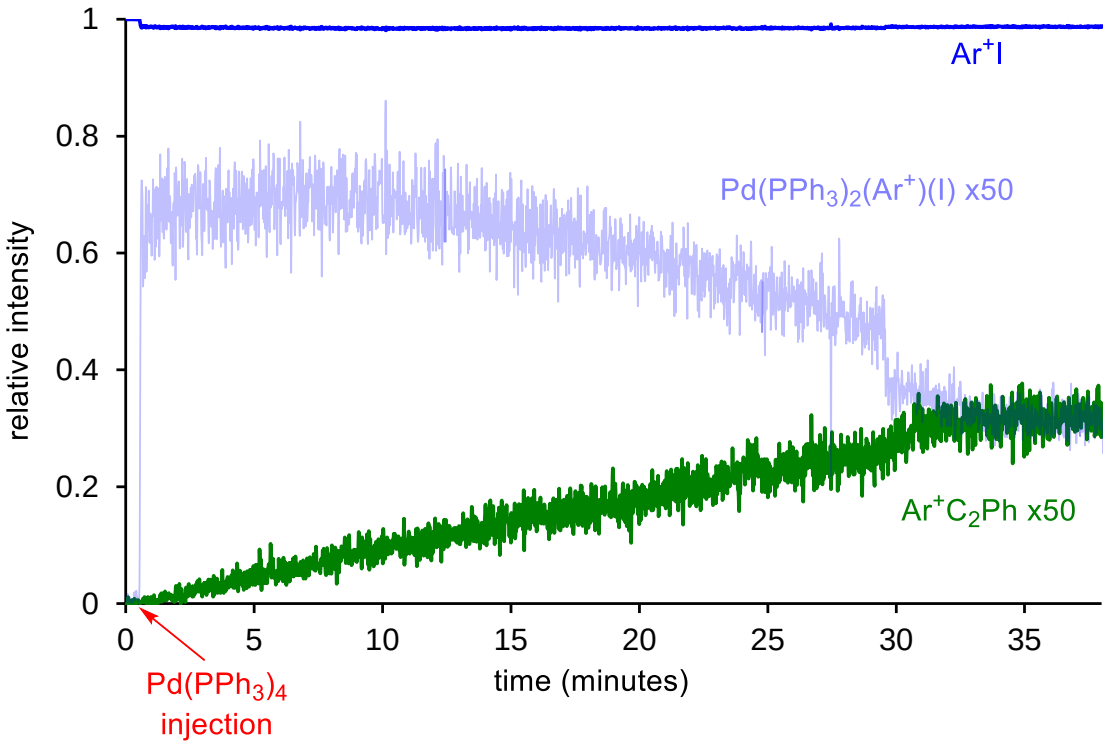

Figure SI6: ESI(+)-MS over time of a reaction performed in the absence of base. The intensities of all observed key species bearing the charged tag are shown, with the intensities of the product and $Pd(PPh_3)_2(Ar^+)(I)$ have been multiplied by 50 for illustrative purposes.

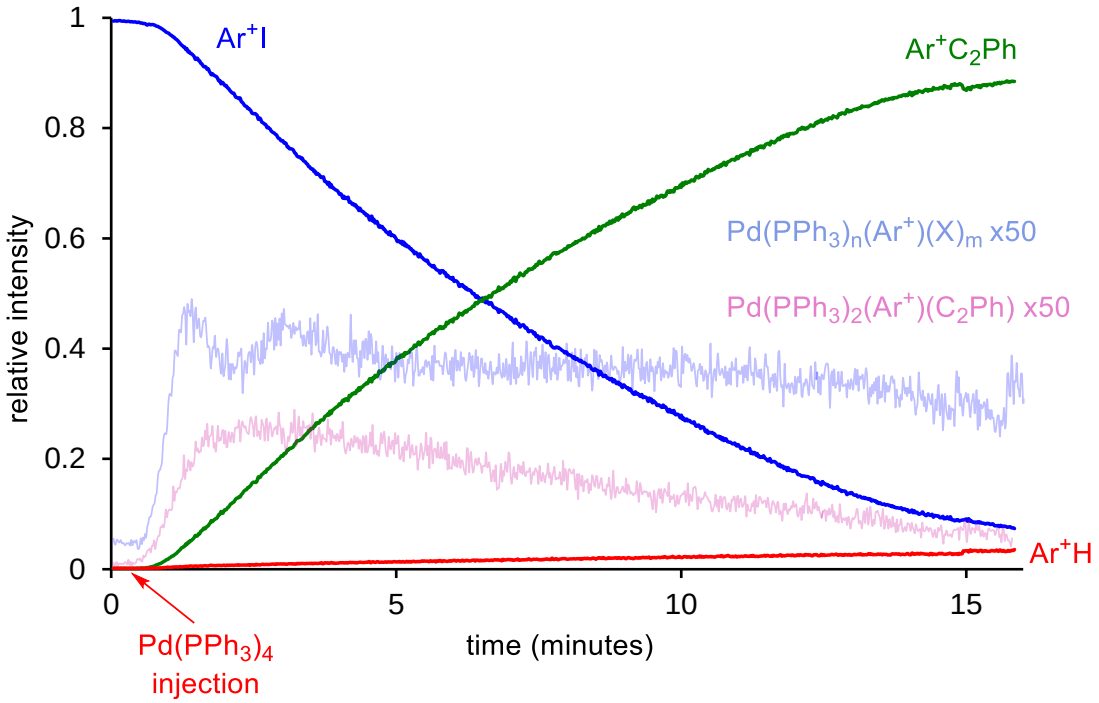

Figure SI7: ESI(+)-MS over time for the intensity of all key species bearing the charged tag for the normal reaction in CH_3OD in the presence of DBU ($Ar^+ = [C_6H_4CH_2PPh_3]^+$). The intensities of the PdP_nArX ($X=I^-$ or DBU) and $PdP_2(Ar)(C_2Ph)$ have been multiplied by 50 for illustrative purposes.

