

Reagents and Apparatus. All reagents were handled in a MBraun Labmaster 130 glovebox (dry N₂) or on a grease-free dual manifold argon and vacuum (base vacuum = 2x10⁻² mbar) Schlenk line. Solvents were dried by distillation from NaK (pentane, hexane, Et₂O) or CaH₂ (CH₂Cl₂). Anhydrous grade MeCN was obtained from Sigma-Aldrich and used without distillation. Prior to use all solvents were stored for at least 48 h over 3 Å molecular sieves, which had been freshly activated at 300 °C under dynamic vacuum for 24 h. PCl₃ (99 %), AsCl₃ (99.99 %), *triphos* (97 %), *dppm* (97 %), *dppe* (99 %) were obtained from Sigma-Aldrich and used without further purification. SbF₃ (98 %) was obtained from Sigma-Aldrich and sublimed prior to use. Bi(OTf)₃ was obtained from Sigma-Aldrich and dried at 160 °C under dynamic vacuum. Deuterated solvents were dried using the same procedure as MeCN. TMSOTf (99%) was obtained from Sigma-Aldrich and distilled before use. Reactions were carried out inside the glovebox in screw-cap glass vials that had been dried at 200 °C for at least 1 h and placed under dynamic vacuum (glovebox antechamber) while still hot. NMR tubes fitted with J-Young valves were charged and sealed inside the glovebox. Infrared spectra were obtained on a Perkin Elmer Frontier instrument equipped with a diamond ATR module. Elemental analyses were carried out by Canadian Microanalytical Ltd. in Delta, British Columbia, Canada. All quantum chemical calculations were carried out using Gaussian 09.¹

Synthesis and Characterization

[(*triphos*-Cl)P][OTf]₂, [1P][OTf]₂: AgOTf (2.00 mmol, 514 mg) and PCl₃ (1.00 mmol, 137 mg) were combined in *ca.* 5 mL CH₂Cl₂ in the dark and stirred for 10 minutes. A solution of *triphos* (1 mmol, 535 mg) in 5 mL CH₂Cl₂ was dropwise added over one minute and the reaction mixture was allowed to stir for 16 hours in the dark. The resulting white suspension was filtered on a G3 frit to remove insoluble AgCl. The filtrate was concentrated to *ca.* 5 mL, layered with pentane and placed in the freezer at -30 °C for one week to obtain white crystalline material. The mother liquor was decanted and the solids were washed twice with 3 mL hexane and dried to constant mass under dynamic vacuum. Yield = 766 mg, 85 %; Melting Point = 168-171 °C; Elemental Analysis (calcd./expt.): C (47.88/47.88) H (4.13/3.91) N(0.00/<0.30); IR (ATR, 298 K, [cm⁻¹]): 215 (s), 220 (w), 233 (m), 244 (m), 255 (m), 279 (w), 289 (w), 343 (w), 354 (w), 379 (w), 419 (vw), 440 (vw), 476 (w), 485 (w), 497 (w), 533 (m), 559 (m), 583 (s), 539 (vs), 703 (m), 797 (s), 825 (w), 1028 (vs), 1170 (s), 1227 (vs), 1237 (vs), 1281 (s), 1458 (w), 1616 (vw); ¹H NMR (CD₃CN, 298 K, 300 MHz): 2.66-2.85 (*m*, 2H), 2.95-3.16 (overlapping *m*, 3H), 3.19-3.52 (overlapping *m*, 3H), 7.44-7.63 (overlapping *m*, 8H), 7.63-7.85 (overlapping *m*, 14H), 7.85-7.95 (*m*, 3H); ¹³C {¹H} NMR (CD₃CN, 298 K, 500 MHz): 23.1 (*dd*, ¹J_{CP} = 43 Hz, ²J_{CP} = 10 Hz), 24.3 (*d*, ¹J_{CP} = 50 Hz), 27.4 (*dt*, ¹J_{CP} = 37 Hz, J_{CP} = 5 Hz), 29.7 (*dt*, ¹J_{CP} = 41 Hz, J_{CP} = 5 Hz), 122.2 (*q*, ¹J_{CF} = 323 Hz), 125.6 (*m*, *Cipso*-P), 126.31 (*ddd*, ¹J_{CP} = 29 Hz, ²J_{CP} = 9 Hz, ³J_{CP} = 4 Hz), 126.9 (*ddd*, ¹J_{CP} = 31 Hz, ²J_{CP} = 8 Hz, ³J_{CP} = 4 Hz), 130.6-130.9 (*m*), 131.7 (*d*, 15 Hz),

