Supplementary data for:

Exchange Chemistry of $t\mathrm{Bu_3PCO_2B(C_6F_5)_2Cl}$

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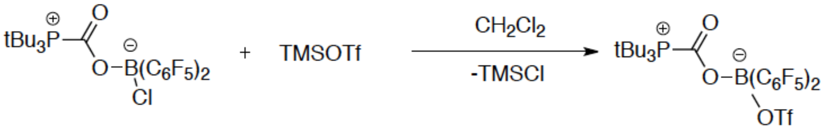
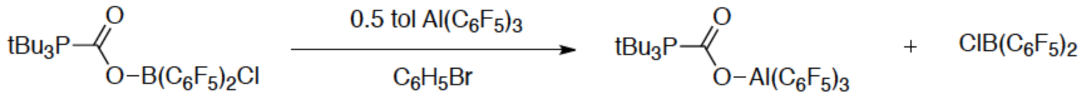
General Considerations: All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing standard Schlenk-line and glovebox techniques. Solvents (CH_2Cl_2, pentane and hexanes) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored under N_2. Bromobenzene was dried over CaH_2 and distilled under N_2 while Cyclohexane was dried over sodium and benzophenone and similarly distilled under N_2. CD_2Cl_2 was vacuum transferred from CaH_2, degassed and stored under N_2. $Me_3SiOSO_2CF_3$ (Sigma-Aldrich) and $[Ph_3C][B(C_6F_5)_4]$ (Sigma-Aldrich) were used as received. 0.5tol·$Al(C_6F_5)_3$[1], Cp_2TiMe_2[2] and $t\mathrm{Bu_3P(CO_2)B(C_6F_5)_2Cl}$[3] were prepared according to literature procedures. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{27}Al and ^{31}P NMR spectra were recorded at 25 °C, unless otherwise stated, on a Varian NMR System 400 MHz or Bruker Avance III 400 MHz spectrometer and were referenced using (residual) solvent resonances relative to $SiMe_4$ (^{1}H and ^{13}C) or relative to an external standard (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$, ^{27}Al: $Al(NO_3)_3$, ^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.



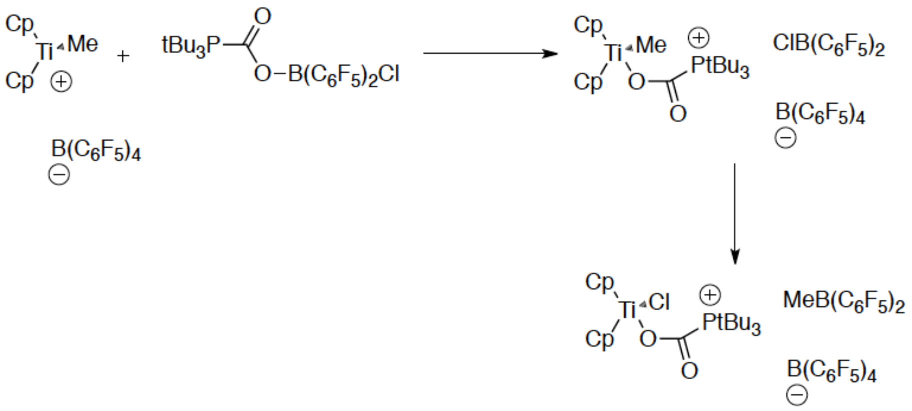
Synthesis of $t\mathbf{Bu_3P(CO_2)B(C_6F_5)_2(OSO_2CF_3)}$ (2): A 20 mL scintillation vial was charged with $t\mathrm{Bu_3P(CO_2)B(C_6F_5)_2Cl}$ (0.080 g, 0.128 mmol) and CH_2Cl_2 (5 mL). $Me_3SiOSO_2CF_3$ (23.1 μL, 0.128 mmol) was added to the clear and colourless solution in a dropwise fashion. The resulting reaction was left stirring for a period of one hour. At this time, the reaction was faintly yellow. All volatiles were then removed *in vacuo* yielding a white solid. The product was washed with hexanes (10 mL) and dried *in vacuo* for a period of one hour. Yield: 0.094 g (99 %). Crystals suitable for X-ray diffraction were grown from a layered solution of CH_2Cl_2 and hexanes. ^{1}H NMR (CD_2Cl_2): δ 1.68 (d, 27H, $^3J_{\text{H-P}}$ = 15 Hz, $P\{C(CH_3)_3\}$). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 3.76 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.08 (d, $^1J_{\text{C-P}}$ = 93 Hz,