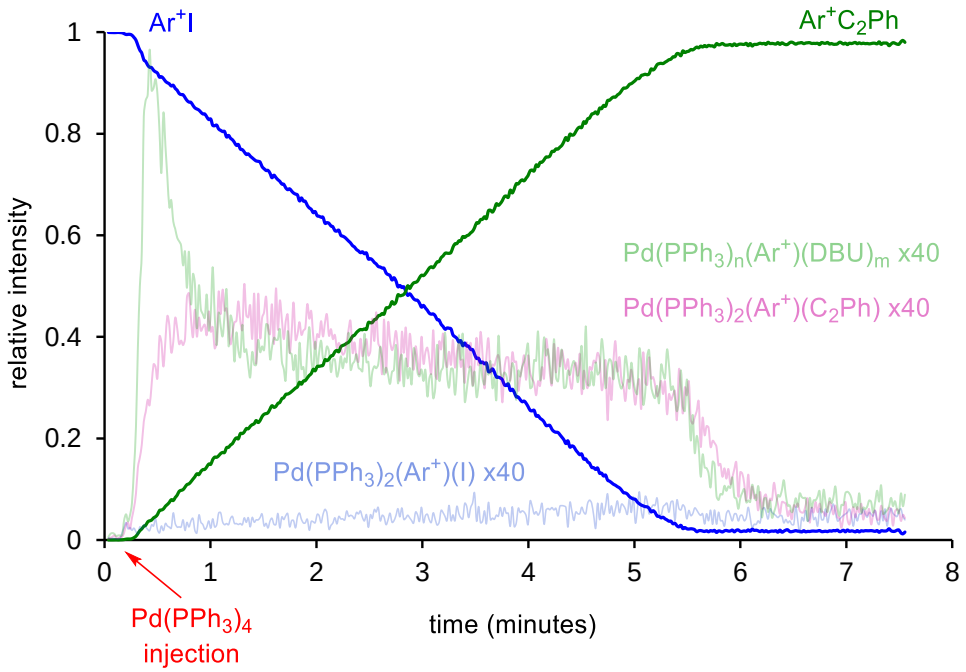

Figure SI8: ESI(+)-MS of reaction with "standard conditions "and three equivalents of phenylacetylene ($Ar^+ = [C_6H_4CH_2PPh_3]^+$). Palladium intermediate species intensities are multiplied by 40 for illustrative purposes.

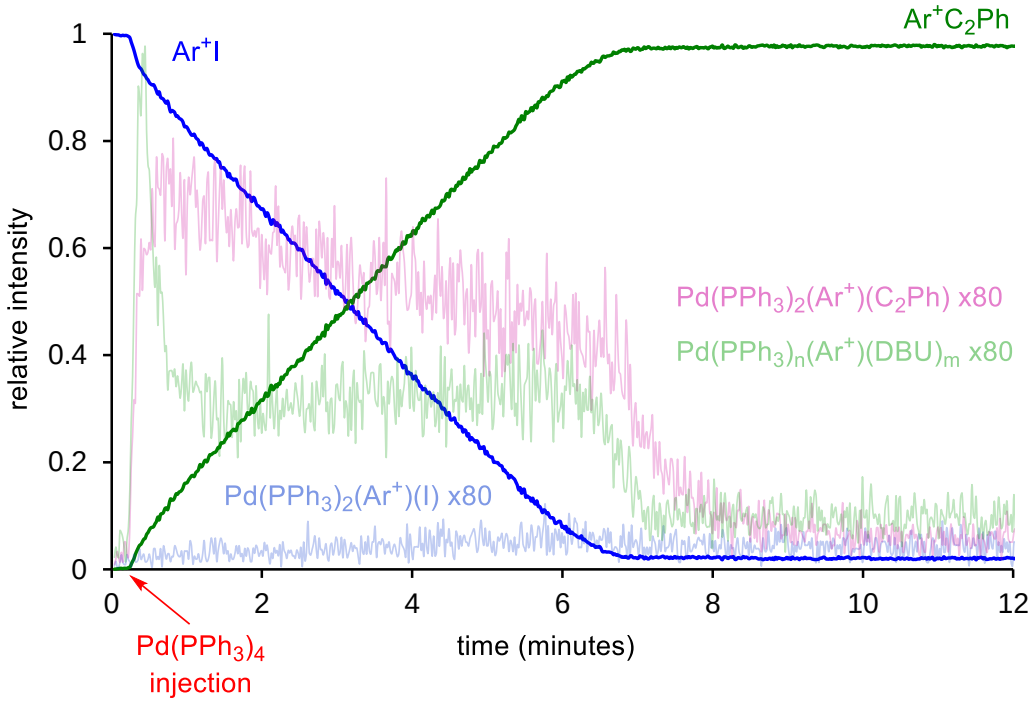

Figure SI9: ESI(+)-MS of reaction with "standard conditions "and six equivalents of phenylacetylene ($Ar^+ = [C_6H_4CH_2PPh_3]^+$). The intensities of the palladium intermediates are multiplied by 80 for illustrative purposes.

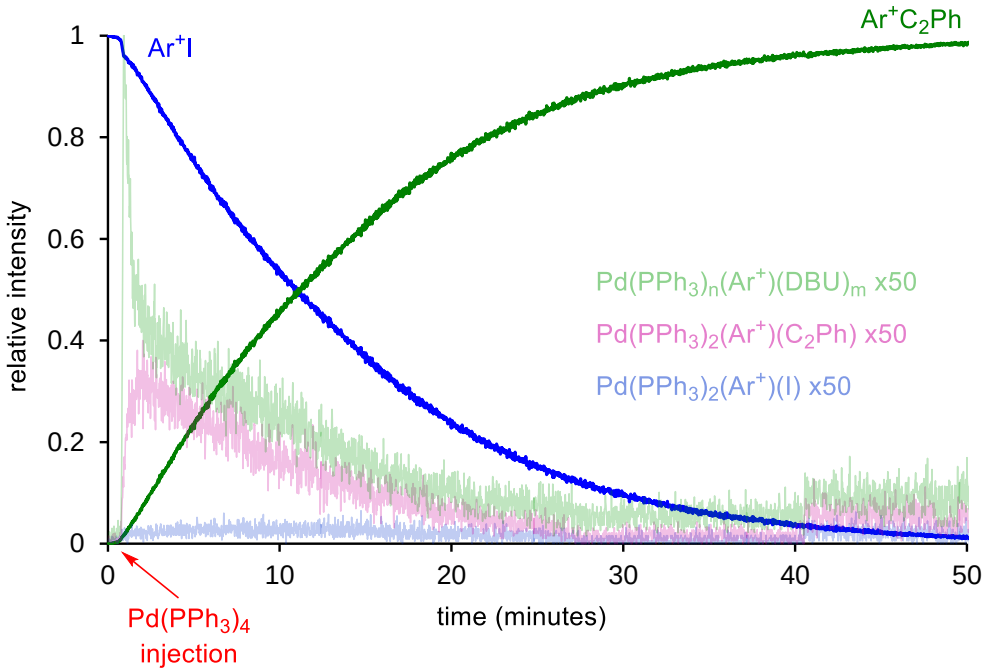

Figure SI10: ESI(+)-MS of reaction with "standard conditions" and three equivalents of biphenylacetylene ($Ar^+ = [C_6H_4CH_2PPh_3]^+$). The intensities of the palladium intermediates are multiplied by 50 for illustrative purposes.

