

Supporting Information: Mechanistic study of the atomic layer deposition of cobalt: A combined mass spectrometric and computational approach

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Synthesis of charged analogs

Two charged tags were prepared, one a terminal alkyne [HCC(CH₂)₄PPh₃][PF₆] (**1**[PF₆]) Figure 1 and the other an internal alkyne [CH₃CC(CH₂)₂PPh₃][PF₆] (**2**[PF₆]) Figure 2.[†] Triphenylphosphonium groups were attached to alkynyl compounds through S_N2 reactions in toluene and the insoluble product was filtered out of solution after 24 hrs at room temperature. We chose hexafluorophosphate as a counterion to eliminate any chance of the halide ion acting as a ligand itself, and to improve the solubility of **1** and **2** in the low-polarity solvents preferred for ESI-MS.

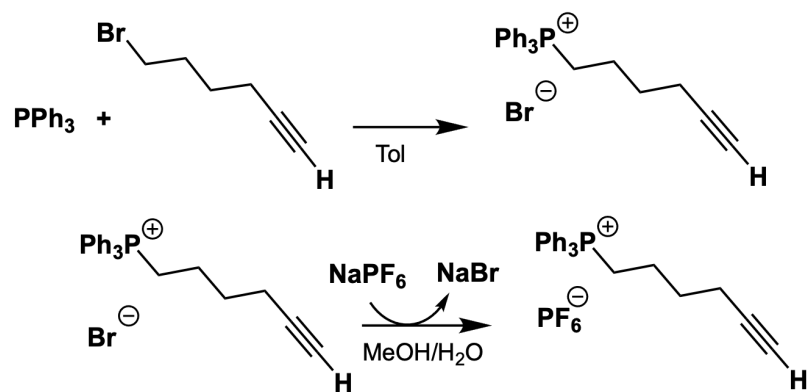


Figure 1: Synthesis of a charged analog ligand of CCTBA [1].

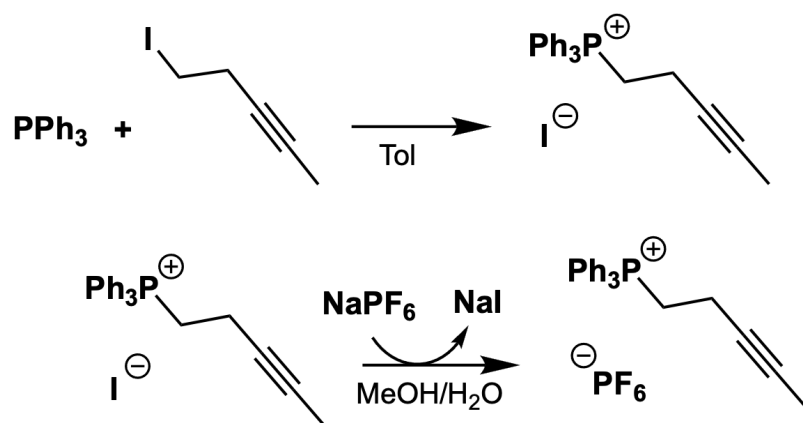


Figure 2: The synthesis of a charged analog ligand of CCTMA [2].

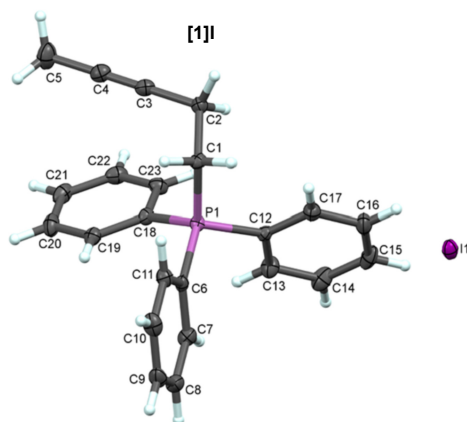
Mass spectrometric parameters

Electrospray ionization mass spectra were collected on a Waters Acquity Triple Quadrupole Detector mass spectrometer in positive ion mode. The capillary voltage was held at 3 kV, cone voltage at 10 V, and extraction cone at 0.5 V. Dichloromethane was used as a solvent for PSI and CID experiments. Due to its low boiling point, the desolvation gas flow rate was kept between 80 and 100 L/h and cone gas flow rate was set to 100 L/h. The source temperature was 40 °C; and desolvation temperature was held between 100 and 120 °C. CID data was collected at a sample rate of one scan per second and plotted data points binned every ten seconds of raw data.