PCO_2); 148.48 (br d, $^1J_{C\text{-}F}$ = 245 Hz, *o*-C_6F_5); 141.08 (br d, $^1J_{C\text{-}F}$ = 249 Hz, *p*-C_6F_5); 137.62 (br d, $^1J_{C\text{-}F}$ = 249 Hz, *m*-C_6F_5); 120.62 (s, OSO_2CF_3); 115.37 (br s, *ipso*-C_6F_5); 41.68 (d, $^1J_{C\text{-}P}$ = 19 Hz, P{*C*(CH_3)}$_3$); 30.64 (s, P{C(*C*H_3)}$_3$). ^{19}F NMR (CD_2Cl_2): δ -78.59 (s, 3F, OSO_2CF_3); -134.40 (dd, 6F, $^3J_{F\text{-}F}$ = 23 Hz, $^4J_{F\text{-}F}$ = 6.8 Hz, *o*-C_6F_5); -157.34 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5); -164.94 (m, 6F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 48.88 (d, $^1J_{P\text{-}C}$ = 93 Hz). IR(KBr): ν 1706 cm^{-1} (C=O). Anal. Calcd. for $C_{26}H_{27}BF_{13}O_5PS$: C, 42.16; H, 3.68. Found: C, 41.67; H, 4.04 %.



Synthesis of ^{t}Bu$_3$P(CO$_2$)Al(C$_6$F$_5$)$_3$ (3): A 20 mL scintillation vial was charged with *t*Bu$_3$P(CO$_2$)B(C$_6$F$_5$)$_2$Cl (0.080 g, 0.128 mmol) in bromobenzene (5 mL) while a second 20 mL vial was charged with 0.5tol·Al(C$_6$F$_5$)$_3$ (0.075 g, 0.129 mmol) in bromobenzene (5 mL). The second solution was added to the first in a dropwise fashion at room temperature. The reaction became faintly yellow upon addition. The resulting solution was stirred for 30 minutes. Following, the solution was divided amongst two 20 mL vials and pentane (15 mL) was added to each slowly precipitating a white solid. The product was allowed to settle and the supernatant was decanted. The material was washed with pentane (2 x 5 mL) and dried *in vacuo* for 30 minutes. Yield: 0.641 g (65 %). Crystals suitable for X-ray diffraction were grown from a layered solution of bromobenzene and cyclohexane. ^{1}H NMR (CD_2Cl_2): δ 1.65 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz, P{C(CH_3)$_3$}). ^{13}C{^{1}H} (CD_2Cl_2): δ 162.61 (d, $^1J_{P\text{-}C}$ = 89 Hz, PCO_2); 149.98 (br d, $^1J_{C\text{-}F}$ = 239 Hz, *o*-C_6F_5); 143.54 (br d, $^1J_{C\text{-}F}$ = 250 Hz, *p*-C_6F_5); 136.80 (br d, $^1J_{C\text{-}F}$ = 253 Hz, *m*-C_6F_5); 125.20 (br s, *ipso*-C_6F_5); 41.16 (d, $^1J_{C\text{-}P}$ = 20 Hz, P{*C*(CH_3)$_3$}); 30.74 (s, P{C(*C*H_3)$_3$). ^{19}F NMR (CD_2Cl_2): δ -123.12 (m, 6F, *o*-C_6F_5); -155.83 (t, 3F, $^3J_{F\text{-}F}$ = 19 Hz, *p*-C_6F_5); -163.39 (m, 6F, *m*-C_6F_5). ^{27}Al{^{1}H} NMR (CD_2Cl_2): silent. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 46.65 (s). IR (KBr pellet): ν 1686 cm^{-1} (C=O). Anal. Calcd. for $C_{31}H_{27}AlF_{15}O_2P$: C, 48.08; H, 3.51. Found: C, 47.69; H, 3.60 %.