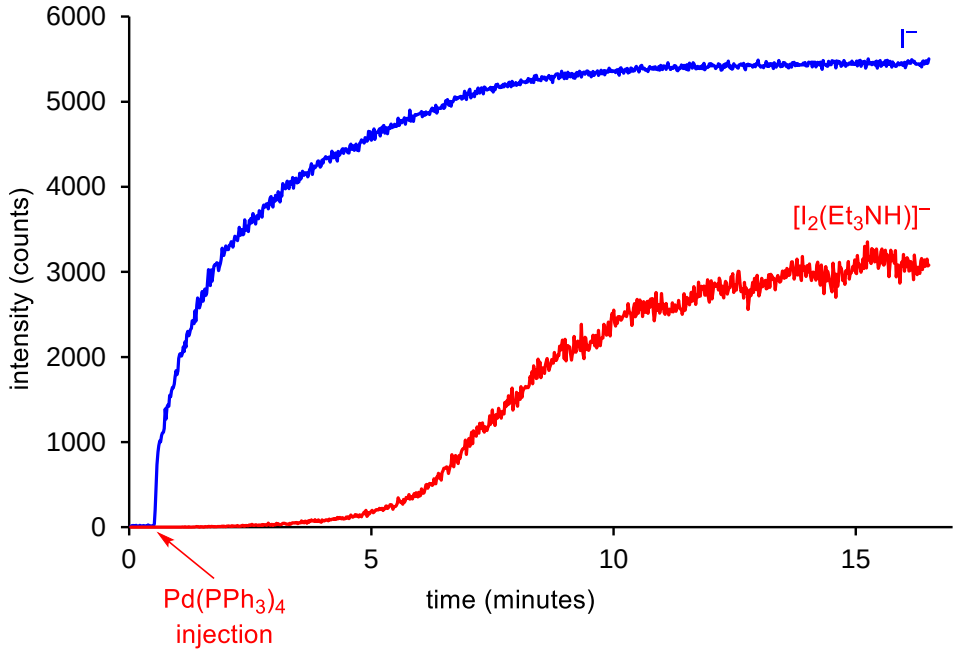

Figure SI11a. ESI(-)-MS intensity data for reaction involving neutral substrates. Release of the iodide and $[I_2(Et_3NH)]^-$ clearly indicates the reaction is proceeding.

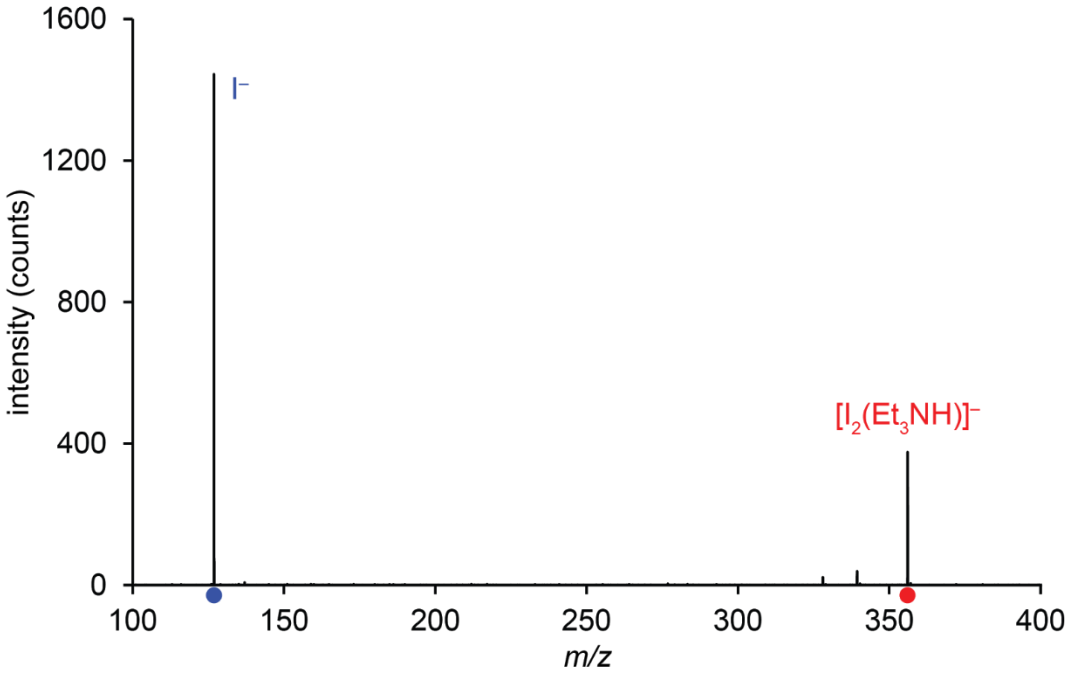

Figure SI11b. ESI(-)-MS intensity data for reaction involving neutral substrates. Release of the iodide and $[I_2(Et_3NH)]^-$ clearly indicates the reaction is proceeding. The above spectrum is a snapshot from the experiment conducted in SI11a, at the 10 minute mark.