133.1 (*dd*, 10.7 Hz, 4 Hz), 133.5 (*dd*, 11 Hz, 2 Hz), 133.6 (*dd*, 11 Hz, 2 Hz), 134.2 (*d*, 13 Hz), 134.7 (*dd*, 14 Hz, 3 Hz), 135.0 (*d*, 3 Hz), 138.4 (*s*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 202.5 MHz): -249.9 (*dd*, $^1J_{\text{PP}} = 442$ Hz), 66.7 (*dd*, $^1J_{\text{PP}} = 442$ Hz, $^2J_{\text{PP}} = 15$ Hz), 72.4 (*ddd*, $^1J_{\text{PP}} = 442$ Hz, $^3J_{\text{PP}} = 67$ Hz, $^2J_{\text{PP}} = 15$ Hz), 75.5 (*d*, $^3J_{\text{PP}} = 68$ Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 282.5 MHz) = -78.5 (*s*).

[(*triphos*-Cd)As][OTf]₂, [1As][OTf]₂: This compound was made using a similar procedure as [1P][OTf]₂, using AsCl₃ (1 mmol, 181 mg) instead of PCl₃ and stirring for 2 hours. The product was obtained as a light yellow powder. Yield = 498 mg, 53 %; Melting Point = 99-101 °C dec.; Elemental Analysis (calcd./expt.): C (45.85/43.27) H (3.53/3.62) N(0.00/<0.30); IR (ATR, 298 K, [cm⁻¹]): 222 (*m*), 235 (*w*), 254 (*w*), 280 (*w*), 356 (*m*), 477 (*s*), 514 (*s*), 571 (*m*), 632 (*vs*), 686 (*s*), 733 (*m*), 996 (*w*), 1023 (*vs*), 1100 (*s*), 1150 (*s*), 1221 (*s*), 1235 (*s*), 1436 (*m*), 1482 (*w*); ^1H NMR (CD_3CN , 298 K, 500 MHz): 2.93-3.16 (*m*, 2H), 3.28-2.58 (*m*, 4H), 3.65-3.86 (*m*, 2H), 7.58 (*dt*, 7.9 Hz, 3.5 Hz, 2H), 7.62-7.69 (overlapping *m*, 4H), 7.69-7.77 (overlapping *m*, 3H), 7.77-7.83 (overlapping *m*, 4H), 7.84-8.04 (overlapping *m*, 9H); $^{13}\text{C}\{^1\text{H}\}$ (CD_3CN , 298 K, 125.81 MHz): 22.9 (*d*, $^1J_{\text{CP}} = 34$ Hz), 23.7 (*d*, $^1J_{\text{CP}} = 48$ Hz), 24.7 (*dd*, $^1J_{\text{CP}} = 33$ Hz, $^2J_{\text{CP}} = 4$ Hz), 28.6 (*dd*, $^1J_{\text{CP}} = 37$ Hz, $^2J_{\text{CP}} = 4$ Hz), 121.2 (*q*, $^1J_{\text{CF}} = 321$ Hz), 123.2 (*dd*, $J_{\text{CP}} = 61$ Hz, $J_{\text{CP}} = 2$ Hz), 124.8 (*dd*, $J_{\text{CP}} = 65$ Hz, $J_{\text{CP}} = 2$ Hz), 130.0, 130.1, 130.2, 130.3, 130.3, 130.4, (overlapping *m*), 130.9 (*dd*, $J_{\text{CP}} = 15$ Hz, $J_{\text{CP}} = 5$ Hz), 132.4 (*d*, $J_{\text{CP}} = 10$ Hz), 132.8 (*d*, $J_{\text{CP}} = 11$ Hz), 133.0 (*d*, $J_{\text{CP}} = 11$ Hz), 133.3 (*dd*, $J_{\text{CP}} = 13$ Hz, $J_{\text{CP}} = 3$ Hz), 134.4 (*dt*, $J_{\text{CP}} = 22$ Hz, $J_{\text{CP}} = 4$ Hz), 137.5 (*s*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 202.5 MHz): 56.6 (*s*), 62.4 (*d*, $^3J_{\text{PP}} = 64$ Hz), 74.7 (*d*, $^3J_{\text{PP}} = 64$ Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 282.5 MHz) = -78.5 (*s*).