Synthesis of ^{t}Bu$_3$P(^{13}CO$_2$)Al(C$_6$F$_5$)$_3$ (3-^{13}C): A small scintillation vial was charged with ^{t}Bu$_3$P(^{13}CO$_2$)B(C$_6$F$_5$)$_2$Cl (0.017 g, 0.027 mmol) and 0.5tol·Al(C$_6$F$_5$)$_3$ (0.016 g, 0.027 mmol) in C_6H_5Br (2 mL). The reaction was allowed to stir for five minutes before the addition of pentane (5 mL), precipitating a white solid. The product was washed with pentane (2 x 2 mL) and dried for ten minutes *in vacuo*. NMR was recorded in CD_2Cl_2. The spectroscopic ^{1}H, ^{13}C, ^{19}F and ^{27}Al NMR data were identical to those observed for ^{t}Bu$_3$P(^{12}CO$_2$)Al(C$_6$F$_5$)$_3$. ^{31}P{^{1}H} (CD_2Cl_2): δ 47.72 (d, $^1J_{P\text{-}C}$ = 89 Hz).



Synthesis of [$^{t}Bu_3P(CO_2)TiCp_2Cl][B(C_6F_5)_4]$ (4): A 20 mL scintillation vial was charged with Cp_2TiMe_2 (0.030 g, 0.144 mml) in bromobenzene (2 mL). A second 10 mL vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (0.133 g, 0.144 mmol) in bromobenzene (5 mL). The solution of trityl borate was added to the titanocene solution yielding a deep red/brown reaction mixture, which was stirred for a further 5 minutes. At this time, dry $tBu_3P(CO_2)B(C_6F_5)_2Cl$ (0.090 g, 0.144 mmol) was added and the resulting solution progressively lightened in colour to a vibrant red over a 30 second period of time. The reaction mixture was allowed to stir at room temperature for an hour after which the reaction was divided amongst two vials and hexanes (15 mL) were added to both fractions precipitating an orange solid. The hexanes were decanted and the resulting solid was washed with further hexanes (2 x 10 mL). The solvents were once again decanted and the solid was dried *in vacuo* for a period of 1 hour. Crystals suitable for X-ray diffraction were grown from a solution of CH_2Cl_2 layered with hexanes. Yield: 0.158 g (96 %). ^1H NMR (CD_2Cl_2): δ 6.65 (s, 10H, Cp); 1.66 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz, $P\{C(CH_3)_3\}$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ -16.65 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 163.59 (d, $^1J_{C\text{-}P}$ = 86 Hz, PCO_2); 148.07 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *o*-C_6F_5); 138.16 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *p*-C_6F_5); 136.23 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *m*-C_6F_5); 124.65 (br s, *ipso*-C_6F_5); 120.53 (s, Cp); 41.56 (d, $^1J_{C\text{-}P}$ = 19 Hz, $P\{C(CH_3\}_3$ 30.97 (s, $P\{C(CH_3\}_3$). ^{19}F NMR (CD_2Cl_2): δ -133.02 (s, 8F, *o*-C_6F_5); -163.03 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5); 167.45 (m, 8F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.09 (d, $^1J_{P\text{-}C}$ = 86 Hz). IR(KBr): ν 1670 cm^{-1} (C=O). Anal. Calcd. for $C_{47}H_{37}BF_{20}O_2PTi$: C, 49.54; H, 3.28. Found: C, 49.10; H, 3.20 %.

References:

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2. G. J. Erskine, D. A. Wilson and J. D. McCowan, *J. Organomet. Chem.*, 1976, 114, 119-125.

3. I. Peuser, R. C. Neu, X. Zhao, M. Ulrich, B. Schirmer, G. Kehr, R. Fröhlich, S. Grimme, G. Erker and D. W. Stephan, *Chem. Eur. J.*, 2011, 17, 9640-9650.