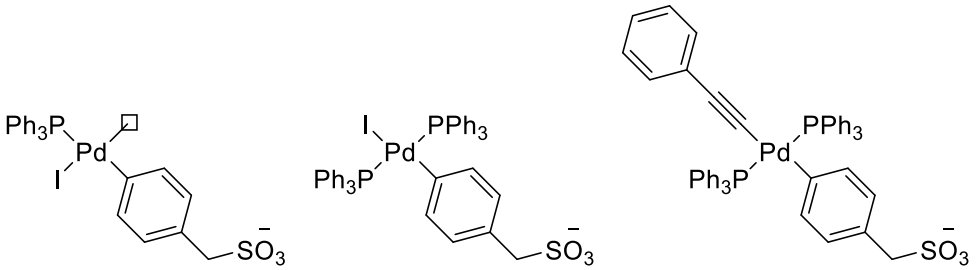

Figure SI12. Proposed structures for the three observed intermediates in ESI(–)-MS: OA product species (left and center) and TM product species (right).

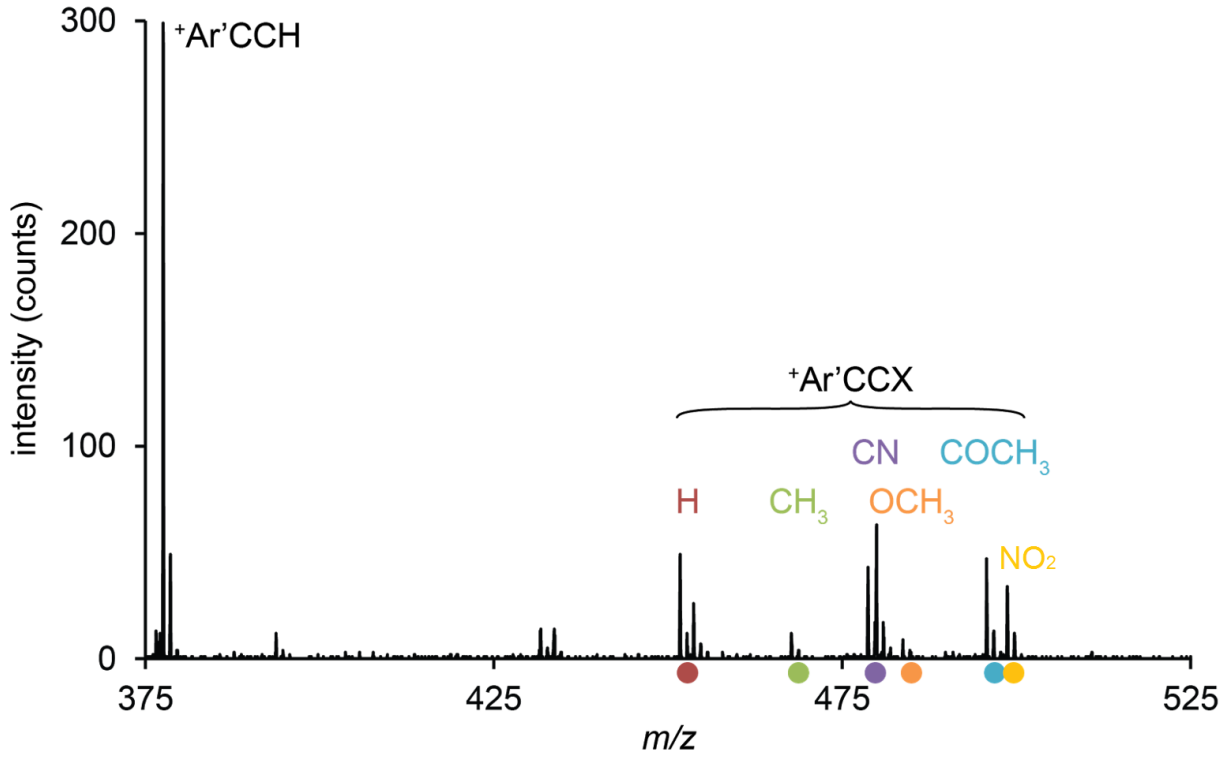

Figure SI13. Snapshot from t = 10 minutes of the multisubstrate screening reaction shown in Figure 4. X = *p*-C_6H_4Y where Y = H, CH_3, CN, OCH_3, $COCH_3$ and NO_2

Table 1. Crystal data and structure refinement for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$.

Identification code	jsm20a
Empirical formula	$C_{33.50}H_{28}F_6O_{0.50}P_2$
Formula weight	614.50
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.7820(12) Å α = 90°
	b = 15.0655(19) Å β = 99.581(2)°
	c = 20.388(3) Å γ = 90°
Volume	2962.7(6) $Å^3$
Z	4
Density (calculated)	1.378 $g.cm^{-3}$
Absorption coefficient (μ)	0.209 mm^{-1}
F(000)	1268
Crystal size	0.30 × 0.21 × 0.14 mm^3
θ range for data collection	1.69 to 26.56°
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-25 \le l \le 25$
Reflections collected	39492
Independent reflections	6151 [R_{int} = 0.0353]
Completeness to θ = 26.56°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6975
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6151 / 0 / 390
Goodness-of-fit on F^2	1.030
Final R indices [I>2σ(I)]	R_1 = 0.0352, wR_2 = 0.0853
R indices (all data)	R_1 = 0.0450, wR_2 = 0.0914
Largest diff. peak and hole	0.456 and -0.333 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	0.09124(4)	0.76798(2)	0.33423(2)	0.018(1)
C(1)	0.08273(16)	0.72780(10)	0.41760(7)	0.021(1)
C(2)	0.04226(16)	0.63087(10)	0.41671(7)	0.021(1)
C(3)	-0.09624(17)	0.60503(11)	0.40599(8)	0.025(1)
C(4)	-0.13121(18)	0.51577(11)	0.40437(8)	0.028(1)
C(5)	-0.02842(18)	0.45072(10)	0.41342(8)	0.027(1)
C(6)	0.11077(18)	0.47663(11)	0.42481(8)	0.029(1)
C(7)	0.14522(17)	0.56598(11)	0.42626(8)	0.026(1)
C(8)	-0.06596(19)	0.35828(11)	0.41299(8)	0.031(1)
C(9)	-0.09951(19)	0.28194(11)	0.41299(8)	0.028(1)
C(10)	-0.13961(17)	0.19023(10)	0.41574(7)	0.023(1)
C(11)	-0.27807(17)	0.16757(11)	0.41565(8)	0.026(1)
C(12)	-0.31541(18)	0.07990(11)	0.42116(8)	0.029(1)
C(13)	-0.21611(18)	0.01358(11)	0.42614(8)	0.029(1)
C(14)	-0.07891(18)	0.03537(11)	0.42540(8)	0.029(1)
C(15)	-0.03978(17)	0.12309(11)	0.42058(8)	0.026(1)
C(16)	-0.07967(15)	0.77860(10)	0.28618(7)	0.021(1)
C(17)	-0.09801(18)	0.76897(11)	0.21714(8)	0.029(1)
C(18)	-0.2271(2)	0.78514(12)	0.17923(9)	0.036(1)
C(19)	-0.33737(19)	0.81007(12)	0.20990(10)	0.039(1)
C(20)	-0.31938(18)	0.81971(12)	0.27839(10)	0.034(1)
C(21)	-0.19054(16)	0.80453(10)	0.31686(8)	0.026(1)
C(22)	0.19071(16)	0.69072(10)	0.29509(7)	0.022(1)
C(23)	0.12985(17)	0.61146(10)	0.26871(8)	0.026(1)
C(24)	0.21073(19)	0.54777(11)	0.24525(8)	0.030(1)
C(25)	0.35119(19)	0.56212(12)	0.24787(9)	0.034(1)
C(26)	0.41202(18)	0.64016(12)	0.27403(9)	0.034(1)
C(27)	0.33210(17)	0.70502(11)	0.29788(8)	0.027(1)
C(28)	0.17289(15)	0.87528(10)	0.33859(7)	0.020(1)
C(29)	0.17368(18)	0.92210(11)	0.27924(8)	0.031(1)
C(30)	0.23532(19)	1.00486(12)	0.28138(9)	0.034(1)
C(31)	0.29531(17)	1.04160(11)	0.34177(9)	0.029(1)
C(32)	0.29419(17)	0.99581(11)	0.40014(8)	0.027(1)
C(33)	0.23375(16)	0.91207(10)	0.39889(8)	0.023(1)