NMR detection of 2P prepared according to Scheme 2F: 1P (0.5 mmol, 449 mg) and powdered magnesium (0.75 mmol, 18 mg) were combined in 3 mL THF and stirred for 1 hour at room temperature to obtain a green suspension. A $^{31}\text{P}\{^1\text{H}\}$ NMR assay of this suspension showed <50 % conversion of starting material. The suspension was stirred for a further 16 hours at room temperature to obtain an orange-brown suspension. Upon filtration, a clear light orange solution was obtained which showed very broad resonances at room temperature in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Upon cooling to -50 °C, well resolved signals were observed (Figure S1) and found to be consistent with the reported NMR data for this compound.² As the cation has been reported previously, this compound was not isolated.

NMR detection of 2P prepared according to Scheme 2E: *triphos* (0.1 mmol, 62 mg) and [(*tbbipy*)₂P][OTf]₃ (0.1 mmol, 101 mg) were combined in 3 mL MeCN and stirred for 2 hours to obtain a light yellow-orange suspension. Upon filtration, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution showed broad peaks at room temperature. Volatiles were removed and the residue was redissolved in CD₂Cl₂. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution at -50 °C showed well-resolved signals which were consistent with reported ^{31}P NMR data for this compound² and with the NMR spectrum obtained for 2P prepared according to Scheme 2F. A number of highly coupled resonances were also observed in this spectrum assigned to the as-yet unidentified oxidation products from this redox reaction.

(*triphos*)Sb(OTf)₃•0.5MeCN, 3Sb•0.5MeCN: Solid SbF₃ (1.00 mmol, 179 mg) was suspended in 5 mL MeCN and TMSOTf (3 mmol, 667 mg) was added as a neat liquid. A clear, pale yellow solution was obtained upon stirring for 16 hours and then all volatiles were removed to obtain a

pale yellow powder. The powder was suspended in 2 mL CH₂Cl₂ and a solution of *triphos* (1 mmol, 535 mg) in CH₂Cl₂ (2 mL) was added to obtain a white suspension. To overcome the low solubility of the solids, 4 mL MeCN was added and after stirring for 1.5 h a clear, pale yellow solution was obtained. This solution was concentrated to half its volume, and allowed to settle overnight at -30 °C. The supernatant was decanted and the solids were washed twice with 2 mL Et₂O and dried to constant mass under vacuum. Yield: 1.012 g, 91 %; Melting Point: 112-113 °C, dec.; Elemental Analysis with half molecule of MeCN (calcd./expt.): C (40.50/40.28) H (3.35/3.03) N(0.62/0.61); IR (ATR, 298 K, [cm⁻¹]): 223 (m), 234 (w), 260 (w), 280 (w), 316 (m), 352 (m), 364 (w), 404 (w), 416 (w), 428 (w), 444 (w), 470 (s), 484 (s), 512 (vs), 573 (m), 629 (vs), 682 (s), 692 (w), 710 (s), 721 (m), 742 (s), 753 (w), 814 (m), 860 (m), 883 (w), 998 (vs), 1017 (vs), 1034 (w), 1094 (s), 1113 (m), 1154 (s), 1192 (vs), 1206 (vs), 1216 (vs), 1230 (s), 1290 (s), 1306 (m), 1343 (w), 1407 (w), 1438 (m), 1487 (w), 1575 (w); ¹H NMR (CD₃CN, 298 K, 300.27 MHz): 3.56 (broad *m*, 4H), 3.84 (broad *m*, 4H), 7.19 (pseudo *tt*, 8 Hz, 4H), 7.43 (pseudo *q*, 8 Hz, 4H), 7.49 (*t*, 8 Hz), 7.61 (*m*, 2 H), 7.64-7.68 (broad *t*, 8 Hz, 4H), 7.58 (broad *t*, 8 Hz, 3H), 7.83-7.90 (overlapping *m*, 2 H), 8.07 (broad *q*, 8 Hz, 4H), ¹³C{¹H} (CD₃CN, 298 K, 125.81 MHz): 120.2 (*dt*, ¹J_{CP} = 59 Hz, ³J_{CP} = 2 Hz), 121.1 (*d*, ¹J_{CP} = 51 Hz), 123.2 (*d*, ¹J_{CP} = 58 Hz), 130.9 (pseudo *d*, J_{CP} = 14 Hz), 131.6-131.9 (overlapping *m*), 133.5 (*t*, J_{CP} = 5 Hz), 134.7 (*t*, J_{CP} = 5 Hz), 135.0 (*d*, J_{CP} = 10 Hz), 135.9 (*d*, J_{CP} = 34 Hz), 136.0 (*s*); ³¹P NMR (CD₃CN, 298 K, 202.5 MHz): 31.1 (*s*, 2P), 53.4 (*s*, 1P). Crystals of **3Sb**•MeCN suitable for diffraction were obtained by slow evaporation of solvent from a concentrated MeCN solution and exhibited the same NMR resonances as the bulk material.