Crystallographic Data

Crystal summary for [1]I

The salt, pent-3-yn-1-yltriphenylphosphonium iodide ([1]I), crystallizes as colorless block-like crystals. There are four molecules of the phosphonium cation and four iodine atoms in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/c$. The structure of the compound is as expected. The pent-3-enyl moiety displays the expected linear characteristics of a triple bond (C–C bond distance = 1.186(3) Å and C–C–C bond angles across the bond = 179.3(2) and 177.9(2)°). The derived metrics within the molecules are otherwise unexceptional. This structure has been added to the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2314737.



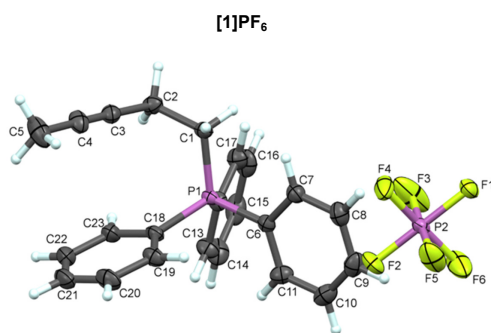
Crystal data for $C_{23}H_{22}IP$: $M_r = 456.27$; Monoclinic; space group $P2_1/c$; $a = 10.606(10)$ Å; $b = 18.313(16)$ Å; $c = 10.750(10)$ Å; $\beta = 90^\circ$; $\alpha = 106.717(12)^\circ$; $\gamma = 90^\circ$; $V = 2000(3)$ Å³; $Z = 4$; $T = 120(2)$ K; $(Mo-K) = 0.71073$ Å; $(Mo-K) = 1.684$ mm⁻¹; $d_{calc} = 1.516$ g.cm⁻³; 31690 reflections collected; 4998 unique ($R_{int} = 0.0387$); giving $R_1 = 0.0222$, $wR_2 = 0.0460$ for 4330 data with $[I \geq 2(I)]$ and $R_1 = 0.0293$, $wR_2 = 0.0486$ for all 4998 data. Residual electron density ($e^- \cdot \text{Å}^{-3}$) max/min: 0.629/−0.463.

An arbitrary sphere of data was collected on a colorless block-like crystal, having approximate dimensions of 0.218 × 0.155 × 0.119 mm, on a Bruker Kappa X8-APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [1]. Data were corrected for absorption and polarization

effects and analyzed for space group determination [2]. The structure was solved by dual-space methods and expanded routinely [3]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [4]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{iso}(H) = 1.5U_{eq}(C)$ for methyl, $1.2U_{eq}(C)$ for all others).

Crystal summary for [1]PF₆

The compound, pent-3-yn-1-yltriphenylphosphonium hexafluorophosphate, crystallizes as colorless block-like crystals. There are four molecules of the phosphonium cation and PF₆ anion in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/c$. The structure of the compound is as expected. Bond distances and angles within the molecules are as expected. The PF₆ anion was found to have positional disorder in the “equatorial” fluorine atoms. These fluorine atoms were modeled over two sites with occupancies summed to unity. This yielded an approximately 0.87:0.13 site ratio. The minor component atoms were modeled with isotropic displacement parameters. The figure shows the major component. This structure has been added to the CCDC under deposition number 2314738.



Crystal data for $C_{23}H_{22}F_6P_2$: $M_r = 474.34$; Monoclinic; space group $P2_1/c$; $a = 11.1886(11)$ Å; $b = 17.4838(16)$ Å; $c = 11.8098(11)$ Å; $\beta = 90^\circ$; $\alpha = 107.4620(10)^\circ$; $\gamma = 90^\circ$; $V = 2203.8(4)$ Å³; $Z = 4$; $T = 120(2)$ K; $(Mo-K) = 0.71073$ Å; $(Mo-K) = 0.255$ mm⁻¹; $d_{calc} = 1.430$ g.cm⁻³; 41837 reflections collected; 5489 unique ($R_{int} = 0.0374$); giving $R_1 = 0.0446$, $wR_2 = 0.1116$ for 4778 data

with $[I_i^2(I)]$ and $R_1 = 0.0520$, $wR_2 = 0.1161$ for all 5489 data. Residual electron density ($e^- \cdot \text{\AA}^{-3}$) max/min: 1.631/−0.313.

An arbitrary sphere of data was collected on a colorless block-like crystal, having approximate dimensions of $0.245 \times 0.213 \times 0.210$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [1]. Data were corrected for absorption and polarization effects and analyzed for space group determination [2]. The structure was solved by dual-space methods and expanded routinely [3]. The model was refined by full-matrix least-squares analysis of F2 against all reflections [4]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{iso}(H) = 1.5U_{eq}(C)$ for methyl, $1.2U_{eq}(C)$ for all others).

References

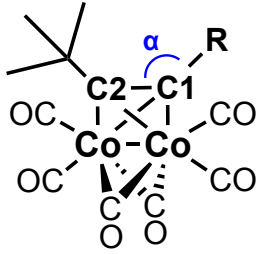
- [1] APEX-3. Bruker AXS. Madison, Wisconsin, USA. 2016.
- [2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke. *J. Appl. Cryst.* 2015 48, 3.
- [3] G. M. Sheldrick. *Acta Cryst.*, 2015, A71, 3.
- [4] G. M. Sheldrick. *Acta Cryst.*, 2015, C71, 3.

Computational details

Table 1: List of sample Cartesian coordinate files available as separate files and brief descriptions. All structures and output files reported in the manuscript are available upon request.

file name	description
terminal.xyz	PBE0/def2-tzvp optimized geometry of CCTBA in the gas phase
internal.xyz	PBE0/def2-tzvp optimized geomtry of CCTMA in the gas phase
T3.xyz	PBE optimized periodic geometry of chemisorbed intermediate of CCTBA
I3.xyz	PBE optimized periodic geometry of chemisorbed intermediate of CCTMA
TS_term.xyz	PBE optimized transition state geometry of a terminal alkyne reacting with Si(111)
TS_int.xyz	PBE optimized transition state geometry of a terminal alkyne reacting with Si(111)

The Si(111) slab consisted of 6 repeating unit cells in the $x - y$ plane and two repeating cells in



compound	d_{C1-C2}	d_{Co-Co}	$\alpha_{R-C1-C2}$
terminal alkyne	1.201		180.0°
internal alkyne	1.203		179.8°
CCTBA	1.336	2.423	142.6°
CCTMA	1.338	2.424	143.3°
$Co_2(CO)_8$ (C_{2v})		2.495	
$Co_2(CO)_8$ (D_{3d})		2.637	

Figure 3: Tabulated bond lengths (Å) and bond angles of computed structures of CCTBA and CCTMA. Values remain consistent across the internal and terminal alkyne and coordination to Co results in lengthening of the C1–C2 bond and departure from a linear C1–C2–R bond angle.

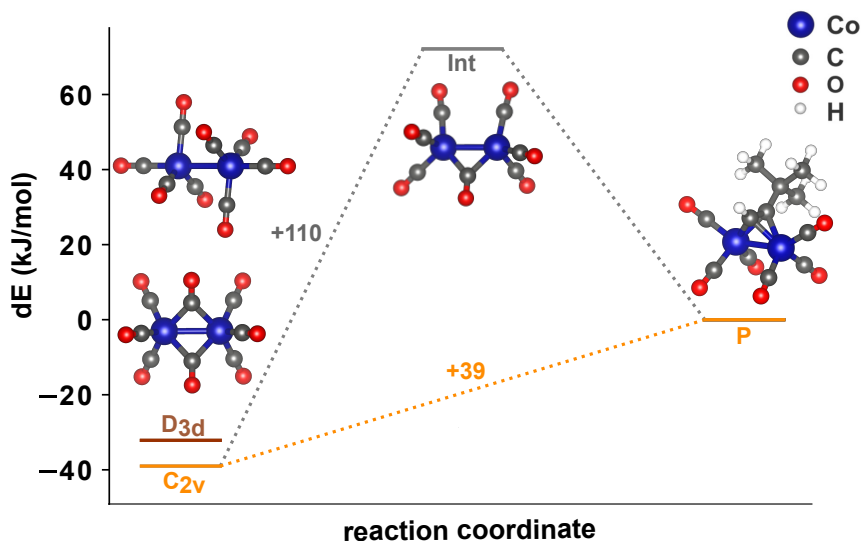


Figure 4: The change in energy (kJ/mol) during formation of CCTBA. The energies of D_{3d} (red) and C_{2v} (orange) isomers of $Co_2(CO)_8$ are shown with respect to the product **P** (CCTBA). The relative energy of a possible $Co_2(CO)_7$ intermediate (**Int**) is shown in grey.

the z direction. Adsorbate geometries were sampled with nose-hoover *AIMD* simulations (50-100 K) to identify and compare local minima relevant to the deposition step.

(111) surface	literature	SIESTA optimized
Si	$a = 5.43$	$a=5.43$

The Si(111) surface unit cell parameters were optimized to

23.037538931057718	0.0	0.0
11.518769465528859	19.951093954968982	0.0
0.0	0.0	88.6212828946741