P(2)	0.59346(4)	0.76111(3)	0.47368(2)	0.024(1)
F(1)	0.43262(10)	0.73436(7)	0.46690(5)	0.035(1)
F(2)	0.60260(11)	0.70679(9)	0.40716(5)	0.048(1)
F(3)	0.75378(10)	0.78796(8)	0.47966(6)	0.042(1)
F(4)	0.63657(12)	0.67388(7)	0.51574(6)	0.049(1)
F(5)	0.58458(12)	0.81380(8)	0.54027(6)	0.052(1)
F(6)	0.55051(12)	0.84731(8)	0.43053(7)	0.060(1)
O(1S)	0.4247(3)	0.5958(2)	0.58424(17)	0.051(1)
C(1S)	0.4987(5)	0.5174(3)	0.5813(4)	0.079(2)
H(1A)	0.1742	0.7357	0.4461	0.026
H(1B)	0.0140	0.7632	0.4369	0.026
H(3A)	-0.1672	0.6488	0.3997	0.031
H(4A)	-0.2261	0.4988	0.3970	0.034
H(6A)	0.1818	0.4330	0.4316	0.034
H(7A)	0.2400	0.5831	0.4338	0.031
H(11A)	-0.3468	0.2127	0.4118	0.031
H(12A)	-0.4096	0.0650	0.4215	0.035
H(13A)	-0.2421	-0.0467	0.4301	0.035
H(14A)	-0.0111	-0.0102	0.4282	0.035
H(15A)	0.0547	0.1377	0.4206	0.031
H(17A)	-0.0225	0.7514	0.1962	0.034
H(18A)	-0.2398	0.7791	0.1322	0.044
H(19A)	-0.4258	0.8206	0.1838	0.046
H(20A)	-0.3955	0.8368	0.2991	0.040
H(21A)	-0.1780	0.8117	0.3638	0.031
H(23A)	0.0334	0.6016	0.2670	0.031
H(24A)	0.1699	0.4939	0.2273	0.036
H(25A)	0.4064	0.5180	0.2316	0.040
H(26A)	0.5086	0.6494	0.2757	0.041
H(27A)	0.3736	0.7586	0.3159	0.032
H(29A)	0.1322	0.8972	0.2379	0.037
H(30A)	0.2366	1.0368	0.2413	0.041
H(31A)	0.3373	1.0985	0.3429	0.034
H(32A)	0.3348	1.0215	0.4414	0.032
H(33A)	0.2341	0.8802	0.4391	0.028
H(1S)	0.4416	0.6307	0.5545	0.061
H(1SA)	0.4855	0.4960	0.5352	0.095
H(1SB)	0.4652	0.4724	0.6095	0.095
H(1SC)	0.5975	0.5284	0.5969	0.095