(triphos)Bi(OTf)₃, 3Bi: Solid *triphos* (1.00 mmol, 535 mg) was added over 10 minutes in five portions to a stirred solution Bi(OTf)₃ (1.00 mmol, 656 mg) in MeCN (12 mL). The resulting dark brown suspension was allowed to stir for 15 minutes to obtain a clear dark orange solution. This solution was concentrated to 6 mL, layered with 4 mL Et₂O and placed at -30 for 48 hours to obtain pale yellow crystalline material. The solid was separated by decanting the mother liquor and washed with an additional 5 mL Et₂O. Removal of all volatiles gave **3Bi** as a fine, beige powder. Yield: 612 mg, 51 %; Melting Point: 173 °C, dec.; Elemental Analysis (calcd./expt.): C (37.32/36.96) H (2.79/2.83) N(0.00/<0.30); ¹H NMR (CD₃CN, 298 K, 300.27 MHz): 3.82 (broad *m*, 4H), 4.06 (broad *m*, 2H), 4.28 (broad *m*, 2H), 7.25 (*m*, 4H), 7.42 (*m*, 6H), 7.68 (*m*, 9H), 7.83 (*m*, 2H), 7.96 (*m*, 4H); ¹³C{¹H} (CD₃CN, 298 K, 75.51 MHz): 29.0 (*t*, J_{CP} = 13 Hz), 30.3 (*d*, J_{CP} = 25 Hz), 121.8 (*q*, ¹J_{CF} = 321 Hz), 123.3 (*d*, J_{CP} = 50 Hz), 125.5 (*m*), 130.9 (*d*, J_{CP} = 13 Hz), 131.7 (*t*, J_{CP} = 6 Hz), 133.6 (*t*, J_{CP} = 5 Hz), 134.9 (*m*), 135.6 (*s*), 136.0 (*d*, J_{CP} = 4Hz); ³¹P NMR (CD₃CN, 298 K, 202.5 MHz): 81.3 (broad *s*, 2P), 108.6 (broad *s*, 1P); ¹⁹F NMR (CD₃CN, 298 K, 282.6 MHz): -79.0 (*s*). Crystals suitable for diffraction were obtained by cooling a saturated MeCN solution to -30 °C and exhibited the same NMR resonances as the bulk material.

(dppm)Sb(MeCN)(OTf)₃: SbF₃ (0.179 g, 1 mmol) and *bis*-(diphenylphosphino)methane (dppm) were combined in a vial equipped with a stir bar and 10 mL of CH₃CN was added. The mixture was stirred for 5 minutes to obtain a white suspension. A solution of TMSOTf (0.666 g, 3 mmol) in 7 mL CH₃CN was added dropwise over 30 seconds to obtain a clear yellow solution, which was allowed to stir for 16 h at room temperature. The cloudy solution was filtered and slow removal of the solvent under dynamic vacuum yielded large colourless blocks identified as **(dppm)Sb(MeCN)(OTf)₃** by X-ray crystallography. A second crop was obtained by storing the