Table 3. Anisotropic displacement parameters ($Å^2$) for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0226(2)	0.0164(2)	0.0155(2)	-0.0004(1)	0.0028(1)	-0.0026(2)
C(1)	0.0284(8)	0.0189(8)	0.0164(7)	0.0008(6)	0.0030(6)	-0.0005(6)
C(2)	0.0320(8)	0.0188(7)	0.0138(7)	0.0005(6)	0.0054(6)	-0.0018(6)
C(3)	0.0303(8)	0.0236(8)	0.0240(8)	0.0019(6)	0.0084(6)	0.0003(7)
C(4)	0.0343(9)	0.0253(9)	0.0269(8)	-0.0001(7)	0.0092(7)	-0.0077(7)
C(5)	0.0448(10)	0.0190(8)	0.0179(7)	-0.0006(6)	0.0102(7)	-0.0044(7)
C(6)	0.0394(10)	0.0210(8)	0.0258(8)	0.0028(6)	0.0057(7)	0.0038(7)
C(7)	0.0292(8)	0.0232(8)	0.0240(8)	0.0024(6)	0.0026(6)	-0.0013(6)
C(8)	0.0478(11)	0.0249(9)	0.0214(8)	-0.0003(7)	0.0110(7)	-0.0039(7)
C(9)	0.0425(10)	0.0229(9)	0.0209(8)	-0.0009(6)	0.0112(7)	-0.0024(7)
C(10)	0.0330(8)	0.0197(8)	0.0160(7)	-0.0018(6)	0.0065(6)	-0.0035(6)
C(11)	0.0299(8)	0.0266(8)	0.0224(8)	-0.0012(6)	0.0059(6)	0.0045(7)
C(12)	0.0279(8)	0.0338(9)	0.0262(8)	-0.0029(7)	0.0064(7)	-0.0070(7)
C(13)	0.0433(10)	0.0193(8)	0.0257(8)	0.0000(6)	0.0074(7)	-0.0060(7)
C(14)	0.0351(9)	0.0242(9)	0.0287(9)	0.0007(7)	0.0054(7)	0.0060(7)
C(15)	0.0256(8)	0.0279(9)	0.0244(8)	-0.0007(7)	0.0052(6)	-0.0021(6)
C(16)	0.0233(8)	0.0180(8)	0.0218(7)	0.0031(6)	0.0008(6)	-0.0042(6)
C(17)	0.0343(9)	0.0283(9)	0.0219(8)	0.0019(7)	0.0010(7)	-0.0073(7)
C(18)	0.0444(11)	0.0332(10)	0.0262(9)	0.0066(7)	-0.0085(8)	-0.0114(8)
C(19)	0.0314(9)	0.0311(10)	0.0471(11)	0.0143(8)	-0.0115(8)	-0.0083(8)
C(20)	0.0253(8)	0.0284(9)	0.0462(11)	0.0113(8)	0.0043(7)	-0.0020(7)
C(21)	0.0280(8)	0.0203(8)	0.0287(8)	0.0043(6)	0.0053(6)	-0.0027(6)
C(22)	0.0282(8)	0.0207(8)	0.0165(7)	-0.0008(6)	0.0049(6)	-0.0007(6)
C(23)	0.0312(8)	0.0234(8)	0.0236(8)	-0.0027(6)	0.0050(6)	-0.0047(7)
C(24)	0.0423(10)	0.0227(8)	0.0252(8)	-0.0056(7)	0.0060(7)	-0.0030(7)
C(25)	0.0415(10)	0.0287(9)	0.0327(9)	-0.0066(7)	0.0119(8)	0.0044(8)
C(26)	0.0306(9)	0.0349(10)	0.0395(10)	-0.0074(8)	0.0117(8)	-0.0004(7)
C(27)	0.0301(8)	0.0243(8)	0.0265(8)	-0.0039(7)	0.0060(7)	-0.0036(7)
C(28)	0.0211(7)	0.0157(7)	0.0236(8)	0.0006(6)	0.0034(6)	-0.0006(6)
C(29)	0.0395(10)	0.0278(9)	0.0225(8)	0.0024(7)	0.0001(7)	-0.0084(7)
C(30)	0.0419(10)	0.0268(9)	0.0317(9)	0.0100(7)	0.0013(7)	-0.0073(7)
C(31)	0.0260(8)	0.0195(8)	0.0393(9)	0.0018(7)	0.0036(7)	-0.0035(6)
C(32)	0.0275(8)	0.0229(8)	0.0289(8)	-0.0049(7)	0.0030(6)	-0.0038(6)
C(33)	0.0251(8)	0.0217(8)	0.0221(8)	-0.0003(6)	0.0033(6)	-0.0011(6)

P(2)	0.0209(2)	0.0246(2)	0.0266(2)	0.0001(2)	0.0025(2)	0.0024(2)
F(1)	0.0240(5)	0.0419(6)	0.0404(6)	-0.0056(5)	0.0082(4)	-0.0054(4)
F(2)	0.0304(6)	0.0774(9)	0.0352(6)	-0.0196(6)	0.0036(4)	0.0010(5)
F(3)	0.0225(5)	0.0503(7)	0.0516(7)	-0.0059(5)	0.0025(4)	-0.0041(5)
F(4)	0.0548(7)	0.0335(6)	0.0524(7)	0.0122(5)	-0.0105(6)	0.0028(5)
F(5)	0.0415(6)	0.0592(8)	0.0561(8)	-0.0326(6)	0.0117(5)	-0.0051(6)
F(6)	0.0429(7)	0.0439(7)	0.0906(10)	0.0342(7)	-0.0002(6)	0.0010(5)
O(1S)	0.0415(16)	0.0453(17)	0.066(2)	0.0113(15)	0.0115(14)	-0.0046(13)
C(1S)	0.043(3)	0.041(3)	0.155(6)	0.024(3)	0.022(3)	0.002(2)

Table 4. Bond lengths [Å] for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$.

atom-atom	distance	atom-atom	distance
P(1)-C(22)	1.7879(16)	P(1)-C(16)	1.7986(15)
P(1)-C(28)	1.7987(15)	P(1)-C(1)	1.8191(15)
C(1)-C(2)	1.512(2)	C(2)-C(3)	1.391(2)
C(2)-C(7)	1.394(2)	C(3)-C(4)	1.387(2)
C(4)-C(5)	1.394(2)	C(5)-C(6)	1.398(2)
C(5)-C(8)	1.440(2)	C(6)-C(7)	1.387(2)
C(8)-C(9)	1.196(2)	C(9)-C(10)	1.440(2)
C(10)-C(11)	1.397(2)	C(10)-C(15)	1.398(2)
C(11)-C(12)	1.380(2)	C(12)-C(13)	1.385(2)
C(13)-C(14)	1.384(2)	C(14)-C(15)	1.384(2)
C(16)-C(21)	1.395(2)	C(16)-C(17)	1.397(2)
C(17)-C(18)	1.388(2)	C(18)-C(19)	1.386(3)
C(19)-C(20)	1.386(3)	C(20)-C(21)	1.388(2)
C(22)-C(27)	1.392(2)	C(22)-C(23)	1.401(2)
C(23)-C(24)	1.379(2)	C(24)-C(25)	1.383(3)
C(25)-C(26)	1.384(2)	C(26)-C(27)	1.389(2)
C(28)-C(33)	1.389(2)	C(28)-C(29)	1.402(2)
C(29)-C(30)	1.382(2)	C(30)-C(31)	1.388(2)
C(31)-C(32)	1.377(2)	C(32)-C(33)	1.392(2)
P(2)-F(6)	1.5855(12)	P(2)-F(4)	1.5875(11)
P(2)-F(5)	1.5875(12)	P(2)-F(2)	1.5990(11)
P(2)-F(3)	1.6044(11)	P(2)-F(1)	1.6077(10)
O(1S)-C(1S)	1.392(5)	C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900	C(3)-H(3A)	0.9500
C(4)-H(4A)	0.9500	C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9500	C(11)-H(11A)	0.9500
C(12)-H(12A)	0.9500	C(13)-H(13A)	0.9500
C(14)-H(14A)	0.9500	C(15)-H(15A)	0.9500
C(17)-H(17A)	0.9500	C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500	C(20)-H(20A)	0.9500
C(21)-H(21A)	0.9500	C(23)-H(23A)	0.9500
C(24)-H(24A)	0.9500	C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9500	C(27)-H(27A)	0.9500
C(29)-H(29A)	0.9500	C(30)-H(30A)	0.9500
C(31)-H(31A)	0.9500	C(32)-H(32A)	0.9500
C(33)-H(33A)	0.9500	O(1S)-H(1S)	0.8400