mother liquor at $-30\text{ }^{\circ}\text{C}$ for 4 days. Yield: 0.711 g, 79 %; Melting Point: $182\text{-}184\text{ }^{\circ}\text{C}$; Elemental Analysis (calcd./expt.): H (2.81/2.59) N (1.56/1.51) – A satisfactory carbon analysis could not be obtained; Raman (int.): 117 (41), 160 (18), 179 (44), 208 (10), 220 (10), 234 (9), 241 (8), 254 (11), 266 (5), 319 (9), 322 (9), 345 (10), 354 (8), 363 (13), 380 (5), 388 (6), 408 (19), 423 (10), 444 (7), 462 (6), 467 (4), 504 (14), 520 (3), 533 (16), 537 (7), 576 (5), 587 (3), 616 (12), 634 (3), 676 (6), 683 (4), 687 (7), 701 (5), 714 (2), 743 (4), 747 (3), 763 (15), 766 (20), 848 (2), 926 (5), 942 (4), 978 (9), 981 (10), 986 (10), 1002 (100), 1028 (7), 1044 (5), 1094 (33), 1103 (16), 1146 (4), 1165 (12), 1197 (6), 1231 (9), 1237 (7), 1315 (3), 1346 (6), 1373 (4), 1440 (6), 1486 (5), 1585 (87), 2255 (7), 2258 (19), 2298 (2), 2858 (4), 2941 (22), 2965 (3), 2996 (7), 3034 (3), 3069 (42), 3077 (26), 3152 (2), 3171 (3); ^1H NMR (CD_3CN , 298 K, 300 MHz): 1.98 (s, 3H), 5.51 (t, 2H, $^2J_{\text{PH}} = 12.6\text{ Hz}$), 7.58-7.85 (m, 10H); ^{31}P NMR (CD_3CN , 75.47 MHz, 298 K): 21.9 (s); ^{19}F NMR (CD_3CN , 298 K, 282.6 MHz): -78.5 (s).

(*dppe*)Sb(OTf)₃: This compound was made using a similar procedure as (*dppm*)Sb(MeCN)(OTf)₃, using *dppe* (1 mmol, 398 mg) instead of *dppm* and stirring for 4 hours. The product was obtained as a light yellow powder upon removal of all volatiles from the recrystallized solid (MeCN, $-30\text{ }^{\circ}\text{C}$). Yield: 612 mg, 63 %; Melting Point: $201\text{-}205\text{ }^{\circ}\text{C}$; IR (ATR, 298 K, [cm^{-1}]): 225 (s), 231 (m), 243 (m), 261 (vw), 282 (vw), 318 (m), 352 (s), 368 (w), 416 (w), 450 (w), 469 (m), 484 (s), 512 (vs), 524 (s), 572 (m), 586 (w), 625 (vs), 664 (vw), 684 (m), 694 (vw), 711 (w), 723 (m), 739 (m), 762 (vw), 819 (m), 869 (w), 919 (w), 938 (vs), 977 (s), 1009 (s), 1027 (vw), 1096 (m), 1110 (m), 1131 (s), 1168 (s), 1183 (vs), 1207 (s), 1229 (m), 1262 (w), 1276 (w), 1306 (m), 1339 (m), 1309 (vw), 1439 (m), 1487 (vw), 1586 (vw), 2927 (vw), 2964 (vw), 3068 (vw); ^1H NMR (CD_3CN , 298 K, 500 MHz): 3.97 (pseudo *d*, 4H), 7.69 (*m*, 8H), 7.78, (*m*, 4H), 7.96 (*m*, 8H); $^{13}\text{C}\{^1\text{H}\}$ (CD_3CN , 298 K, 125.81 MHz): 23.6 (*d*, $^1J_{\text{CP}} = 32\text{ Hz}$), 120.9 (*q*, $^1J_{\text{CF}} = 319\text{ Hz}$), 121.2 (*d*, $^1J_{\text{CP}} = 57\text{ Hz}$), 131.7 (*m*), 135.1 (*m*), 136.0 (*s*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 202.5 MHz): 46.0 (s); $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 298 K, 282.6 MHz): -78.7 (s). Crystals were obtained upon cooling a saturated MeCN solution to $-30\text{ }^{\circ}\text{C}$ and exhibited the same NMR resonances as the bulk product.