C(1S)-H(1SA)	0.9800	C(1S)-H(1SB)	0.9800
C(1S)-H(1SC)	0.9800		

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$.

atom-atom-atom	angle	atom-atom-atom	angle
C(22)-P(1)-C(16)	109.90(7)	C(22)-P(1)-C(28)	109.69(7)
C(16)-P(1)-C(28)	108.17(7)	C(22)-P(1)-C(1)	108.26(7)
C(16)-P(1)-C(1)	110.83(7)	C(28)-P(1)-C(1)	109.99(7)
C(2)-C(1)-P(1)	111.27(10)	C(3)-C(2)-C(7)	119.19(14)
C(3)-C(2)-C(1)	121.21(14)	C(7)-C(2)-C(1)	119.60(14)
C(4)-C(3)-C(2)	120.33(15)	C(3)-C(4)-C(5)	120.59(16)
C(4)-C(5)-C(6)	119.12(15)	C(4)-C(5)-C(8)	120.10(16)
C(6)-C(5)-C(8)	120.76(16)	C(7)-C(6)-C(5)	120.07(15)
C(6)-C(7)-C(2)	120.70(16)	C(9)-C(8)-C(5)	178.7(2)
C(8)-C(9)-C(10)	177.78(17)	C(11)-C(10)-C(15)	119.29(15)
C(11)-C(10)-C(9)	120.33(15)	C(15)-C(10)-C(9)	120.35(15)
C(12)-C(11)-C(10)	120.24(15)	C(11)-C(12)-C(13)	120.29(16)
C(14)-C(13)-C(12)	119.83(15)	C(15)-C(14)-C(13)	120.49(16)
C(14)-C(15)-C(10)	119.84(15)	C(21)-C(16)-C(17)	120.12(15)
C(21)-C(16)-P(1)	120.15(12)	C(17)-C(16)-P(1)	119.44(12)
C(18)-C(17)-C(16)	119.70(17)	C(19)-C(18)-C(17)	120.06(17)
C(20)-C(19)-C(18)	120.34(16)	C(19)-C(20)-C(21)	120.21(17)
C(20)-C(21)-C(16)	119.56(16)	C(27)-C(22)-C(23)	120.23(15)
C(27)-C(22)-P(1)	119.48(12)	C(23)-C(22)-P(1)	119.88(12)
C(24)-C(23)-C(22)	119.65(15)	C(23)-C(24)-C(25)	120.09(16)
C(24)-C(25)-C(26)	120.55(16)	C(25)-C(26)-C(27)	120.11(16)
C(26)-C(27)-C(22)	119.37(15)	C(33)-C(28)-C(29)	120.01(14)
C(33)-C(28)-P(1)	121.59(12)	C(29)-C(28)-P(1)	118.41(12)
C(30)-C(29)-C(28)	119.45(15)	C(29)-C(30)-C(31)	120.36(16)
C(32)-C(31)-C(30)	120.26(15)	C(31)-C(32)-C(33)	120.17(15)
C(28)-C(33)-C(32)	119.75(15)	F(6)-P(2)-F(4)	179.02(8)
F(6)-P(2)-F(5)	91.02(8)	F(4)-P(2)-F(5)	89.96(7)
F(6)-P(2)-F(2)	89.76(8)	F(4)-P(2)-F(2)	89.26(7)
F(5)-P(2)-F(2)	179.21(8)	F(6)-P(2)-F(3)	90.07(6)
F(4)-P(2)-F(3)	89.95(6)	F(5)-P(2)-F(3)	90.04(6)
F(2)-P(2)-F(3)	90.09(6)	F(6)-P(2)-F(1)	89.57(6)
F(4)-P(2)-F(1)	90.40(6)	F(5)-P(2)-F(1)	90.39(6)
F(2)-P(2)-F(1)	89.48(6)	F(3)-P(2)-F(1)	179.44(7)
C(2)-C(1)-H(1A)	109.4	P(1)-C(1)-H(1A)	109.4
C(2)-C(1)-H(1B)	109.4	P(1)-C(1)-H(1B)	109.4
H(1A)-C(1)-H(1B)	108.0	C(4)-C(3)-H(3A)	119.8