Supporting Figures and Tables

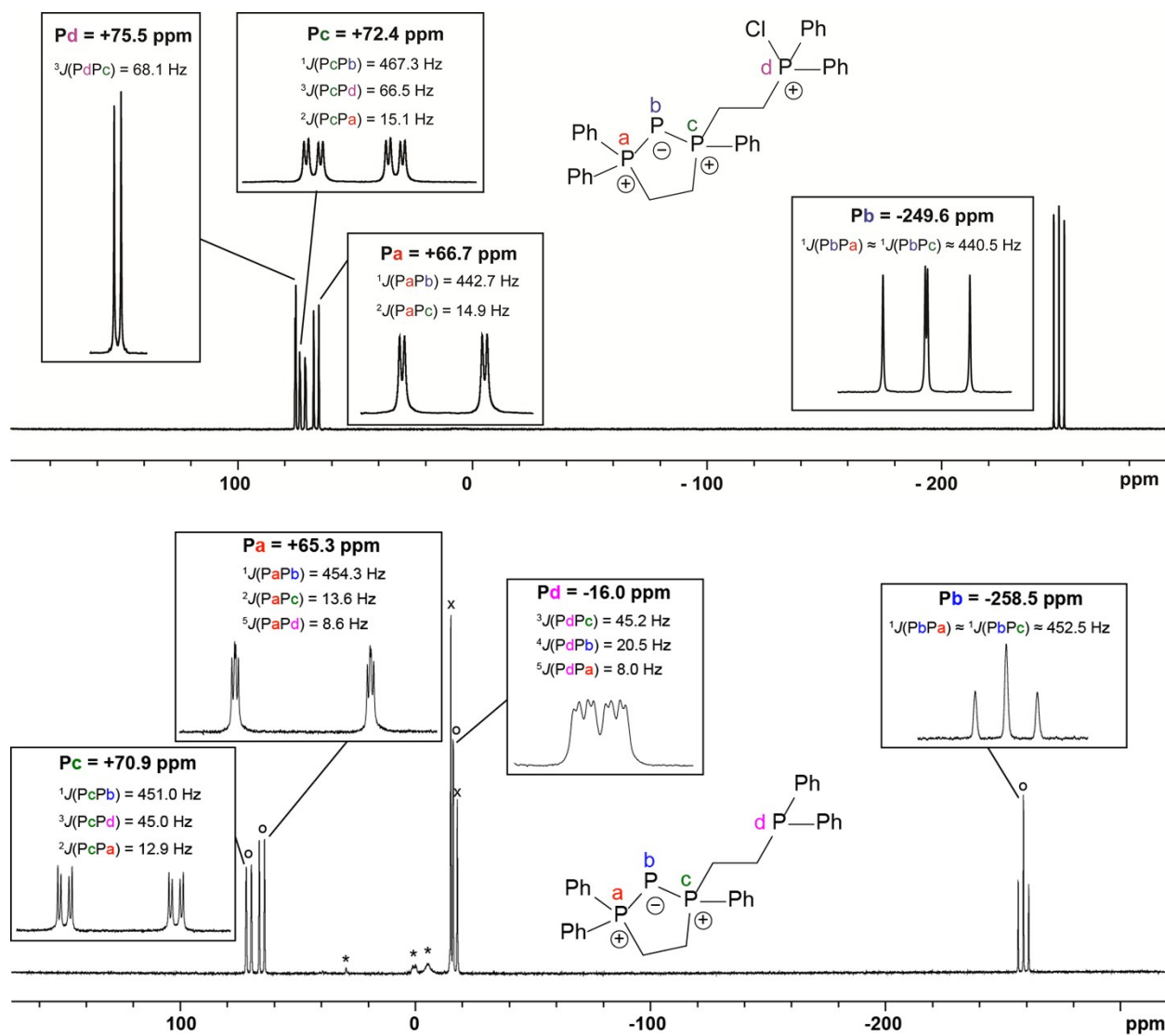


Figure S1. Top: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1P** at room temperature. Bottom: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (THF, -50 °C) of the crude reaction mixture containing equimolar amounts of **1P** and magnesium. Symbols denote resonances due to **2P** (o), *triphos* (x), and unidentified byproducts (*).

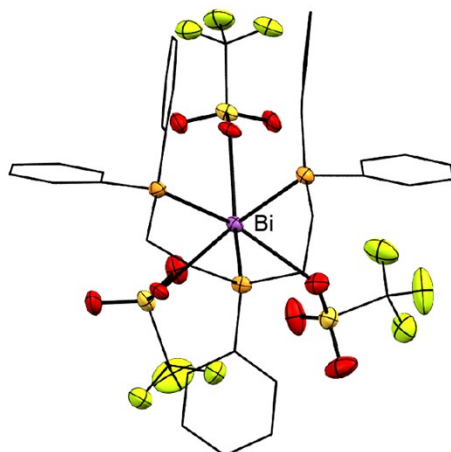


Figure S3. Molecular structure of **3Bi** in the solid state. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms have been omitted for clarity. The crystal showed severe twinning and the diffraction data is only suitable for establishing connectivity.

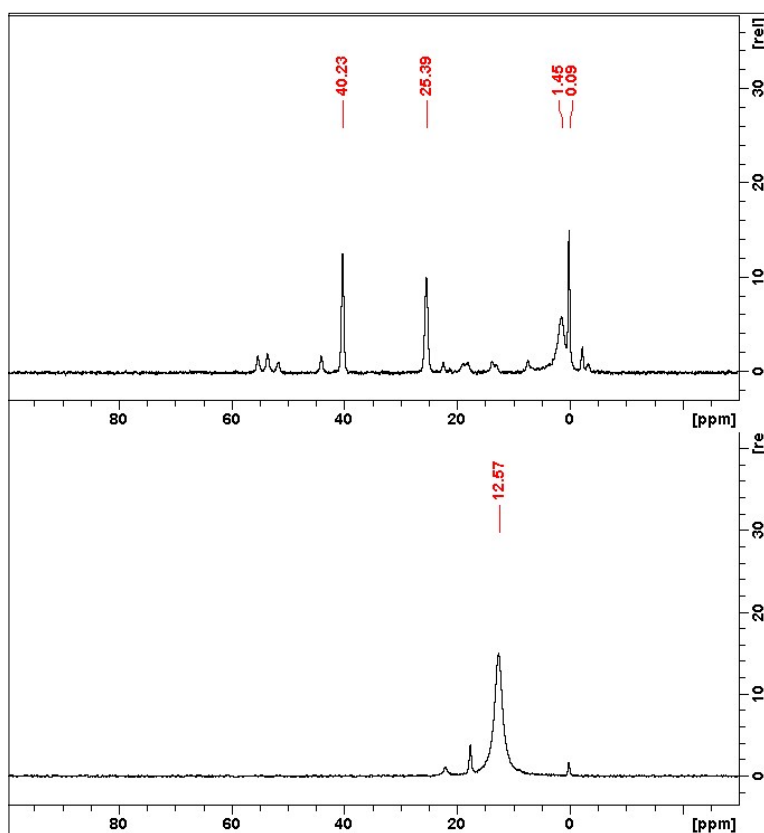


Figure S3. ^{31}P NMR (CD_3CN , 298 K) spectra of the reaction mixture containing $\text{Sb}(\text{OTf})_3$ and PPh_3 in a 1:3 stoichiometry after 5 minutes (bottom) and 16 hours (top) of stirring.

Table S1. Crystallographic Experimental Details for *(triphos)Sb(OTf)₃•MeCN* (CCDC No.: 1417711)

A. Crystal Data

formula	C ₃₉ H ₃₆ F ₉ NO ₉ P ₃ S ₃ Sb
formula weight	1144.53
crystal dimensions (mm)	0.26 × 0.12 × 0.05
crystal system	orthorhombic
space group	<i>Pbcn</i> (No. 60)
unit cell parameters ^a	
<i>a</i> (Å)	12.2821 (2)
<i>b</i> (Å)	16.7365 (3)
<i>c</i> (Å)	44.4675 (8)
<i>V</i> (Å ³)	9140.7 (3)
<i>Z</i>	8
ρ_{calcd} (g cm ⁻³)	1.663
μ (mm ⁻¹)	7.874

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD ^b
radiation (λ [Å])	Cu K α (1.54178) (microfocus source)
temperature (°C)	-100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	145.83
total data collected	60603 ($-15 \leq h \leq 15$, $-20 \leq k \leq 20$, $-54 \leq l \leq 52$)
independent reflections	9109 ($R_{\text{int}} = 0.0426$)
number of observed reflections (<i>NO</i>)	8613 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (<i>SHELXT-2014^c</i>)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-2014^d</i>)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7724–0.2269
data/restraints/parameters	9109 / 0 / 587
goodness-of-fit (<i>S</i>) ^e [all data]	1.191
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0415
<i>wR</i> ₂ [all data]	0.0956
largest difference peak and hole	0.913 and -0.811 e Å ⁻³

^aObtained from least-squares refinement of 9996 reflections with $8.22^\circ < 2\theta < 145.24^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cSheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.

^dSheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0184P)^2 + 23.4699P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Crystallographic Experimental Details for **(*dppe*)Sb(OTf)₃**
(CCDC No.:1417713)

A. Crystal Data

formula	C ₂₉ H ₂₄ F ₉ O ₉ P ₂ S ₃ Sb
formula weight	967.35
crystal dimensions (mm)	0.18 × 0.08 × 0.07
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])
unit cell parameters ^a	
<i>a</i> (Å)	13.3718 (4)
<i>b</i> (Å)	17.5496 (6)
<i>c</i> (Å)	15.4871 (5)
β (deg)	102.9604 (15)
<i>V</i> (Å ³)	3541.8 (2)
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.814
μ (mm ⁻¹)	9.601

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD ^b
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	−100
scan type	ω and φ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.43
total data collected	24895 (−16 ≤ <i>h</i> ≤ 16, −21 ≤ <i>k</i> ≤ 21, −19 ≤ <i>l</i> ≤ 19)
independent reflections	7200 (<i>R</i> _{int} = 0.0514)
number of observed reflections (<i>NO</i>)	6370 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]
structure solution method	intrinsic phasing (<i>SHELXT-2014</i> ^c)
refinement method	full-matrix least-squares on <i>F</i> ² (<i>SHELXL-2014</i> ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7029–0.3990
data/restraints/parameters	7200 / 0 / 536
goodness-of-fit (<i>S</i>) ^e [all data]	1.059
final <i>R</i> indices ^f	
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0416
<i>wR</i> ₂ [all data]	0.1119

largest difference peak and hole

1.686 and $-1.542 \text{ e } \text{\AA}^{-3}$

^aObtained from least-squares refinement of 9853 reflections with $7.72^\circ < 2\theta < 148.12^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cSheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.

^dSheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0637P)^2 + 4.2404P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

$\int R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table S3. Crystallographic Experimental Details for **(dppm)Sb(MeCN)(OTf)₃** (CCDC No.:1417712)

A. Crystal Data

formula	C ₃₀ H ₂₅ F ₉ NO ₉ P ₂ S ₃ Sb
formula weight	994.38
crystal dimensions (mm)	0.43 × 0.26 × 0.21
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])
unit cell parameters ^a	
<i>a</i> (Å)	9.1263 (5)
<i>b</i> (Å)	19.3196 (10)
<i>c</i> (Å)	21.6426 (11)
β (deg)	99.3749 (6)
<i>V</i> (Å ³)	3765.0 (3)
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.754
μ (mm ⁻¹)	1.081

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD ^b
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	-100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	55.02
total data collected	32826 (-11 ≤ <i>h</i> ≤ 11, -25 ≤ <i>k</i> ≤ 24, -27 ≤ <i>l</i> ≤ 28)
independent reflections	8639 (<i>R</i> _{int} = 0.0259)
number of observed reflections (<i>NO</i>)	7632 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]

structure solution method	Patterson/structure expansion (<i>DIRDIF-2008</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-97</i> ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8049–0.6531
data/restraints/parameters	8639 / 0 / 497
goodness-of-fit (S) ^e [all data]	1.034
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0233
wR_2 [all data]	0.0568
largest difference peak and hole	0.517 and -0.407 e \AA^{-3}

^aObtained from least-squares refinement of 9642 reflections with $4.36^\circ < 2\theta < 48.88^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cBeurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

^dSheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0240P)^2 + 2.4047P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

¹ Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

² S. Lochschmidt, and A. Schmidpeter, *Z. Anorg. Allg. Chem.*, **1985**, *40B*, 765-773.