C(2)-C(3)-H(3A)	119.8	C(3)-C(4)-H(4A)	119.7
C(5)-C(4)-H(4A)	119.7	C(7)-C(6)-H(6A)	120.0
C(5)-C(6)-H(6A)	120.0	C(6)-C(7)-H(7A)	119.7
C(2)-C(7)-H(7A)	119.7	C(12)-C(11)-H(11A)	119.9
C(10)-C(11)-H(11A)	119.9	C(11)-C(12)-H(12A)	119.9
C(13)-C(12)-H(12A)	119.9	C(14)-C(13)-H(13A)	120.1
C(12)-C(13)-H(13A)	120.1	C(15)-C(14)-H(14A)	119.8
C(13)-C(14)-H(14A)	119.8	C(14)-C(15)-H(15A)	120.1
C(10)-C(15)-H(15A)	120.1	C(18)-C(17)-H(17A)	120.2
C(16)-C(17)-H(17A)	120.2	C(19)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18A)	120.0	C(20)-C(19)-H(19A)	119.8
C(18)-C(19)-H(19A)	119.8	C(19)-C(20)-H(20A)	119.9
C(21)-C(20)-H(20A)	119.9	C(20)-C(21)-H(21A)	120.2
C(16)-C(21)-H(21A)	120.2	C(24)-C(23)-H(23A)	120.2
C(22)-C(23)-H(23A)	120.2	C(23)-C(24)-H(24A)	120.0
C(25)-C(24)-H(24A)	120.0	C(24)-C(25)-H(25A)	119.7
C(26)-C(25)-H(25A)	119.7	C(25)-C(26)-H(26A)	119.9
C(27)-C(26)-H(26A)	119.9	C(26)-C(27)-H(27A)	120.3
C(22)-C(27)-H(27A)	120.3	C(30)-C(29)-H(29A)	120.3
C(28)-C(29)-H(29A)	120.3	C(29)-C(30)-H(30A)	119.8
C(31)-C(30)-H(30A)	119.8	C(32)-C(31)-H(31A)	119.9
C(30)-C(31)-H(31A)	119.9	C(31)-C(32)-H(32A)	119.9
C(33)-C(32)-H(32A)	119.9	C(28)-C(33)-H(33A)	120.1
C(32)-C(33)-H(33A)	120.1	C(1S)-O(1S)-H(1S)	109.5
O(1S)-C(1S)-H(1SA)	109.5	O(1S)-C(1S)-H(1SB)	109.5
H(1SA)-C(1S)-H(1SB)	109.5	O(1S)-C(1S)-H(1SC)	109.5
H(1SA)-C(1S)-H(1SC)	109.5	H(1SB)-C(1S)-H(1SC)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(22)-P(1)-C(1)-C(2)	-48.47(13)	C(16)-P(1)-C(1)-C(2)	72.13(12)
C(28)-P(1)-C(1)-C(2)	-168.31(11)	P(1)-C(1)-C(2)-C(3)	-86.62(16)
P(1)-C(1)-C(2)-C(7)	92.85(15)	C(7)-C(2)-C(3)-C(4)	-0.4(2)
C(1)-C(2)-C(3)-C(4)	179.03(14)	C(2)-C(3)-C(4)-C(5)	0.0(2)
C(3)-C(4)-C(5)-C(6)	0.6(2)	C(3)-C(4)-C(5)-C(8)	178.74(15)
C(4)-C(5)-C(6)-C(7)	-0.7(2)	C(8)-C(5)-C(6)-C(7)	-178.85(15)
C(5)-C(6)-C(7)-C(2)	0.3(2)	C(3)-C(2)-C(7)-C(6)	0.3(2)
C(1)-C(2)-C(7)-C(6)	-179.16(14)	C(4)-C(5)-C(8)-C(9)	-25(9)
C(6)-C(5)-C(8)-C(9)	153(9)	C(5)-C(8)-C(9)-C(10)	-66(12)
C(8)-C(9)-C(10)-C(11)	84(5)	C(8)-C(9)-C(10)-C(15)	-94(5)
C(15)-C(10)-C(11)-C(12)	0.8(2)	C(9)-C(10)-C(11)-C(12)	-177.22(15)
C(10)-C(11)-C(12)-C(13)	-0.7(2)	C(11)-C(12)-C(13)-C(14)	-0.2(2)
C(12)-C(13)-C(14)-C(15)	0.8(2)	C(13)-C(14)-C(15)-C(10)	-0.6(2)
C(11)-C(10)-C(15)-C(14)	-0.2(2)	C(9)-C(10)-C(15)-C(14)	177.87(15)
C(22)-P(1)-C(16)-C(21)	154.35(12)	C(28)-P(1)-C(16)-C(21)	-85.92(13)
C(1)-P(1)-C(16)-C(21)	34.73(15)	C(22)-P(1)-C(16)-C(17)	-31.72(15)
C(28)-P(1)-C(16)-C(17)	88.02(14)	C(1)-P(1)-C(16)-C(17)	-151.33(12)
C(21)-C(16)-C(17)-C(18)	-0.1(2)	P(1)-C(16)-C(17)-C(18)	-174.07(13)
C(16)-C(17)-C(18)-C(19)	-0.5(3)	C(17)-C(18)-C(19)-C(20)	0.5(3)
C(18)-C(19)-C(20)-C(21)	0.0(3)	C(19)-C(20)-C(21)-C(16)	-0.7(2)
C(17)-C(16)-C(21)-C(20)	0.7(2)	P(1)-C(16)-C(21)-C(20)	174.60(12)
C(16)-P(1)-C(22)-C(27)	144.74(12)	C(28)-P(1)-C(22)-C(27)	25.94(15)
C(1)-P(1)-C(22)-C(27)	-94.09(13)	C(16)-P(1)-C(22)-C(23)	-42.63(14)
C(28)-P(1)-C(22)-C(23)	-161.43(12)	C(1)-P(1)-C(22)-C(23)	78.55(14)
C(27)-C(22)-C(23)-C(24)	-0.3(2)	P(1)-C(22)-C(23)-C(24)	-172.83(13)
C(22)-C(23)-C(24)-C(25)	0.1(2)	C(23)-C(24)-C(25)-C(26)	0.1(3)
C(24)-C(25)-C(26)-C(27)	-0.1(3)	C(25)-C(26)-C(27)-C(22)	-0.1(3)
C(23)-C(22)-C(27)-C(26)	0.3(2)	P(1)-C(22)-C(27)-C(26)	172.87(13)
C(22)-P(1)-C(28)-C(33)	-111.45(13)	C(16)-P(1)-C(28)-C(33)	128.68(13)
C(1)-P(1)-C(28)-C(33)	7.51(15)	C(22)-P(1)-C(28)-C(29)	68.79(14)
C(16)-P(1)-C(28)-C(29)	-51.07(15)	C(1)-P(1)-C(28)-C(29)	-172.25(13)
C(33)-C(28)-C(29)-C(30)	0.0(3)	P(1)-C(28)-C(29)-C(30)	179.73(14)
C(28)-C(29)-C(30)-C(31)	-0.3(3)	C(29)-C(30)-C(31)-C(32)	0.1(3)
C(30)-C(31)-C(32)-C(33)	0.5(3)	C(29)-C(28)-C(33)-C(32)	0.6(2)
P(1)-C(28)-C(33)-C(32)	-179.13(12)	C(31)-C(32)-C(33)-C(28)	-0.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for $[Ph(C_2)C_6H_4CH_2PPh_3]^+$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1S)-H(1S)...F(1)	0.84	2.36	3.186(3)	166.6
O(1S)-H(1S)...F(4)	0.84	2.28	2.931(3)	135.0

Symmetry transformations used to generate equivalent atoms: