Synthesis and Structure of Intermediates in Copper-Catalyzed Alkylation of Diphenylphosphine

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Supporting Information Part 2

1. Additional experimental information

2. NMR Spectra

3. DFT Calculations

1. Additional experimental information

Cu-Catalyzed Alkylation of Diphenylphosphine (Table 2). See the manuscript experimental section for the other entries.

Entry 1. $[Cu(NCMe)_4][PF_6]$-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in CH_2Cl_2 A slurry of $[Cu(NCMe)_4][PF_6]$ (**1**; 10 mg, 0.027 mmol) in a few drops of CH_2Cl_2 was treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of CH_2Cl_2, resulting in a homogeneous solution, to

which benzyl bromide (32 μL, 0.27 mmol) was added. This mixture was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2, giving a bright yellow color, which dissipated within a couple of minutes leaving a clear solution with a white precipitate. ^{31}P NMR spectroscopy revealed full conversion within 15 min and the reaction mixture was pumped down under vacuum. The residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, the solution was passed through a silica plug, and the filtrate was pumped down again giving a white solid (54 mg, 0.20 mmol, 73%).

Entry 4. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in THF A slurry of [Cu(triphos)(NCMe)][PF_6] (**2**; 23 mg, 0.027 mmol) in a few drops of THF was treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of THF; the resulting white slurry was treated with a solution of benzyl bromide (32 μL, 0.27 mmol) in 1 mL of THF. A solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of THF was added, resulting in immediate precipitation; the reaction was complete in less than 15 min as observed by ^{31}P NMR spectroscopy. The reaction mixture was pumped down under vacuum and the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution. The solution was passed through a silica plug and pumped down under vacuum giving a white solid (66 mg, 0.24 mmol, 89%).

Entry 5. Cu(XantPhos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in CD_2Cl_2 A solution of [Cu(XantPhos)(NCMe)][PF_6] (**3**; 22 mg, 0.027 mmol) in a few drops of CD_2Cl_2 was treated with $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of CD_2Cl_2, then with dry, degassed $PhCH_2Br$ (32 μL, 0.27 mmol). This mixture was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CD_2Cl_2 and within a minute the clear solution became a very cloudy pale-brown and a precipitate formed. ^{31}P NMR spectroscopy showed the catalysis to be complete in less than 15 min. The reaction mixture was pumped down under vacuum; the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, and the solution was passed through a silica plug. The resulting solution was pumped down under vacuum giving a white solid (60 mg, 0.22 mmol, 81%).

Entry 6. Cu(XantPhos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in THF A slurry of [Cu(XantPhos)(NCMe)][PF_6] (**3**; 22 mg, 0.027 mmol) in less than 1 mL of THF was treated with a

solution of $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of THF, then with $PhCH_2Br$ (32 μL, 0.27 mmol), resulting in a homogeneous solution. A solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of THF was added, resulting in a bright yellow solution and precipitation. Within a minute, the yellow color had subsided and the solution was clear with a large amount of precipitate. ^{31}P NMR spectroscopy showed full conversion to Ph_2PCH_2Ph in less than 15 min; the reaction mixture was pumped down under vacuum. The residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, the solution was passed through a silica plug, and the resulting solution was pumped down again giving a white solid (73 mg, 0.26 mmol, 98%).

Entry 7. Cu(dtbp)(Cl)-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in CD_2Cl_2 A solution of Cu(dtbp)(Cl) (**5**; 20 mg, 0.051 mmol) in a few drops of CD_2Cl_2 was treated with a solution of $PHPh_2$ (95 mg, 0.51 mmol) in 1 mL of CD_2Cl_2, then with $PhCH_2Br$ (61 μL, 0.51 mmol. This mixture was added to a stirring solution of $NaOSiMe_3$ (57 mg, 0.51 mmol) in 1 mL of CD_2Cl_2, resulting in a flash of yellow color, which dissipated within a minute to give a very cloudy pale-brown solution. ^{31}P NMR spectroscopy confirmed the catalysis to be complete in less than 15 min. The reaction mixture was then pumped down under vacuum. The residue was dissolved in 10 mL of petroleum ether and passed through a silica plug. The resulting clear solution was pumped down and analyzed by ^{31}P and ^{1}H NMR spectroscopy; the only phosphorus-containing product was PPh_2CH_2Ph. The ^{1}H NMR spectrum showed free dtbp.

Entry 8. Cu(dtbp)(OTf)-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in CD_2Cl_2 A solution of Cu(dtbp)(OTf) (**6**; 24 mg, 0.047 mmol) in a few drops of CD_2Cl_2 was treated with a solution of $PHPh_2$ (88 mg, 0.47 mmol) in 1 mL of CD_2Cl_2, then with $PhCH_2Br$ (57 μL, 0.47 mmol). This mixture was added to a stirring solution of $NaOSiMe_3$ (53 mg, 0.47 mmol) in 1 mL of CD_2Cl_2, resulting in a flash of yellow color and some frothiness, which dissipated within a minute to give a very cloudy pale-brown solution. ^{31}P NMR spectroscopy confirmed the catalysis to be complete in less than 15 min. The reaction mixture was pumped down under vacuum; the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, and the solution was passed through a silica plug. The resulting clear

solution was pumped down and analyzed by ^{31}P and ^{1}H NMR spectroscopy; the only phosphorus-containing product was Ph_2PCH_2Ph, but the ^{1}H NMR spectrum ($CDCl_3$) showed free dtbp.

Entry 9. CuCl-Catalyzed Reaction of $PHPh_2$ with Benzyl Bromide in CH_2Cl_2 A few drops of CH_2Cl_2 was added to CuCl (3 mg, 0.03 mmol) generating a slurry, which was treated with $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of CH_2Cl_2 resulting in a homogeneous solution, to which benzyl bromide (32 μL, 0.27 mmol) was added. This mixture was added to a stirring slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2 giving a bright yellow solution. The color of the solution faded within a minute and was replaced by a pale-brown cloudy solution. The catalysis was monitored by ^{31}P NMR spectroscopy and shown to be complete within 15 min. The reaction mixture was pumped down under vacuum; the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution and passed through a silica plug. The resulting solution was again pumped down under vacuum giving a white solid (62 mg, 0.22 mmol, 84%), which was Ph_2PCH_2Ph containing a trace of $Ph_2P\text{-}PPh_2$.

Entry 10. Background Reaction of $PHPh_2$ with $NaOSiMe_3$ and Benzyl Bromide in CD_2Cl_2 A solution of $PHPh_2$ (50 mg, 0.27 mmol) and benzyl bromide (32 μL, 0.27 mmol) in 1 mL of CD_2Cl_2 was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2 and the mixture was monitored by ^{31}P NMR spectroscopy. After 15 min, 22% conversion to a 2:1 mixture of Ph_2PCH_2Ph and the quaternary salt $[Ph_2P(CH_2Ph)_2][Br]$ (δ 24.2) had occurred.[1] After 25 min, only 12% of the reaction mixture was $PHPh_2$ and 74% was Ph_2PCH_2Ph. Further product formation occurred over 2 h, when no more reaction was observed.

Entry 11. Background Reaction of $PHPh_2$ with $NaOSiMe_3$ and Benzyl Bromide in THF A solution of $PHPh_2$ (50 mg, 0.27 mmol) and benzyl bromide (32 μL, 0.27 mmol) in 1 mL of THF was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of THF and the combined solution was monitored by ^{31}P NMR spectroscopy. After 15 min, there was 61% conversion to a 25:1 mixture of Ph_2PCH_2Ph and the quaternary salt $[Ph_2P(CH_2Ph)_2][Br]$ (δ 26.8). Further reaction occurred over 2 h (90% conversion), when no more conversion was observed.

Entry 12. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Chloride in CH_2Cl_2 [Cu(triphos)(NCMe)][PF_6] (**2**; 23 mg, 0.027 mmol) was dissolved in a few drops of CH_2Cl_2 and treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of CH_2Cl_2, then with dry, degassed benzyl chloride (31 μL, 0.27 mmol). This mixture was added to a stirring slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2; the catalysis was monitored by ^{31}P NMR spectroscopy and shown to be complete in 1 h, yielding a mixture of PPh_2CH_2Ph (**4**, major product) and PPh_2CH_2Cl (**7**). The reaction mixture was pumped down under vacuum; the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution and passed through a silica plug. Pumping down the filtrate gave an oily white solid of 93% purity by ^{31}P NMR spectroscopy (56 mg, 0.20 mmol, 75%; mostly **4** with a little of **7**).

Entry 13. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Chloride in THF A slurry of [Cu(triphos)(NCMe)][PF_6] (**2**; 23 mg, 0.027 mmol) in a few drops of THF was treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of THF, then with a solution of dry, degassed benzyl chloride (31 μL, 0.27 mmol) in 1 mL of THF. To the resulting white slurry was added a solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of THF, giving a bright yellow solution. The yellow color dissipated within 5 min, and was replaced by a clear solution with a large amount of precipitate. The catalysis was shown to be complete within 15 min by ^{31}P NMR spectroscopy. The reaction mixture was pumped down under vacuum. The residue was dissolved in 10 mL of a 10% THF/petroleum ether solution and passed through a silica plug. The resulting solution was pumped down under vacuum to give a white solid (69 mg, 0.25 mmol, 93%).

Entry 14. Cu(XantPhos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Chloride in CH_2Cl_2 [Cu(XantPhos)(NCMe)][PF_6] (**3**; 22 mg, 0.027 mmol) was dissolved in a few drops of CH_2Cl_2 and treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of CH_2Cl_2, affording a homogeneous solution, to which was added dry, degassed benzyl chloride (31 μL, 0.27 mmol). This mixture was added to a stirring slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of CH_2Cl_2 giving a bright yellow solution. ^{31}P NMR monitoring showed that the catalysis was complete within 15 min, but formation of PPh_2CH_2Ph (**4**) was accompanied by liberation of some XantPhos and formation of Ph_2PCH_2Cl (**7**) as a

side product. The reaction mixture was pumped down under vacuum. The residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, and the solution was passed through a silica plug. The resulting solution was pumped down giving an oily white solid of 97% purity (56 mg, 0.20 mmol, 75% yield; mostly **4** with **7** as an impurity).

Entry 15. Cu(XantPhos)-Catalyzed Reaction of $PHPh_2$ with Benzyl Chloride in THF [Cu(XantPhos)(NCMe)][PF_6] (**3**; 22 mg, 0.027 mmol) was dissolved in 1 mL of THF and treated with a solution of $PHPh_2$ (50 mg, 0.27 mmol) in 2 mL of THF giving a homogeneous solution, to which a solution of dry, degassed benzyl chloride (31 μL, 0.27 mmol) in 1 mL of THF was added. A solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of THF was added, resulting in a bright yellow solution, and the reaction was monitored by ^{31}P NMR spectroscopy. After 15 min, some conversion to PPh_2CH_2Ph had occurred; significant XantPhos dissociation was observed. After 27 h, full conversion occurred and most of the XantPhos had re-coordinated to the Cu(I) center. The reaction mixture was pumped down. The residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, and the solution was passed through a silica plug. The resulting solution was pumped down under vacuum to give a white solid (74 mg, 0.27 mmol, 100%).

Entry 16. Background Reaction of $PHPh_2$ with Benzyl Chloride and $NaOSiMe_3$ in CD_2Cl_2 A solution of $PHPh_2$ (50 mg, 0.27 mmol) and benzyl chloride (31 μL, 0.27 mmol) in 1 mL of CD_2Cl_2 was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CD_2Cl_2 and the combined solution was monitored by ^{31}P NMR spectroscopy. After 72 h, conversion to the product PPh_2CH_2Ph was less than 5%.

Entry 17. Background Reaction of $PHPh_2$ with Benzyl Chloride and $NaOSiMe_3$ in THF A solution of $PHPh_2$ (50 mg, 0.27 mmol) and benzyl chloride (31 μL, 0.27 mmol) in 1 mL of THF was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of THF and the combined solution was monitored by ^{31}P NMR spectroscopy. After three h, 5% conversion to the product PPh_2CH_2Ph had occurred. In 16.5 h conversion was 14% and in 40.5 h, conversion reached 23%. After 72 h, the reaction was no longer monitored and conversion was 28%.

Entry 19. Background Reaction of $PHPh_2$ with $NaOSiMe_3$ in CH_2Cl_2 A solution of $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of CH_2Cl_2 was transferred to a rapidly stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2. The reaction mixture was placed in an NMR tube and monitored by ^{31}P NMR spectroscopy. No conversion was seen after 48 hours.

Entry 21. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with PhCHMe(Br) and $NaOSiMe_3$ in CH_2Cl_2 A solution of [Cu(triphos)(NCMe)][PF_6] (**2**; 23 mg, 0.027 mmol), $PHPh_2$ (50 mg, 0.27 mmol) and (1-bromoethyl)benzene (37 μL, 0.27 mmol) in 1 mL of CH_2Cl_2 was added to a stirring solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 1 mL of CH_2Cl_2. The mixture was transferred to an NMR tube and analyzed by ^{31}P NMR spectroscopy. Within 20 min, complete conversion of $PHPh_2$ gave $PPh_2CH(Me)Ph$, PPh_2CH_2Cl, and Ph_2P-PPh_2 in a ratio of 68:28:4.

Entry 22. Background Reaction of $PHPh_2$ with PhCHMe(Br) and $NaOSiMe_3$ in THF A solution of (1-bromoethyl)benzene (37 μL, 0.27 mmol) and $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of THF was added to a slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in less than 1 mL of THF, resulting in a homogeneous solution. Within minutes, precipitation began to occur. The reaction was monitored by ^{31}P NMR spectroscopy. After 15 min, Ph_2P-PPh_2 (**9**) was observed, along with a small amount of $PPh_2CH(Me)Ph$ (**8**). In 6 h, ^{31}P NMR spectroscopy revealed 22% conversion from $PHPh_2$; 18% conversion to Ph_2P-PPh_2 and only 4% conversion to $PPh_2CH(Me)Ph$. At 23 h, conversion from $PHPh_2$ had reached 32%: 8% tertiary phosphine and 24% biphosphine. In 48 h, the reaction had proceeded no further and was no longer monitored.

Entry 23. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with PhCHMe(Cl) and $NaOSiMe_3$ in THF To a stirring slurry of [Cu(triphos)(NCMe)][PF_6] (**2**; 23 mg, 0.027 mmol), $PHPh_2$ (50 mg, 0.27 mmol), and (1-chloroethyl)benzene (36 μL, 0.27 mmol) in 2 mL of THF was added a solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of THF, resulting in a bright yellow homogeneous solution. The catalysis was monitored by ^{31}P NMR spectroscopy, which revealed minimal conversion in 1 h and dissociation of triphos. Full conversion was achieved in 72 h accompanied by the disappearance of the yellow color. The reaction mixture was then pumped down under vacuum and the residue was dissolved in 10 mL of a

10% THF/petroleum ether solution. The solution was passed through a silica plug and the fitrate was pumped down again affording an oily solid of $PPh_2CHMe(Ph)$ (**8**; 58 mg, 0.20 mmol, 74%) in 94% purity by ^{31}P NMR spectroscopy. The other phosphorus-containing products were $Ph_2P\text{-}PPh_2$ (**9**; δ -13.9, 4%), an unidentified product (δ -21.4, <1%), and triphos (δ -24.9, 1%).

Entry 24. Background Reaction of $PHPh_2$ with PhCHMe(Cl) and $NaOSiMe_3$ in THF A solution of (1-chloroethyl)benzene (36 μL, 0.27 mmol) and $PHPh_2$ (50 mg, 0.27 mmol) in 1 mL of THF was added to a slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in less than 1 mL of THF, resulting in a homogeneous solution; the reaction was monitored by ^{31}P NMR spectroscopy. The reaction reached less than 2% conversion to $PPh_2CH(Me)Ph$ in 23 h. In 75 h, conversion from $PHPh_2$ had only reached 3% and the reaction was no longer monitored.

Entry 25. Cu(triphos)-Catalyzed Reaction of $PHPh_2$ with Dibromoethane in THF An NMR tube was charged with a slurry of $[Cu(triphos)(NCMe)][PF_6]$ (**2**; 23 mg, 0.027 mmol), $PHPh_2$ (50 mg, 0.27 mmol), and dry, degassed 1,2-dibromoethane (12 μL, 0.13 mmol) in about 2 mL of THF. A solution of $NaOSiMe_3$ (30 mg, 0.27 mmol) in 2 mL of THF was added to the slurry giving a bright yellow color. Precipitation occurred and the catalysis was shown to be complete in 15 min by ^{31}P NMR spectroscopy. The reaction mixture was pumped down under vacuum; the residue was dissolved in 10 mL of a 10% THF/petroleum ether solution, and the resulting solution was passed through a silica plug. The filtrate was pumped down under vacuum affording a white solid (38 mg, 0.10 mmol, 77% yield), which was mostly $Ph_2P\text{-}PPh_2$, and also contained trace amounts of $Ph_2P\text{-}P(O)Ph_2$, an unidentified peak at 24.7 ppm, and $PHPh_2$ as observed by ^{31}P NMR spectroscopy.

Entry 27. Background Reaction of $PHPh_2$, dibromoethane, and $NaOSiMe_3$ in THF An NMR tube was charged with $PHPh_2$ (50 mg, 0.27 mmol) and 1,2-dibromoethane (12 μL, 0.27 mmol) in 1 mL of THF. The mixture was then added to a slurry of $NaOSiMe_3$ (30 mg, 0.27 mmol) in less than 1 mL of THF, resulting in a homogeneous solution. Within minutes, precipitation began to occur. The reaction was monitored by ^{31}P NMR spectroscopy. In 15 min, there was negligible conversion and even after 48

h, the reaction had not proceeded past 2% conversion to Ph_2P-PPh_2 (**9**). After 48 h, the reaction was no longer monitored.

[Cu(PPh$_2$CH$_2$Ph)$_3$][PF$_6$] (21) A slurry of [Cu(NCMe)$_4$][PF$_6$] (**1**; 25 mg, 0.067 mmol) in 2 mL of THF was treated with a solution of benzyldiphenylphosphine (74 mg, 0.27 mmol, 4 equiv) in 2 mL of THF. The rapidly stirred solution became clear and homogeneous immediately, but was stirred for one hour to ensure complete conversion. The resulting solution was pumped down under vacuum, washed with petroleum ether (2x10 mL), and recrystallized from methylene chloride layered with petroleum ether at –30 °C yielding a crystalline, semi-transparent solid (65 mg, 0.063 mmol, 93%). Crystals suitable for elemental analysis and X-ray crystallography were obtained by slow diffusion of petroleum ether vapors into a CH_2Cl_2 solution at -30 °C.

Anal. Calcd. for $C_{57}H_{51}CuP_4F_6$: C, 65.99; H, 4.95. Found: C, 65.59; H, 5.10. HRMS m/z calcd for $C_{57}H_{51}CuP_3$ (M+): 891.2500. Found: 891.2519. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -1.4 (PPh_2CH_2Ph), -143.5 (septet, J = 711, PF_6). ^1H NMR (CD_2Cl_2): δ 7.50 (t, J = 7, 6H, Ph), 7.29 (t, J = 7, 12H, Ph), 7.26 (m, 3H, Ph), 7.13 (t, J = 7, 6H, Ph), 7.00 (br, 12H, Ph), 6.63 (d, J = 7, 6H, Ph), 3.28 (6H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.8 (Ph), 133.0 (br, Ph), 131.4 (Ph), 130.6 (m, Ph), 129.7 (br, Ph), 129.4 (br, Ph), 129.1 (Ph), 127.7 (Ph), 34.6 (CH_2).

Conductivity Measurements Approximately 0.03 mmol of each compound was weighed out and dissolved in 30 mL of CH_3NO_2 affording ~$1x10^{-3}$ M solutions. Using a Fischer Scientific digital Conductivity meter, the probe was placed in the solution and the corresponding conductivity value in $\mu\Omega^{-1}$/cm was recorded. The units were converted to molar conductivity.

Table S1. Conductivity Data

Cu(I) Complex	**Concentration (M)**	**Molar Conductivity ($\Omega^{-1}\bullet cm^2\bullet mol^{-1}$)**
[Cu(dtbp)($PHPh_2$)][OTf] (**20a)**	$1.01x10^{-3}$	138.8
[Cu(dtbp)($PHPh_2$)][Cl] (**20b**)	$9.81x10^{-4}$	54.4
[Cu(dtbp)(NCMe)][PF_6] [2]	$9.84x10^{-4}$	148.6
Neat CH_3NO_2	- - -	7.0
[NEt_4][I]	$0.5x10^{-3}$	97.0 (lit)[3]
[NEt_4][I]	$0.5x10^{-3}$	100.0

References

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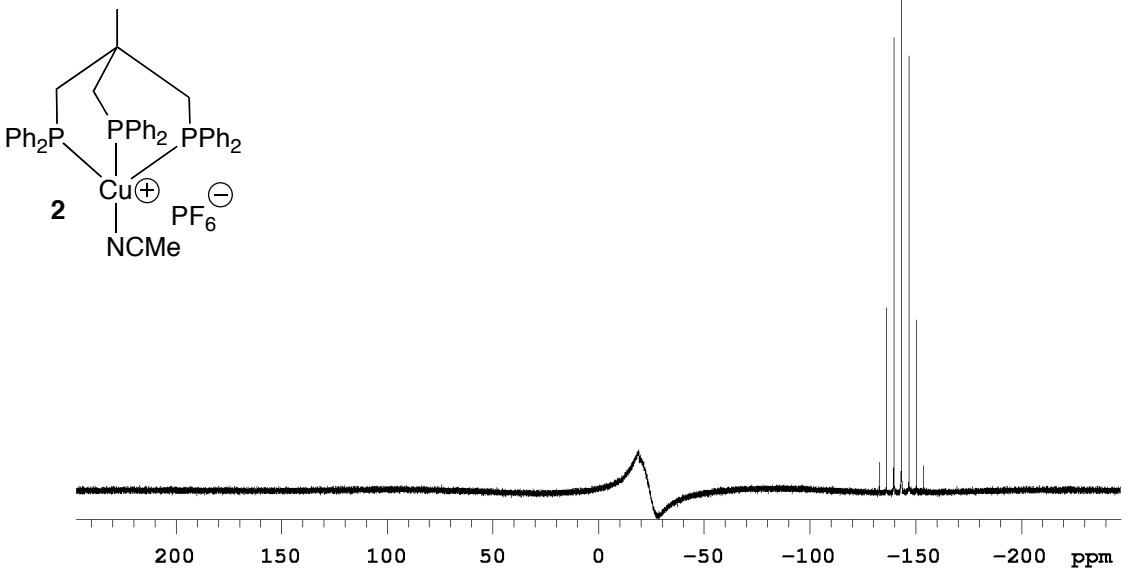
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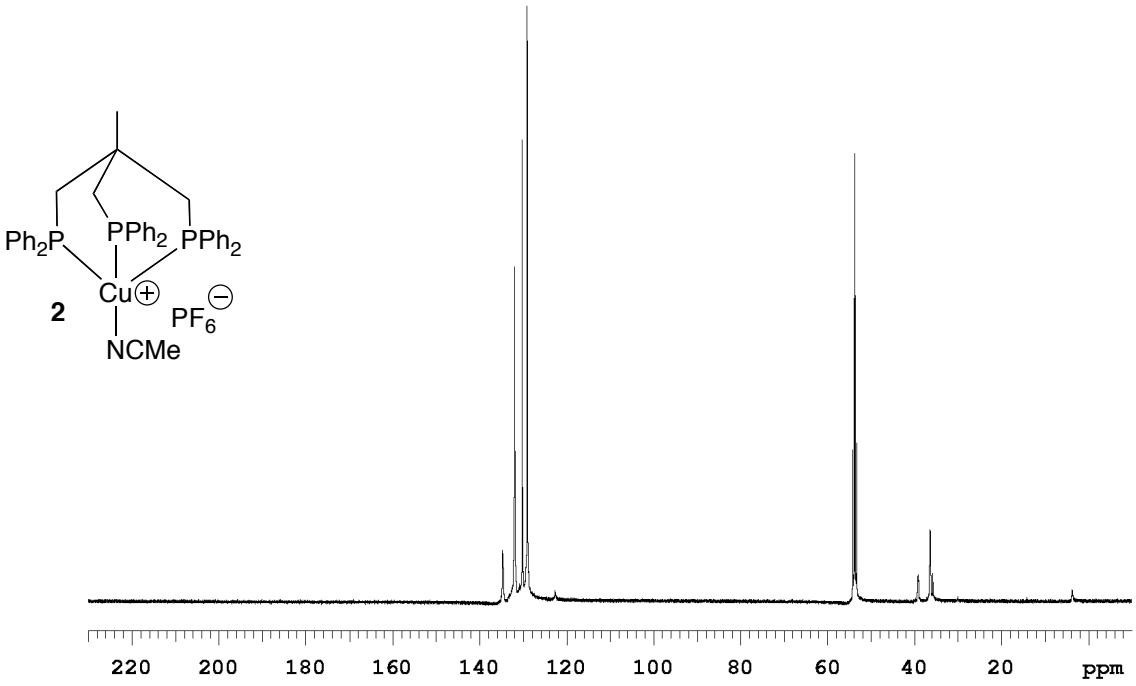
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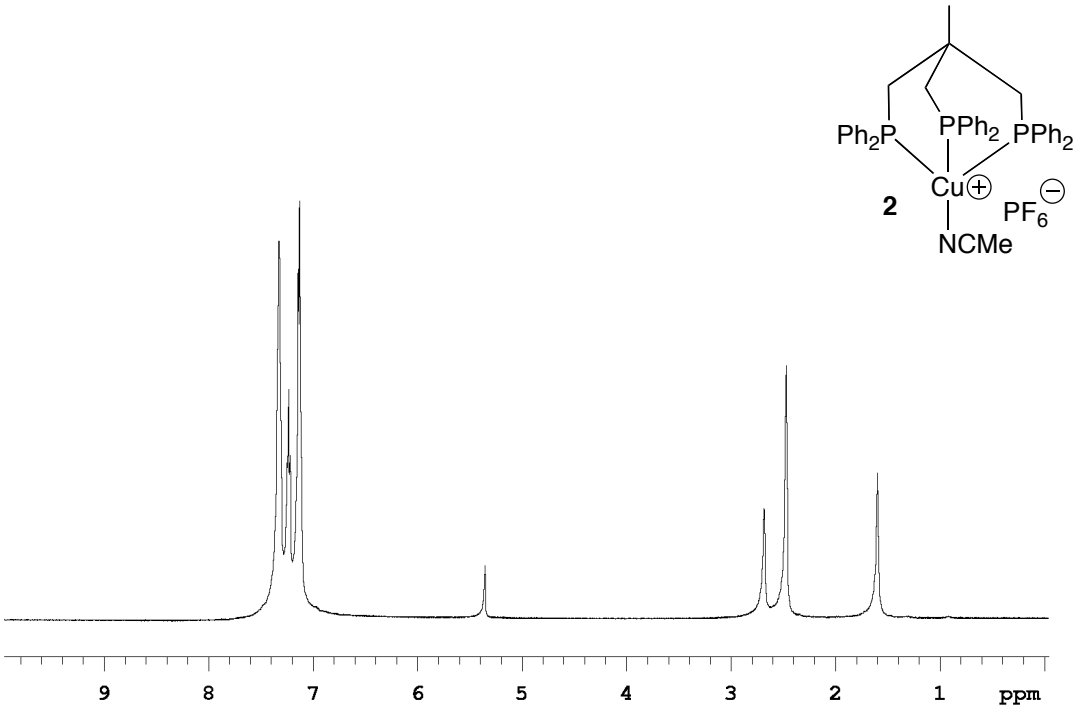
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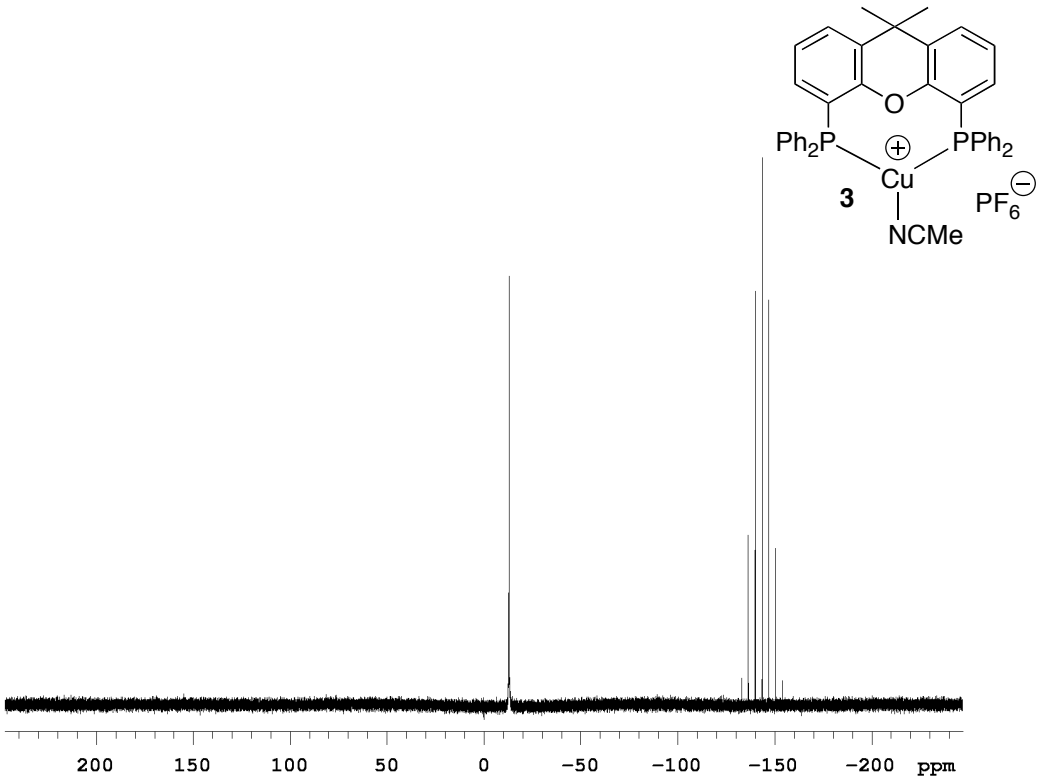
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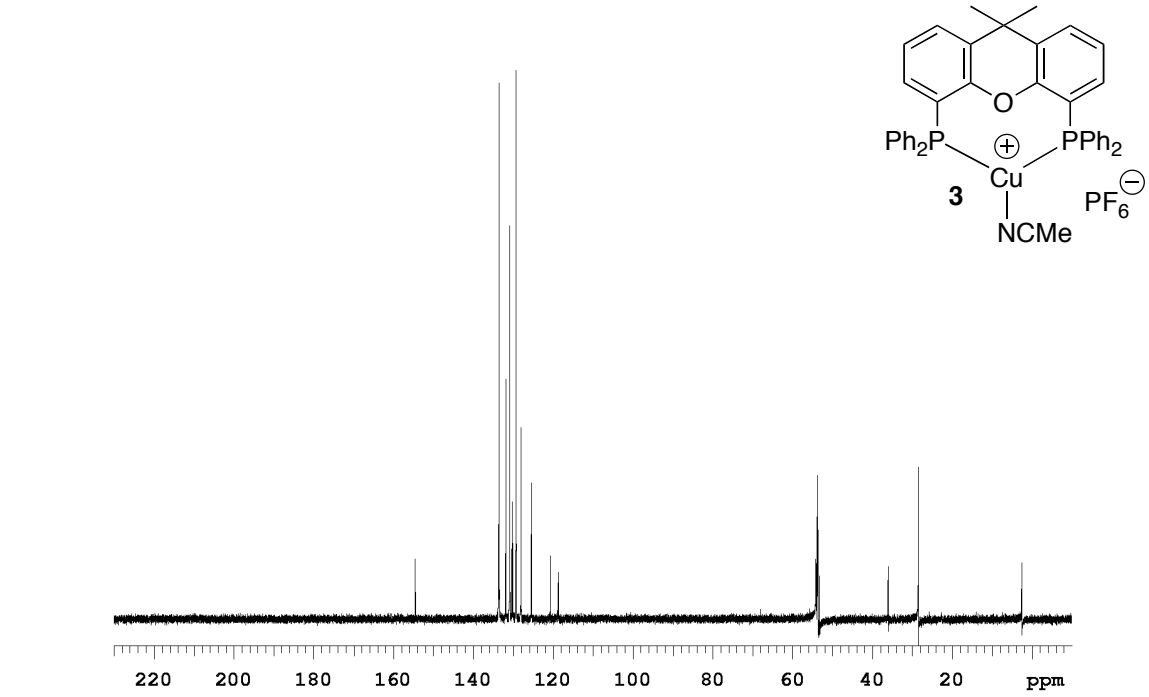
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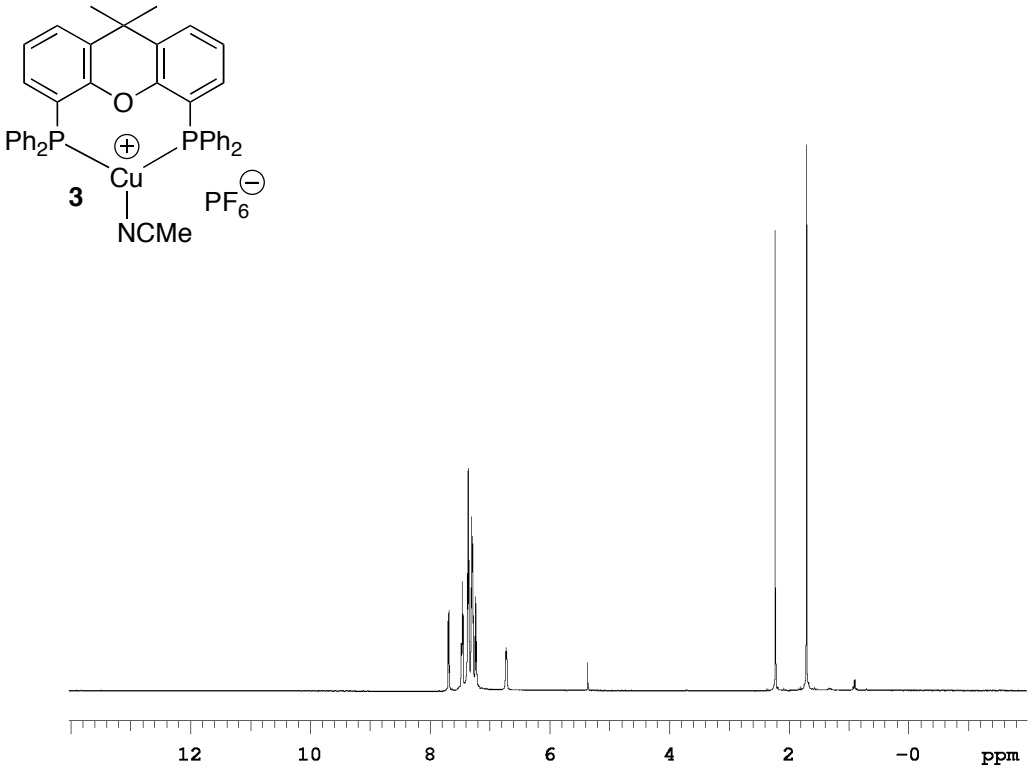
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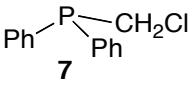
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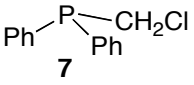
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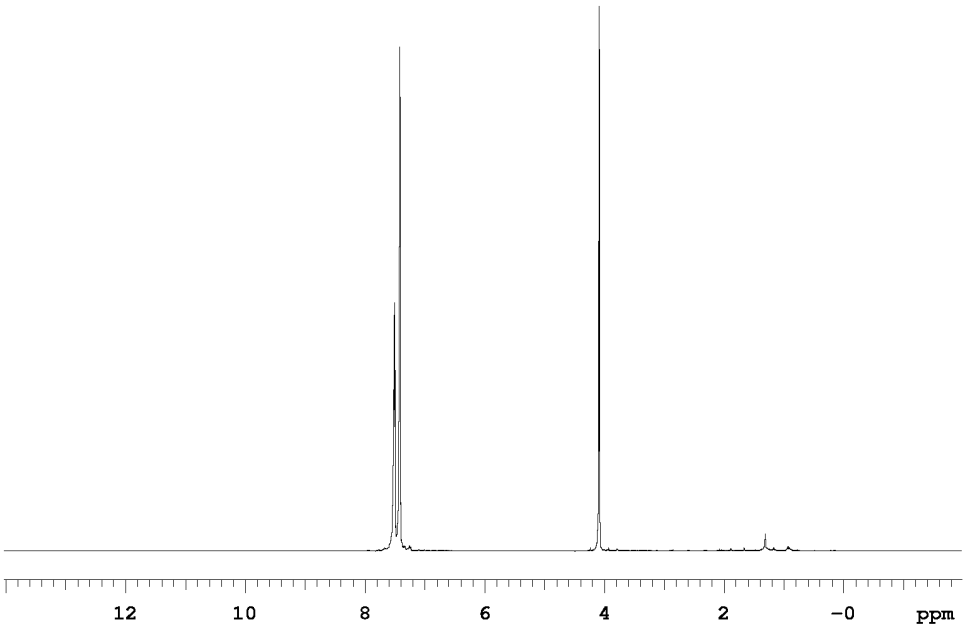
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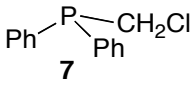
P
CH2Cl
Ph
Ph

7

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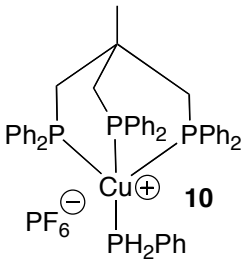
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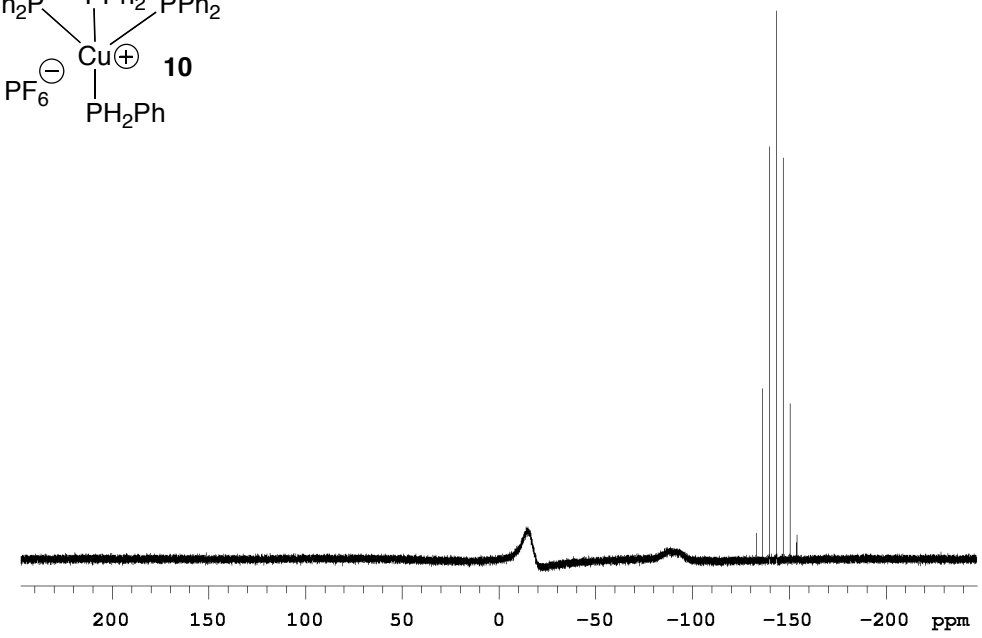
PPh2
PPh2
Cu
PF6
PH2Ph

10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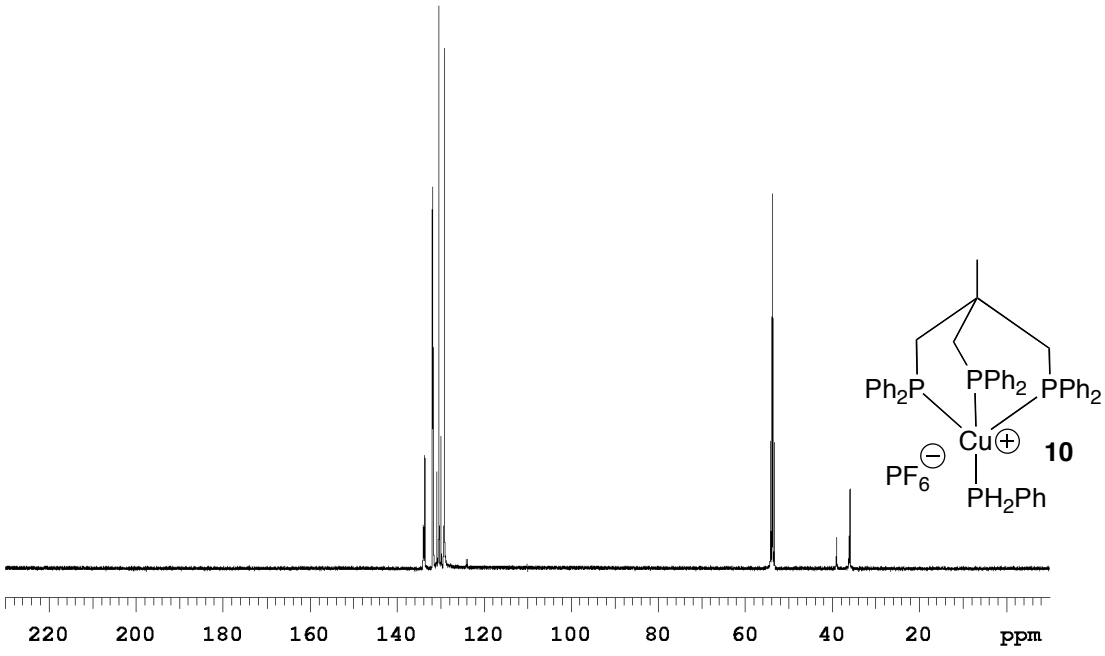
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PPh2
Cu
PF6
PH2Ph
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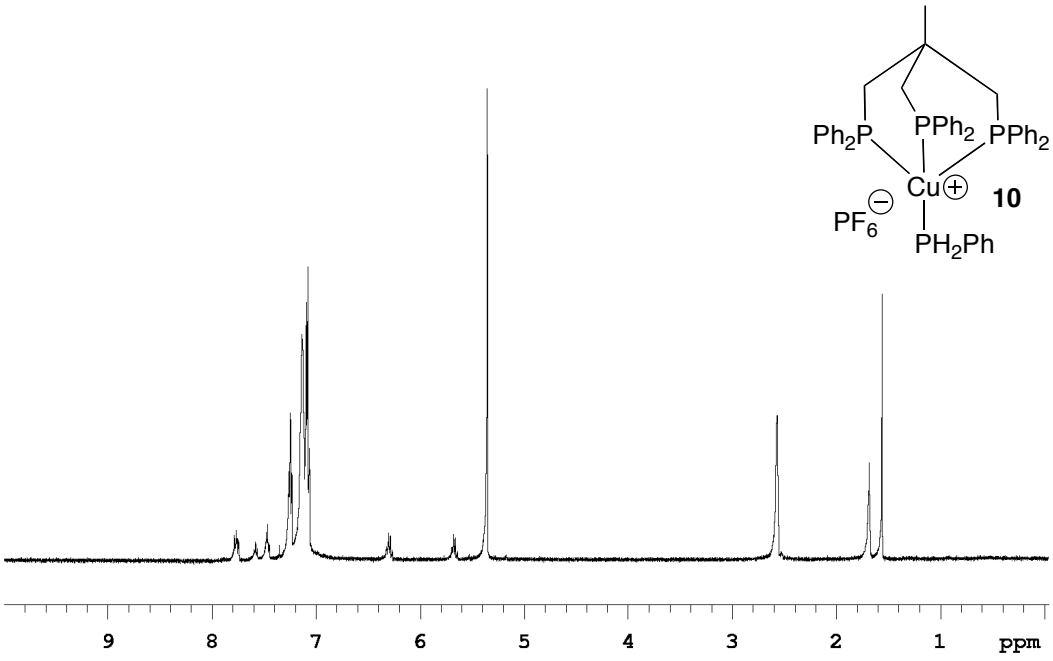
20
ppm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PPh2
PPh2
Cu
PF6
PH2Ph
10
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8
7
6
5
4
3
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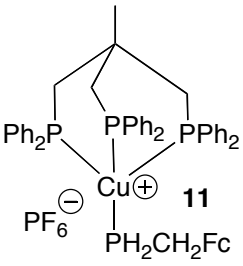
ppm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PPh2
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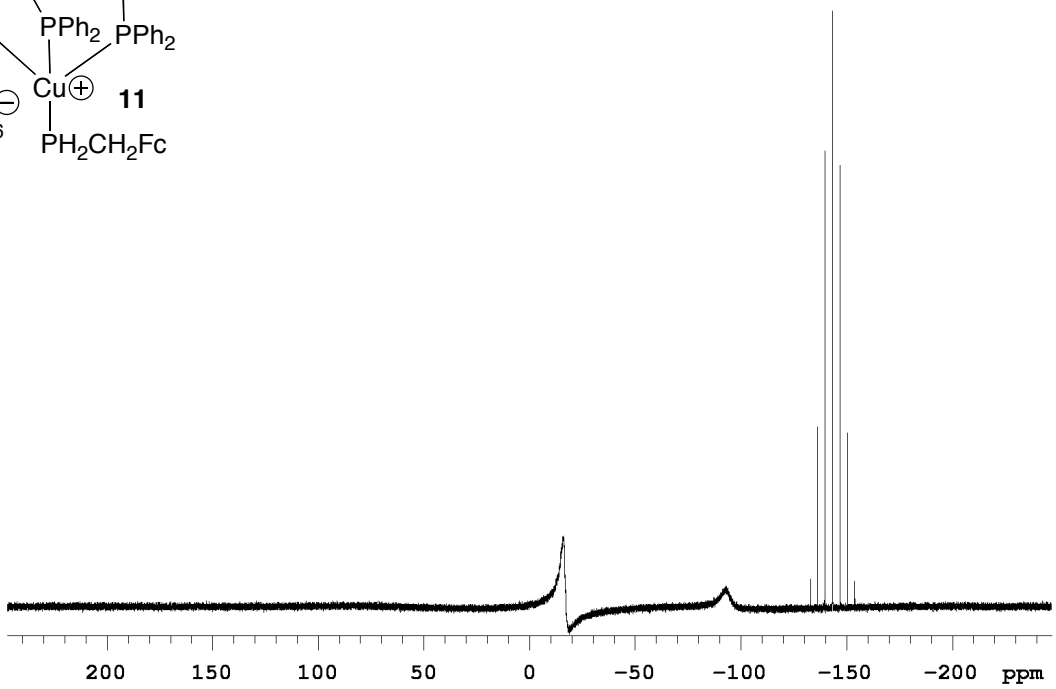
Cu
PF6
PH2CH2Fc

11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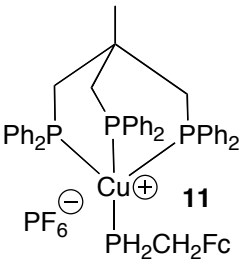
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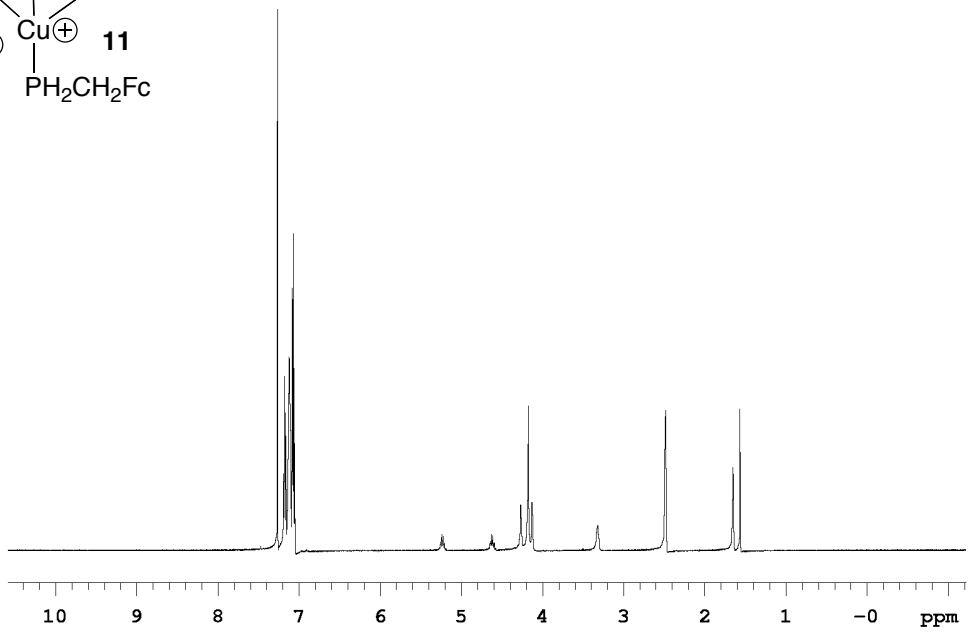
PPh2
Cu
PF6
PH2CH2Fc

11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4
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2
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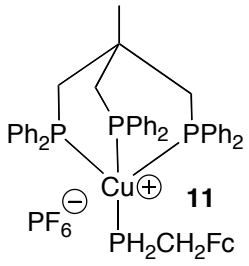
ppm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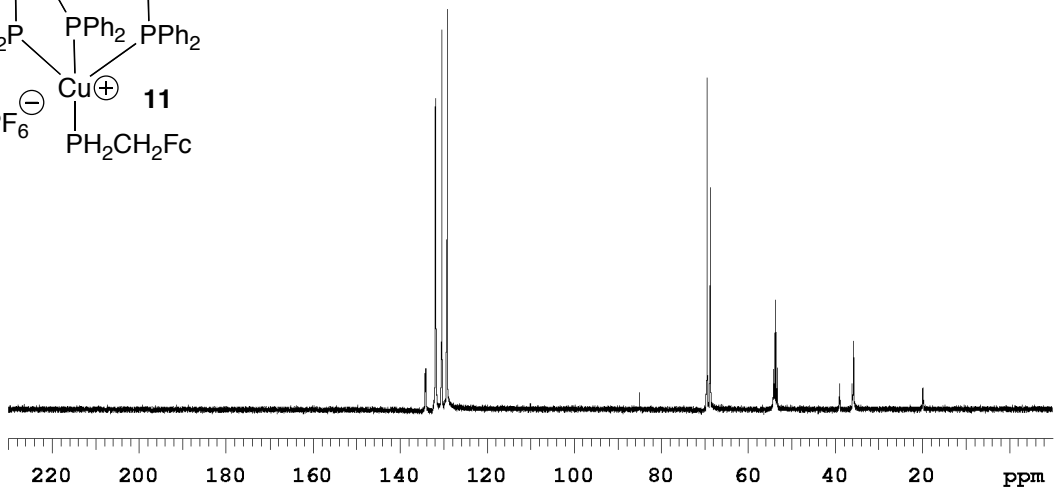
PPh2
PPh2
Cu
PF6
PH2CH2Fc

11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60
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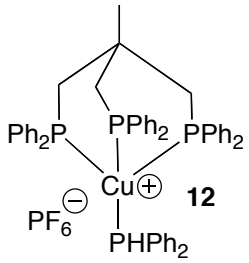
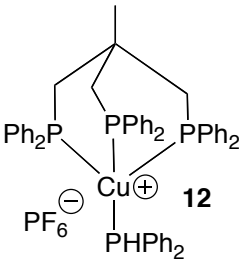
20
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PHPh2

12

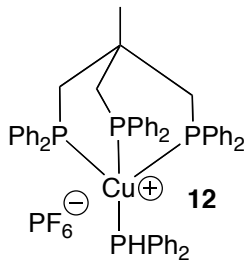
200
150
100
50
0
−50
−100
−150
−200
ppm



12

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ -16.0 (broad, triphos), -19.4 (broad, $PHPh_2$), -143.7 (septet, J = 711 Hz, PF_6)

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2), -70 °C



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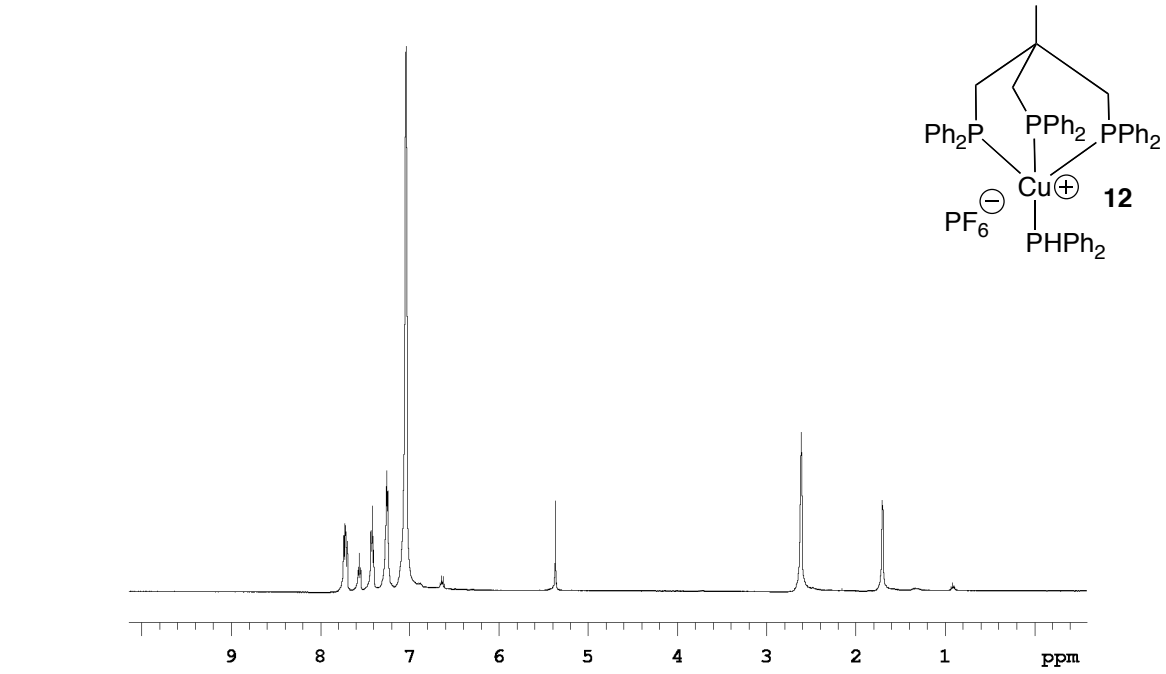
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PPh2
PPh2
Cu
PF6
PHPh2
12
9
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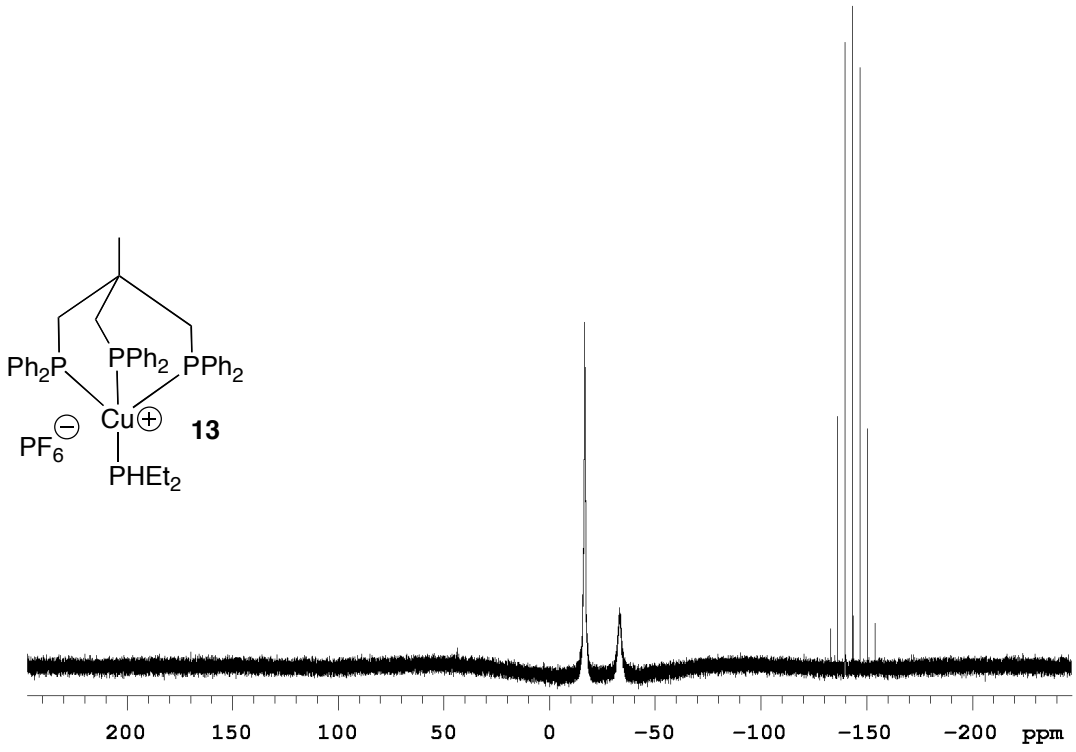
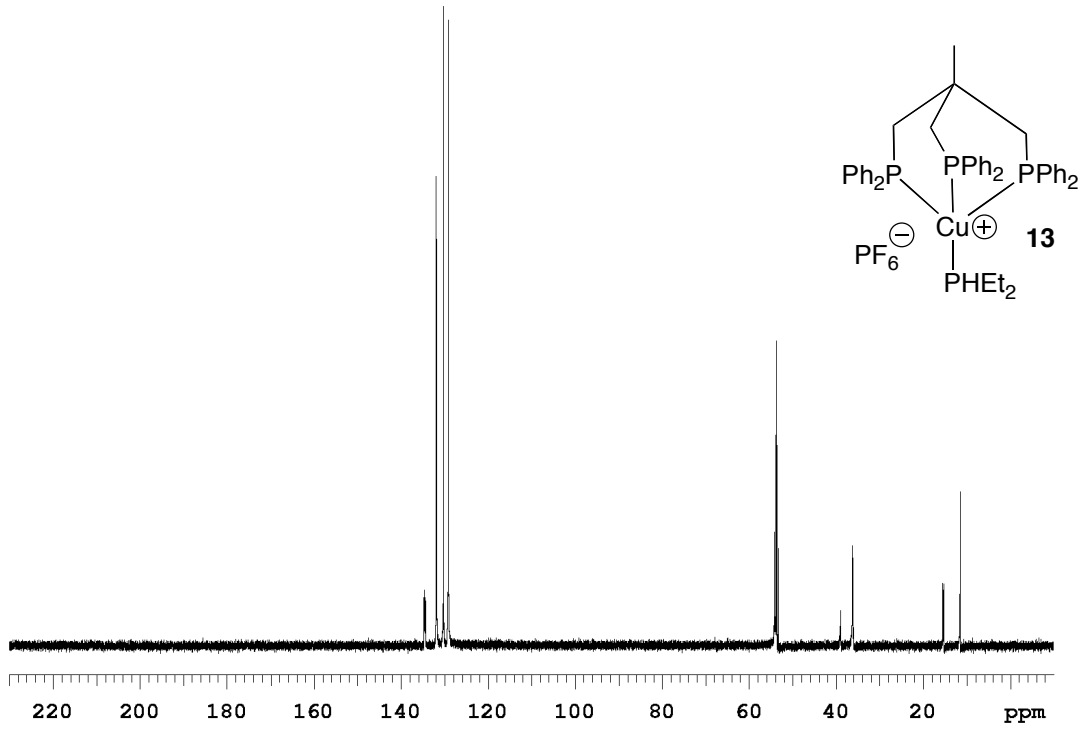
7
6
5
4
3
2
1
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PHEt2
13
200
150
100
50
0
−50
−100
−150
−200
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PHEt2
13
220
200
180
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140
120
100
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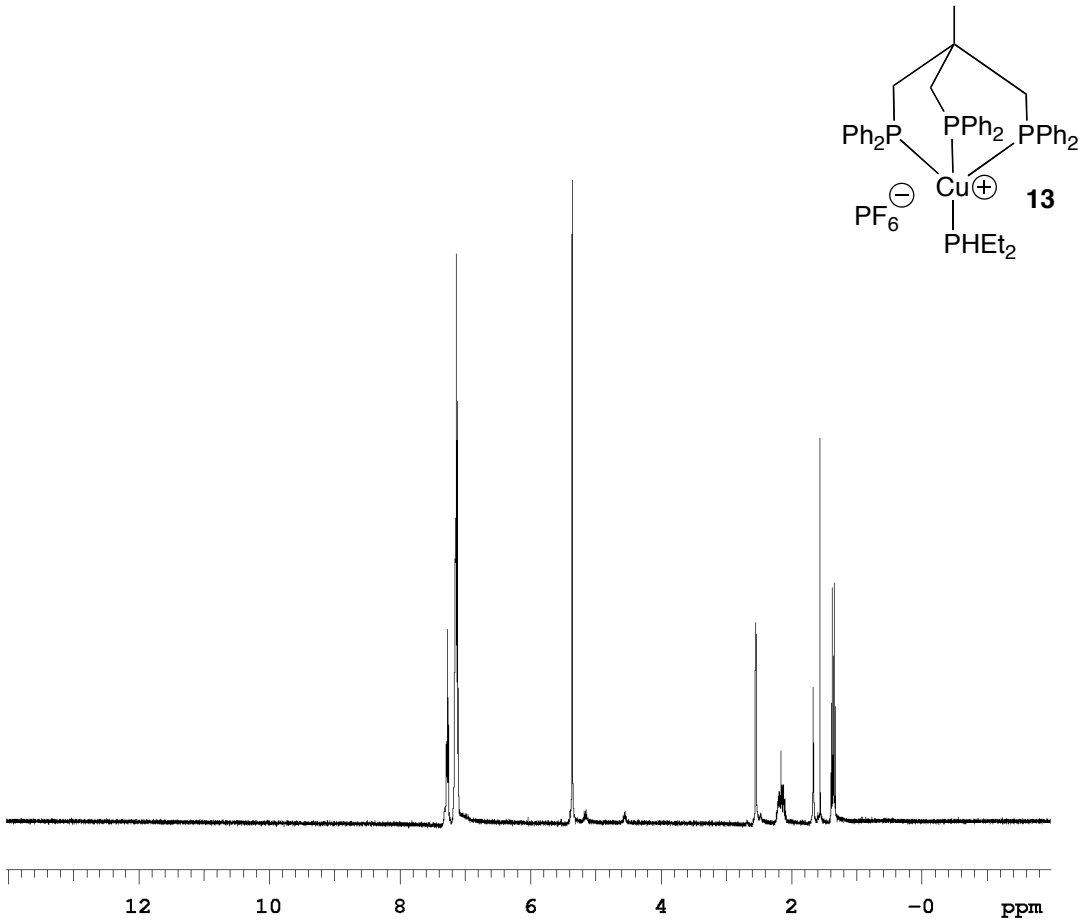
60
40
20
ppm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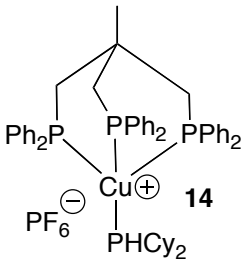
PPh2
PPh2
Cu
PF6
PHEt2
13
12
10
8
6
4
2
−0
ppm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PPh2
PPh2
Cu
PF6
PHCy2

14

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150
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50
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−50
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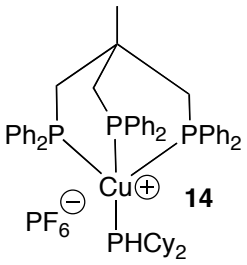
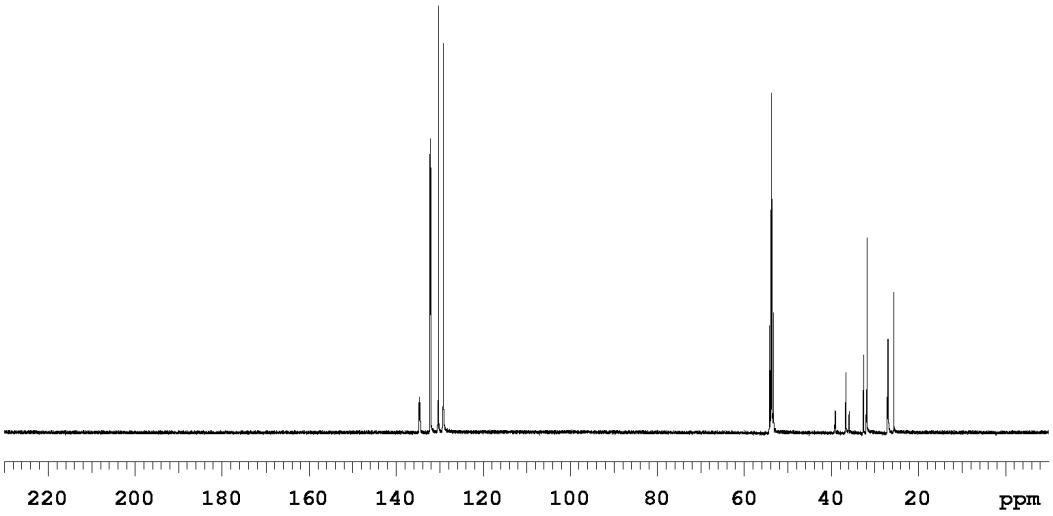
−200
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PHCy2

14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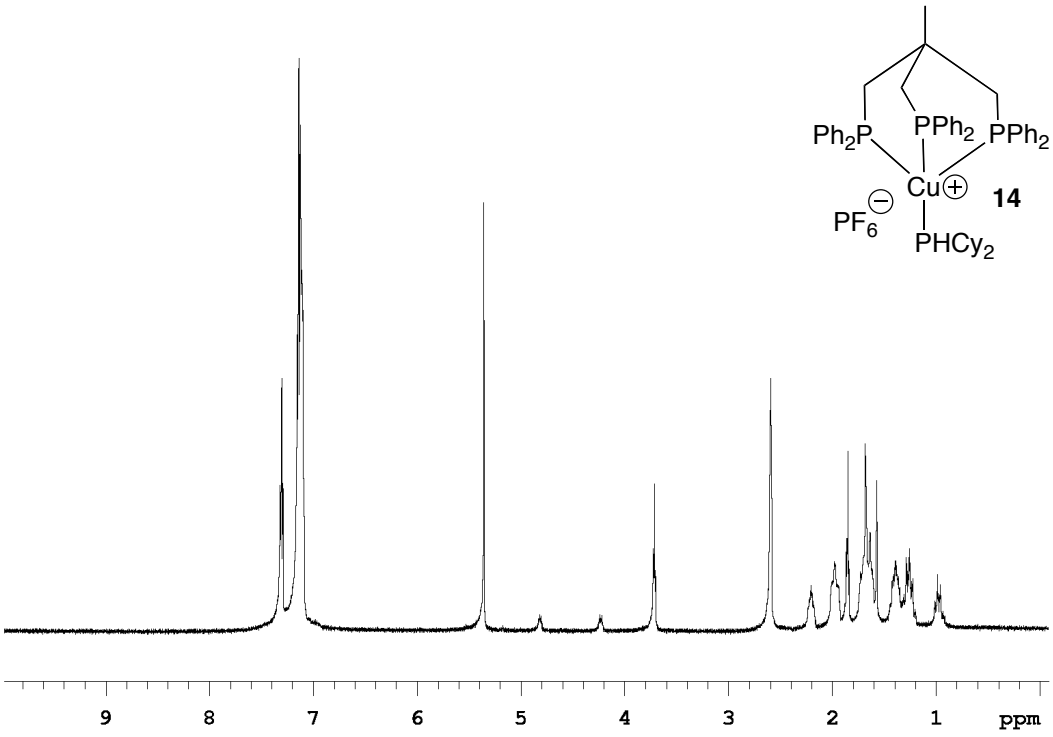
120
100
80
60
40
20
ppm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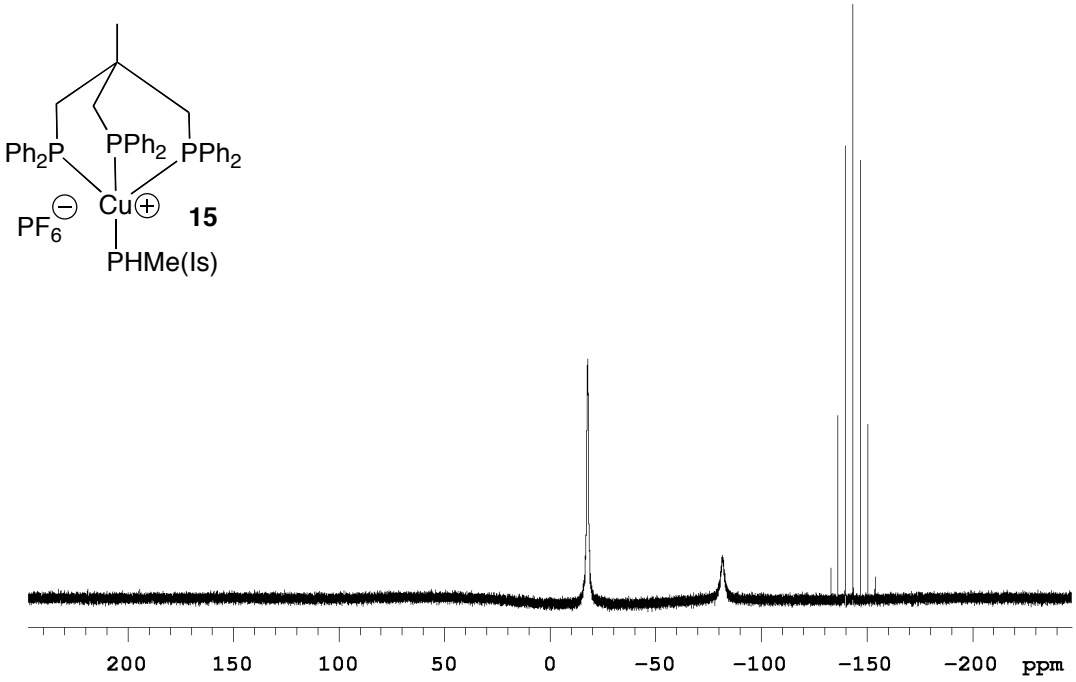
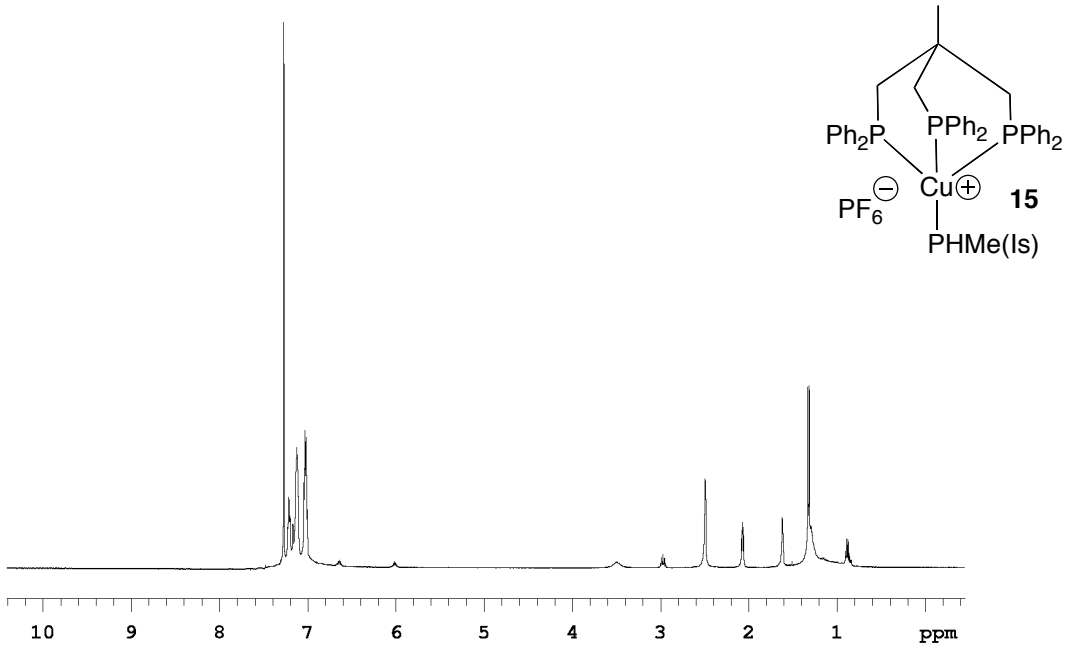
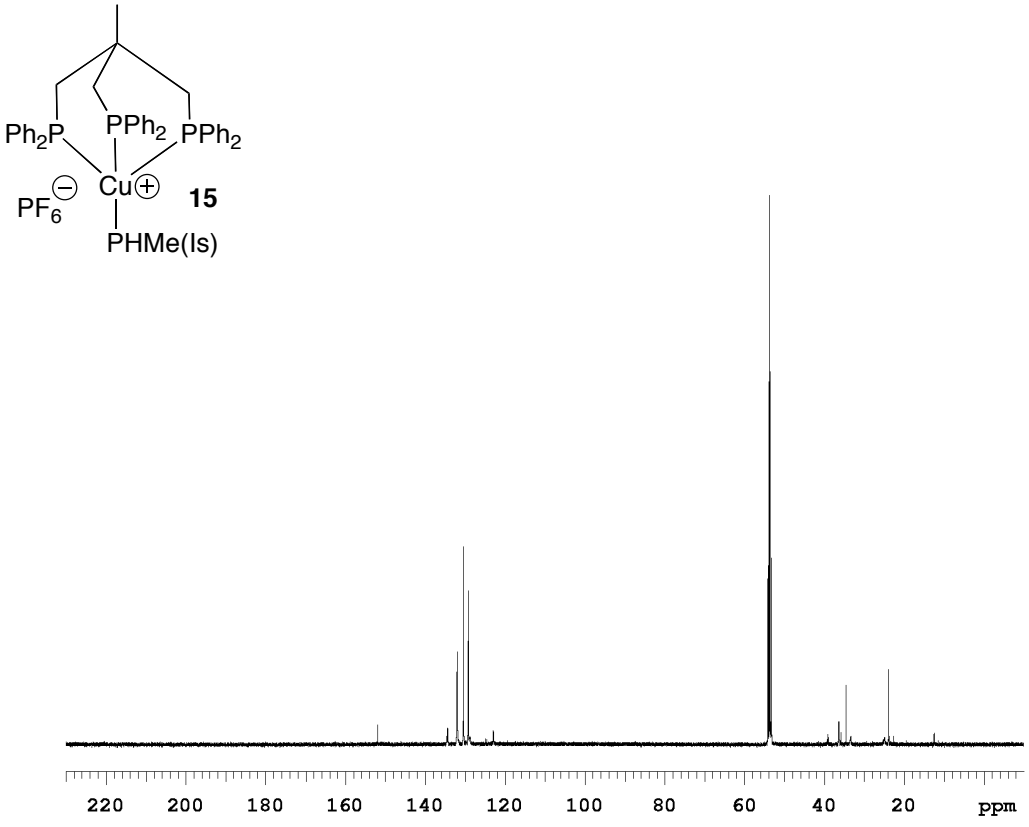
PPh2
PPh2
Cu
PF6
PHCy2
14
9
8
7
6
5
4
3
2
1
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PHMe(Is)
15
200
150
100
50
0
−50
−100
−150
−200
ppm


Ph2P
PPh2
PPh2
PF6
Cu
PHMe(Is)
15
10
9
8
7
6
5
4
3
2
1
ppm


Ph2P
PPh2
PPh2
PF6
Cu
PHMe(Is)
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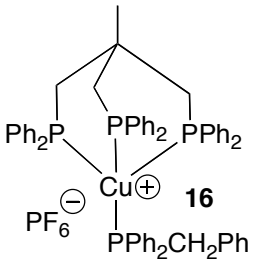
60
40
20
ppm


Ph2P
PPh2
PPh2
Cu
PF6
PPh2CH2Ph

16

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0
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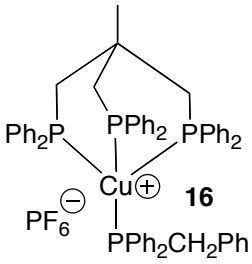
−150
−200
ppm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Cu
PF6
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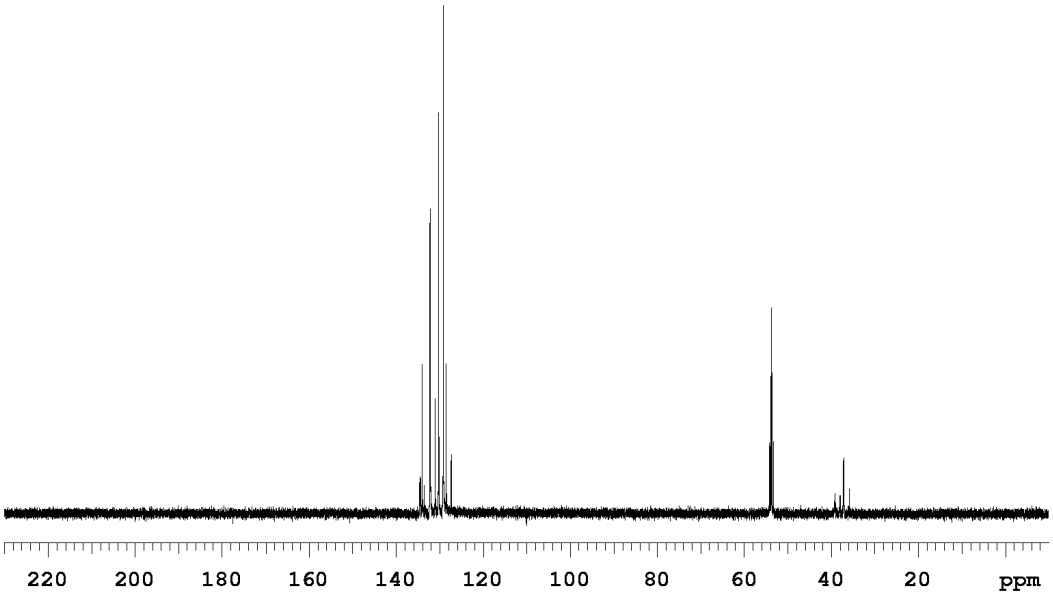
16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20
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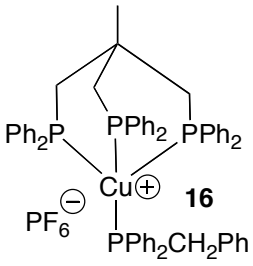
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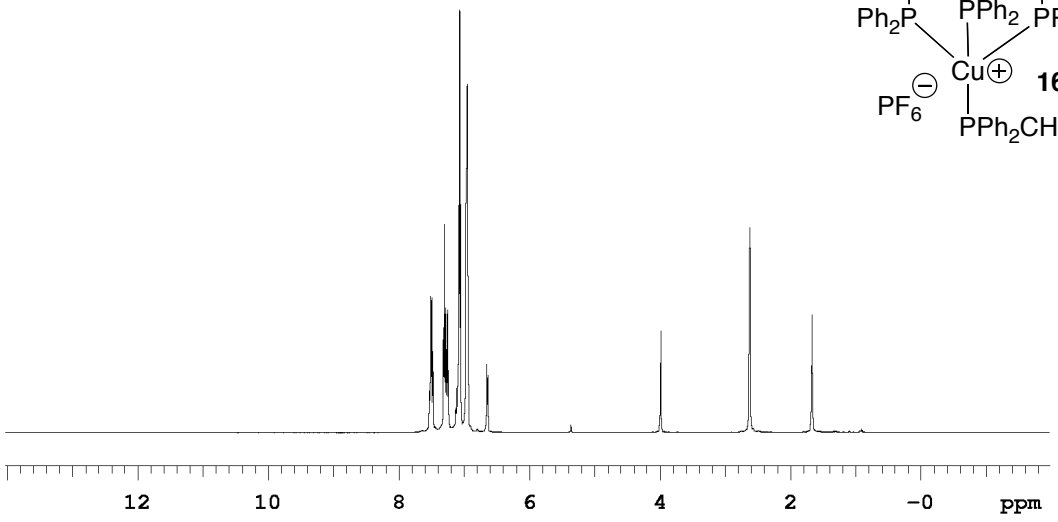
PPh2
Cu
PF6
PPh2CH2Ph

16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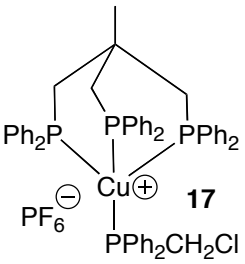
Ph2P
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PPh2
Cu
PF6
PPh2CH2Cl

17

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0
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−150
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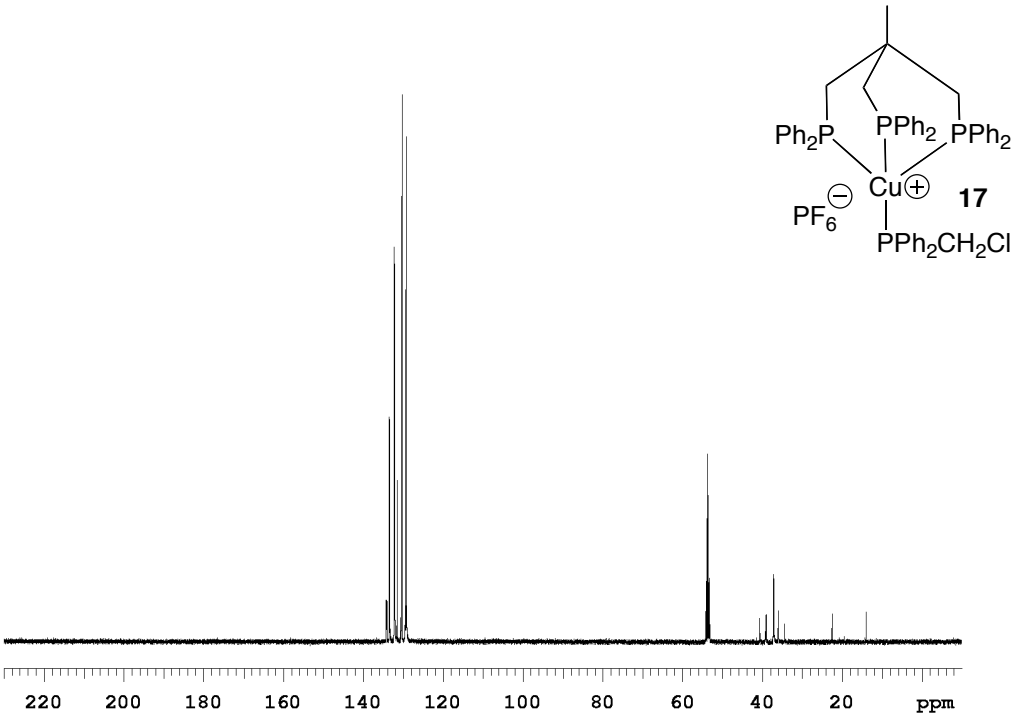
ppm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PPh2
PPh2
Cu
PF6
17
PPh2CH2Cl
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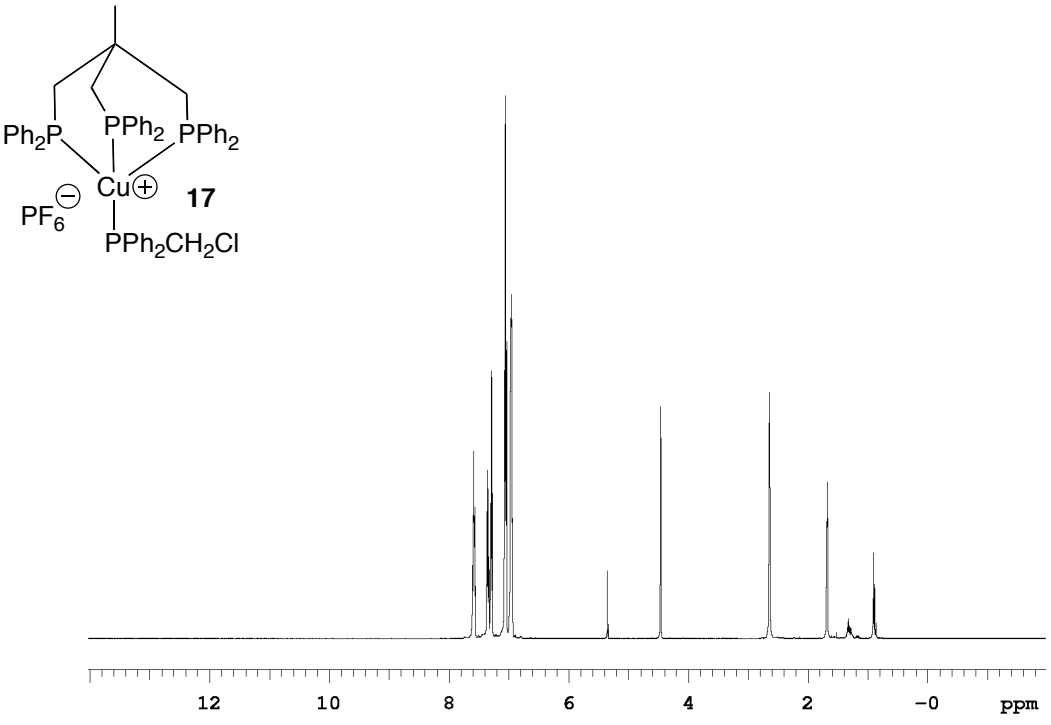
20
ppm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PPh2
Cu
PF6
17
PPh2CH2Cl
12
10
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4
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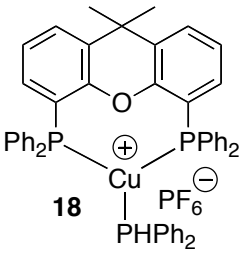
−0
ppm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Ph2P
PPh2
Cu
PF6
PHPh2

18

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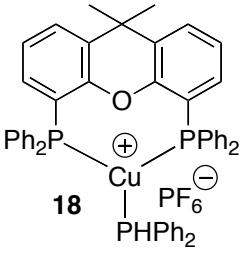
ppm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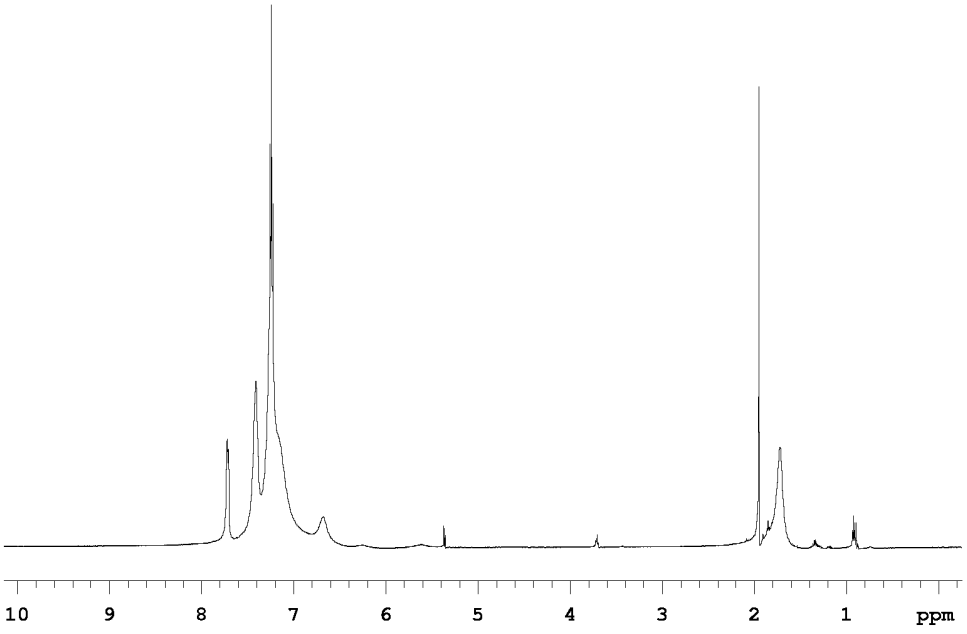
Cu
PF6
PHPh2

18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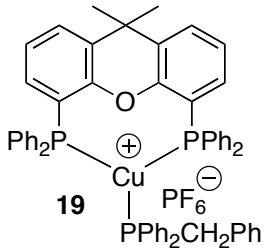
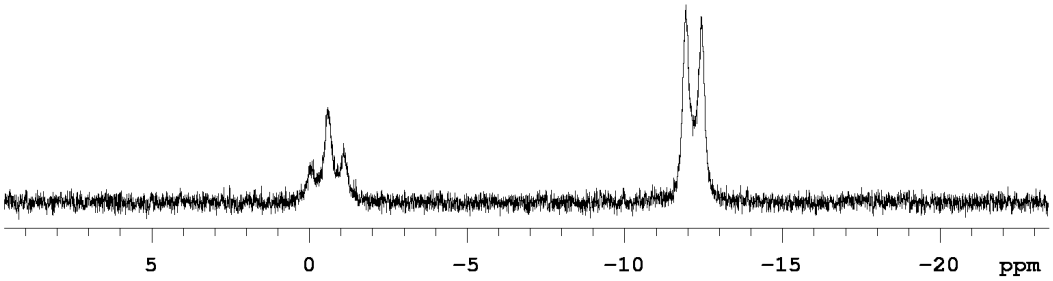
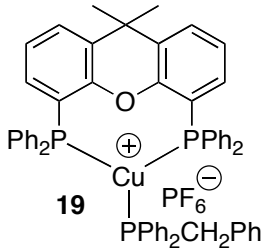
ppm



19

Zoomed in ^{31}P NMR Spectrum





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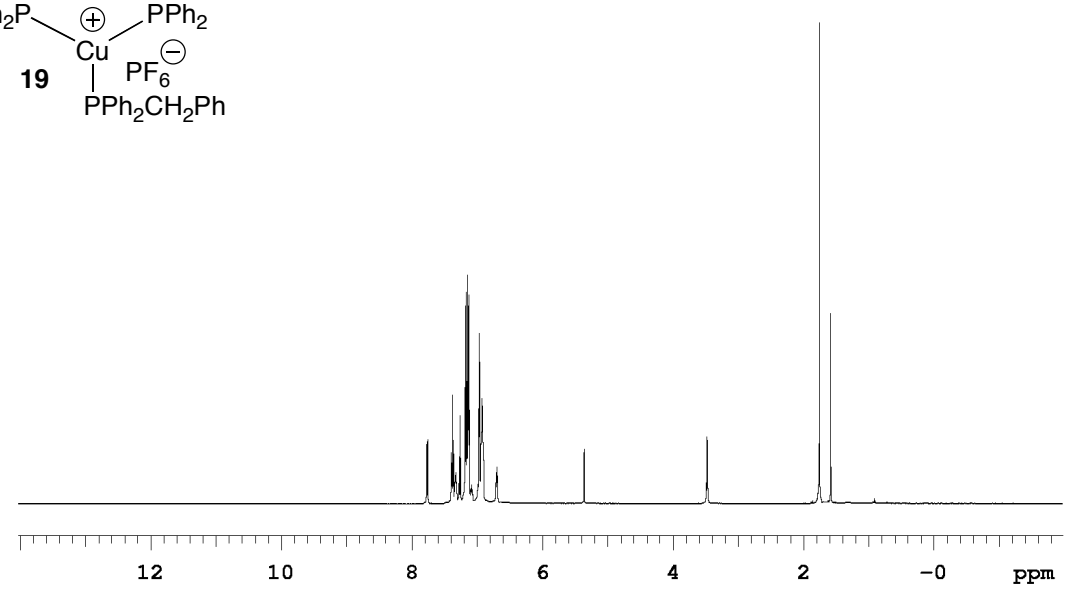
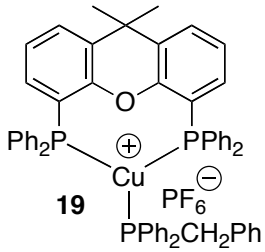
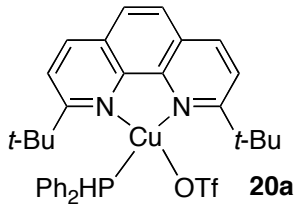


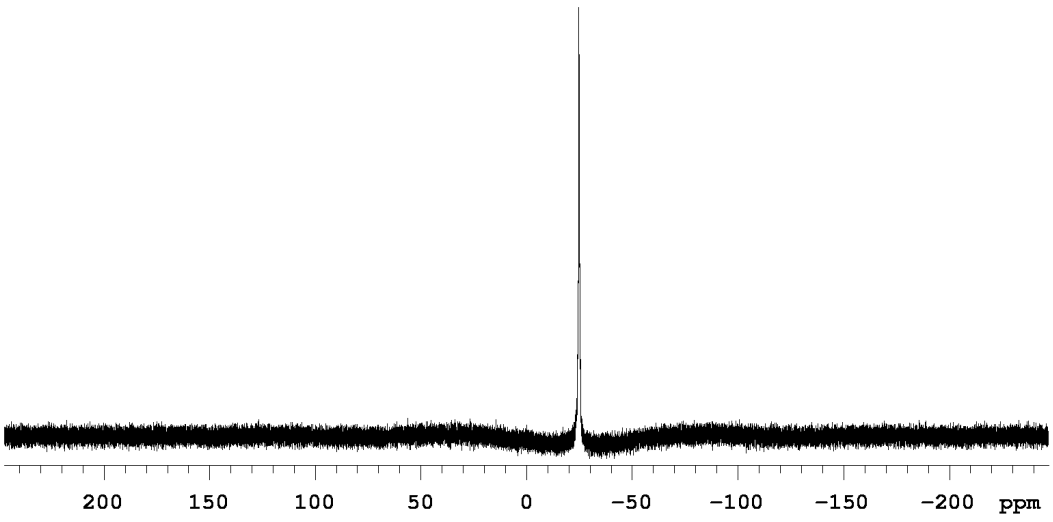

O
Ph2P
PPh2
Cu
PF6
PPh2CH2Ph

19

220
200
180
160
140
120
100
80
60
40
20
ppm


N
N
t-Bu
t-Bu
Cu
Ph2HP
OTf

20a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0
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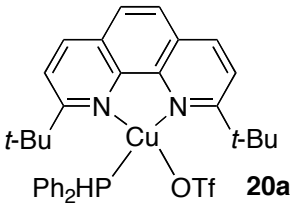
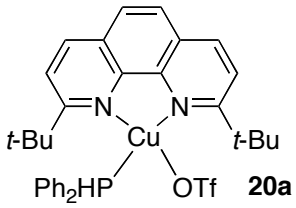
−100
−150
−200
ppm

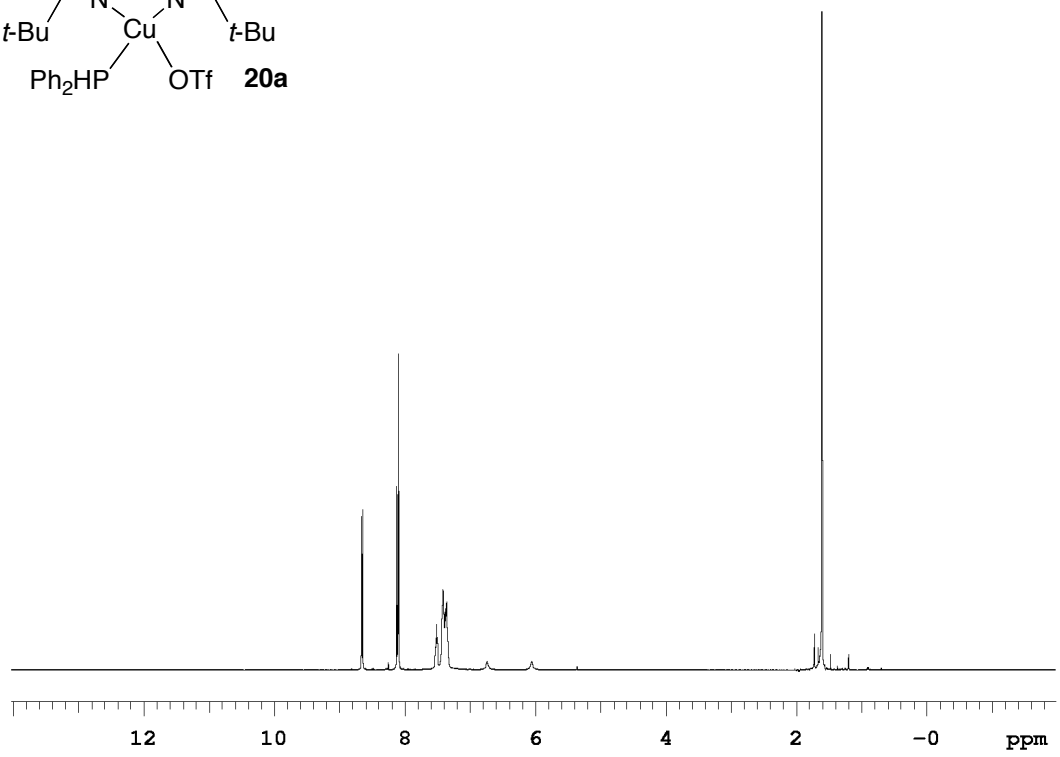

N
N
Cu
t-Bu
t-Bu
Ph2HP
OTf

20a

220
200
180
160
140
120
100
80
60
40
20
ppm


N
N
Cu
t-Bu
t-Bu
Ph2HP
OTf

20a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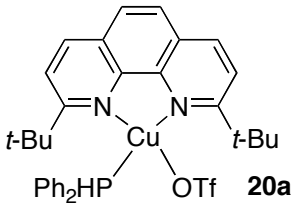
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Cu
t-Bu
t-Bu
Ph2HP
OTf

20a

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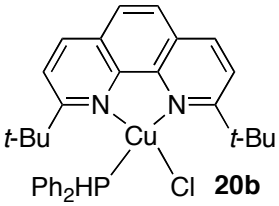
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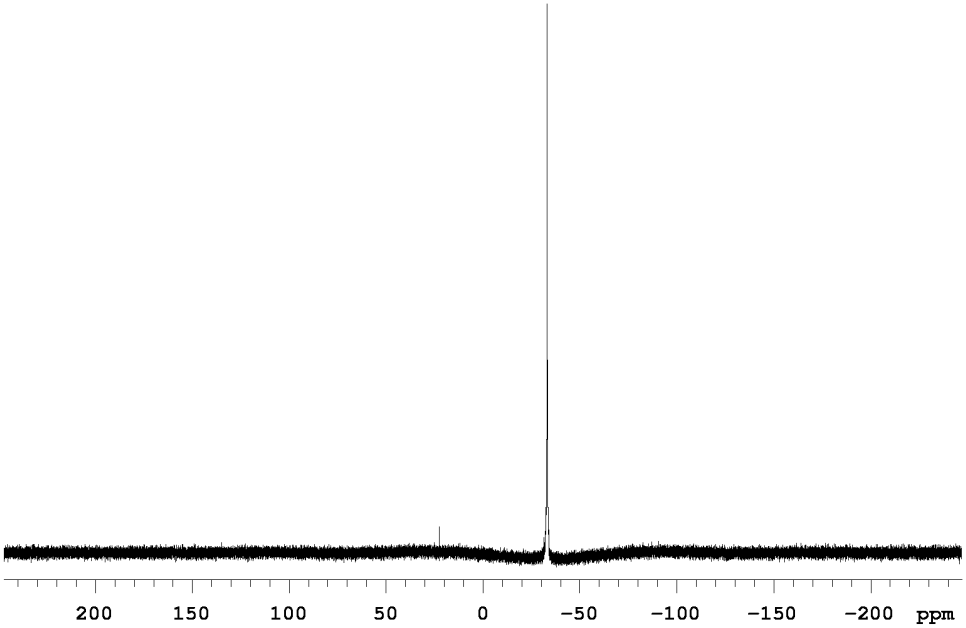
Ph2HP
Cl

20b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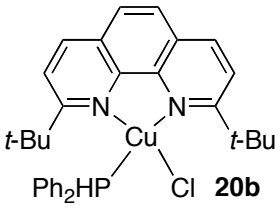
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t-Bu
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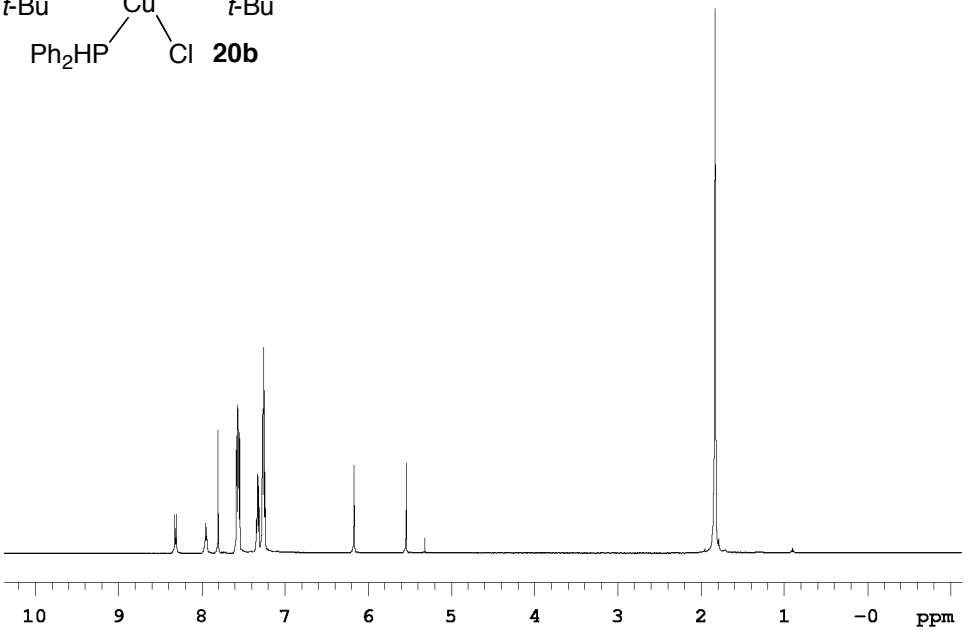
Cl

20b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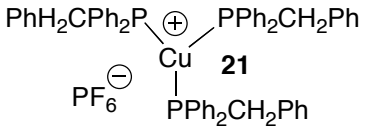
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PPh2CH2Ph
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PF6
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21

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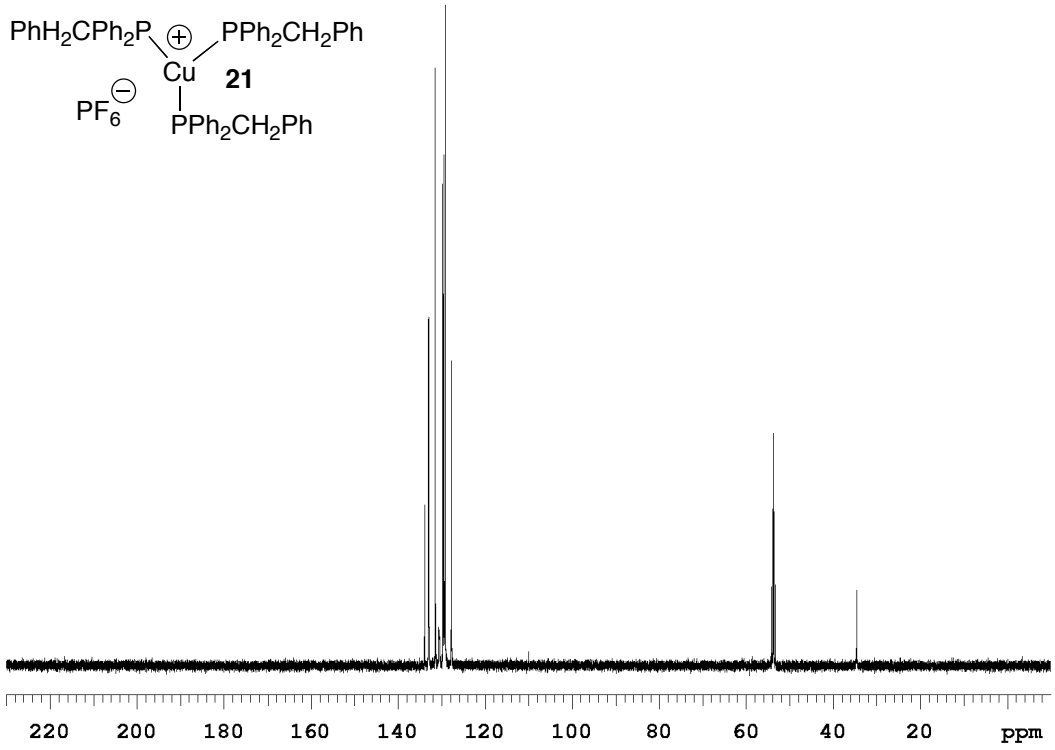
ppm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PF6
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80
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40
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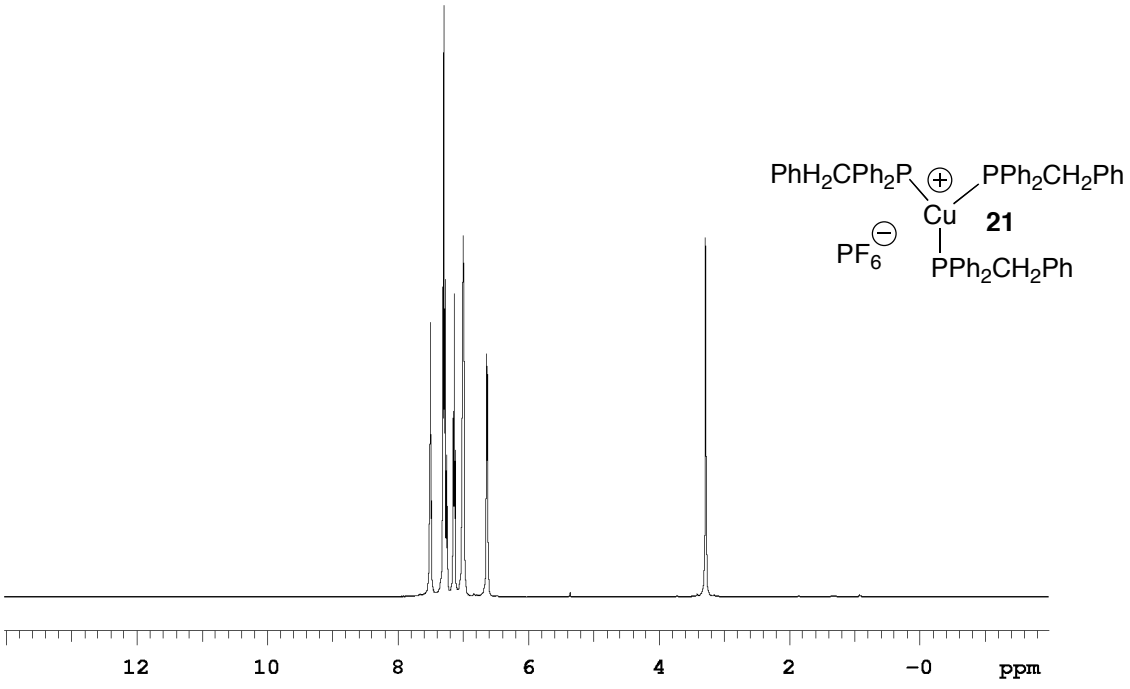
ppm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21
PF6
PPh2CH2Ph
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10
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6
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2
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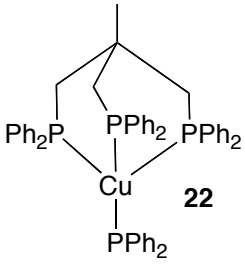
ppm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PPh2
PPh2
Cu
PPh2

22

triphos
PPh2
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−22
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−26
−28
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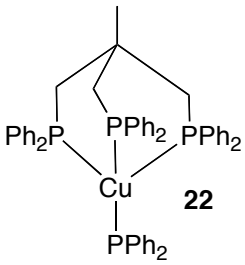
ppm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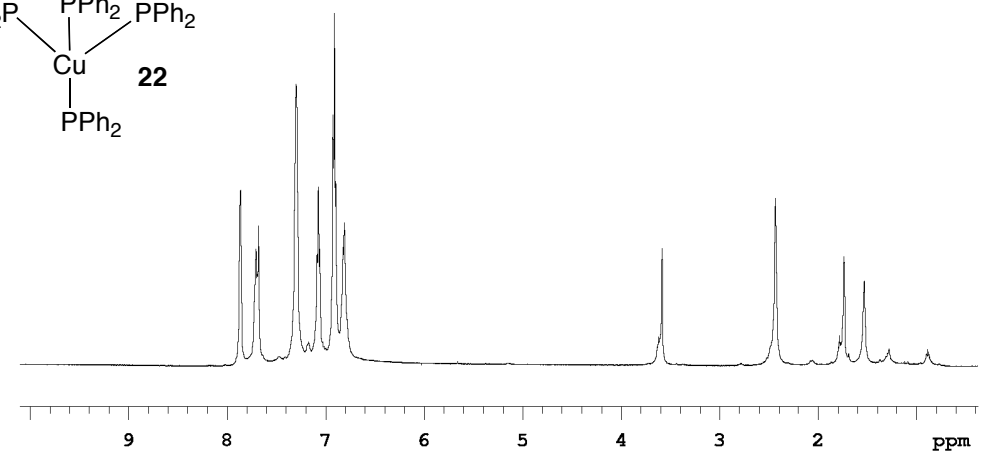
PPh2
Cu
PPh2

22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8
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4
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2
ppm

Computational (DFT) Supporting Information.

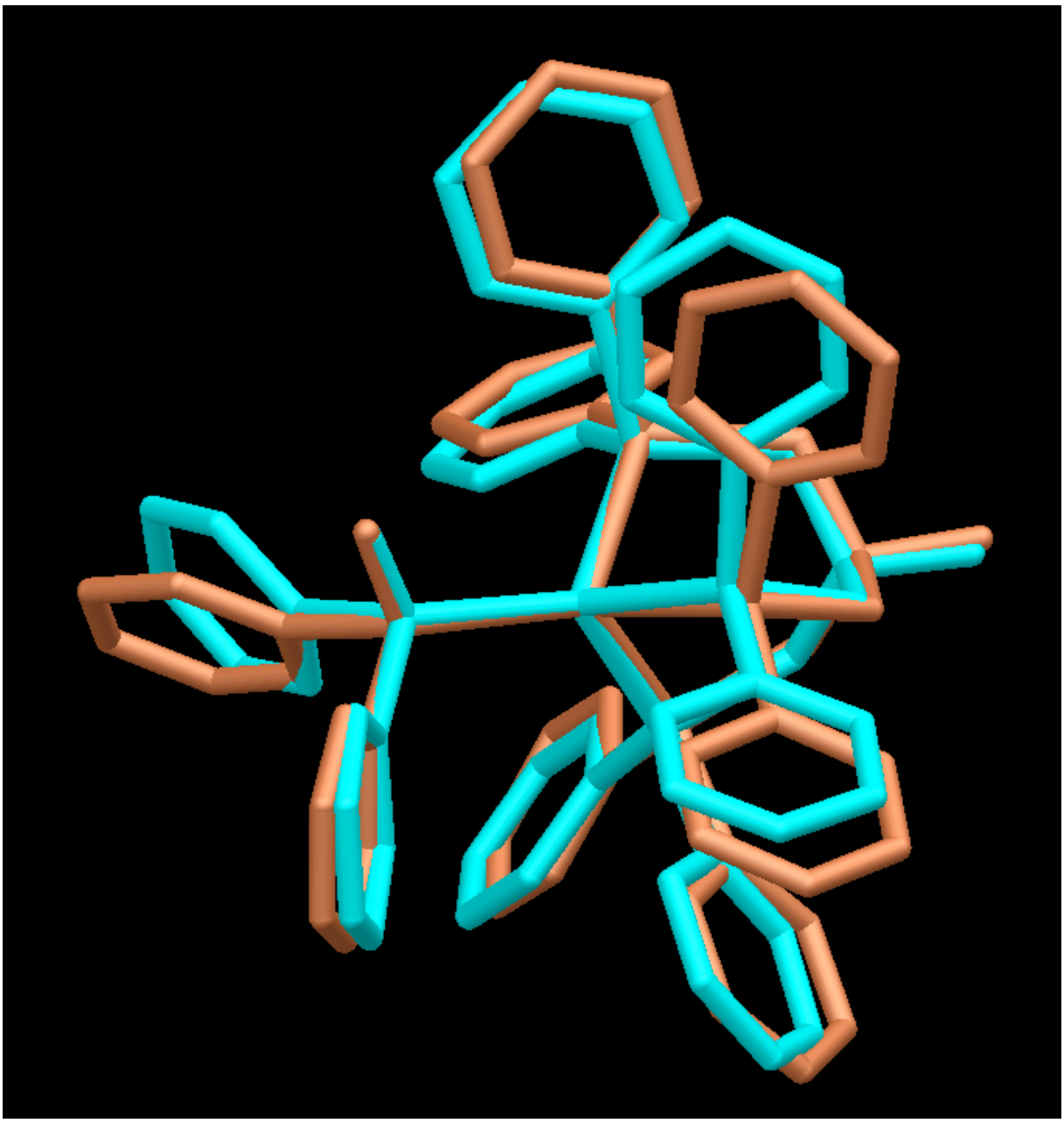

Figure S1. Superposition of the X-ray structure (blue) and DFT (B3LYP/LACV3P**++) calculated structure (bronze) of $[Cu(triphosPh_6)(PHPh_2)]^+$ cation. All H atoms except for the P-H are omitted for clarity.

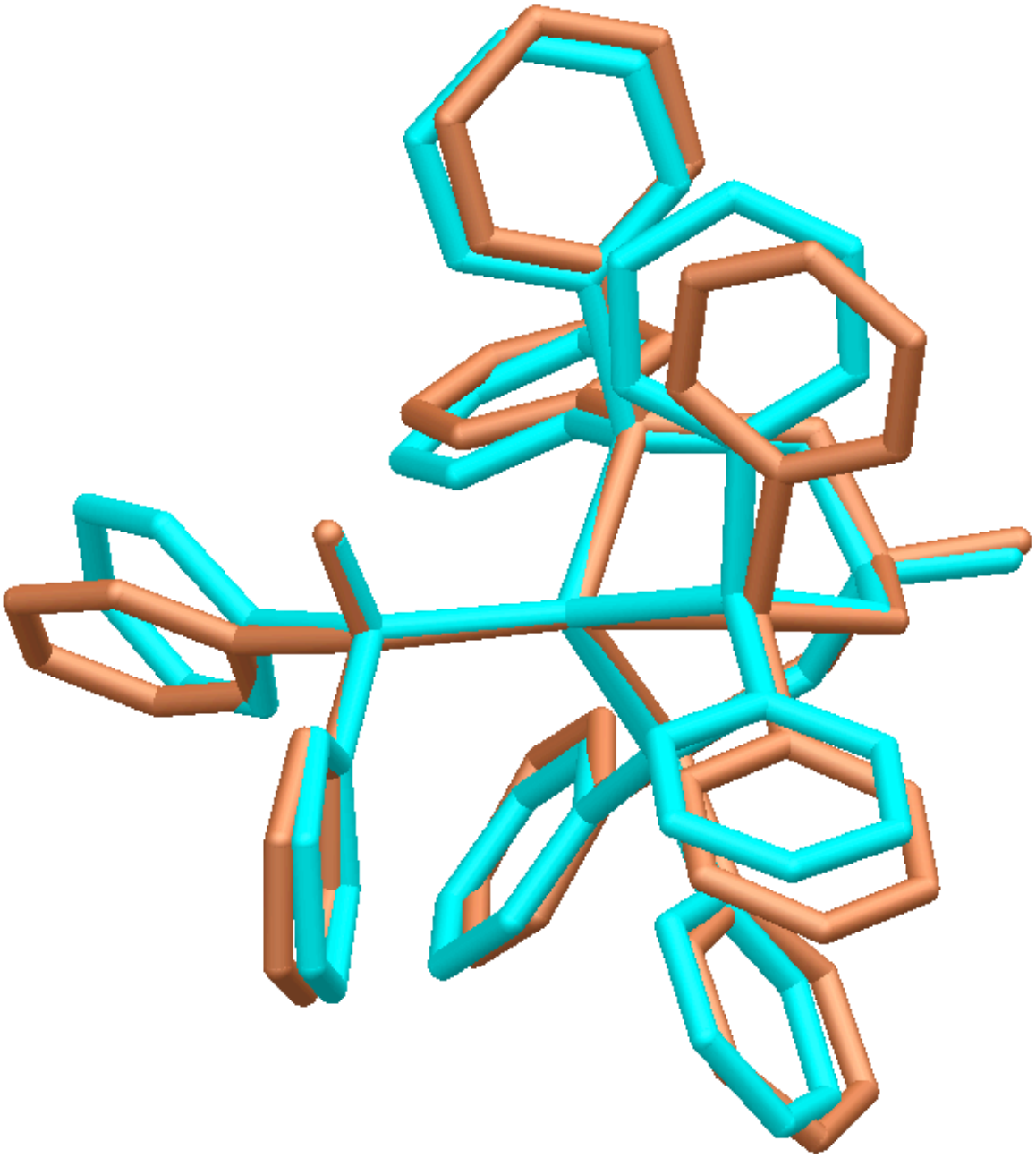

Figure S2. Superposition of the X-ray structure (blue) and DFT (B3LYP/LACV3P**++) calculated structure (bronze) of $[Cu(triphosPh_6)(PHPh_2)]^+$ cation. All H atoms except for the P-H are omitted for clarity.

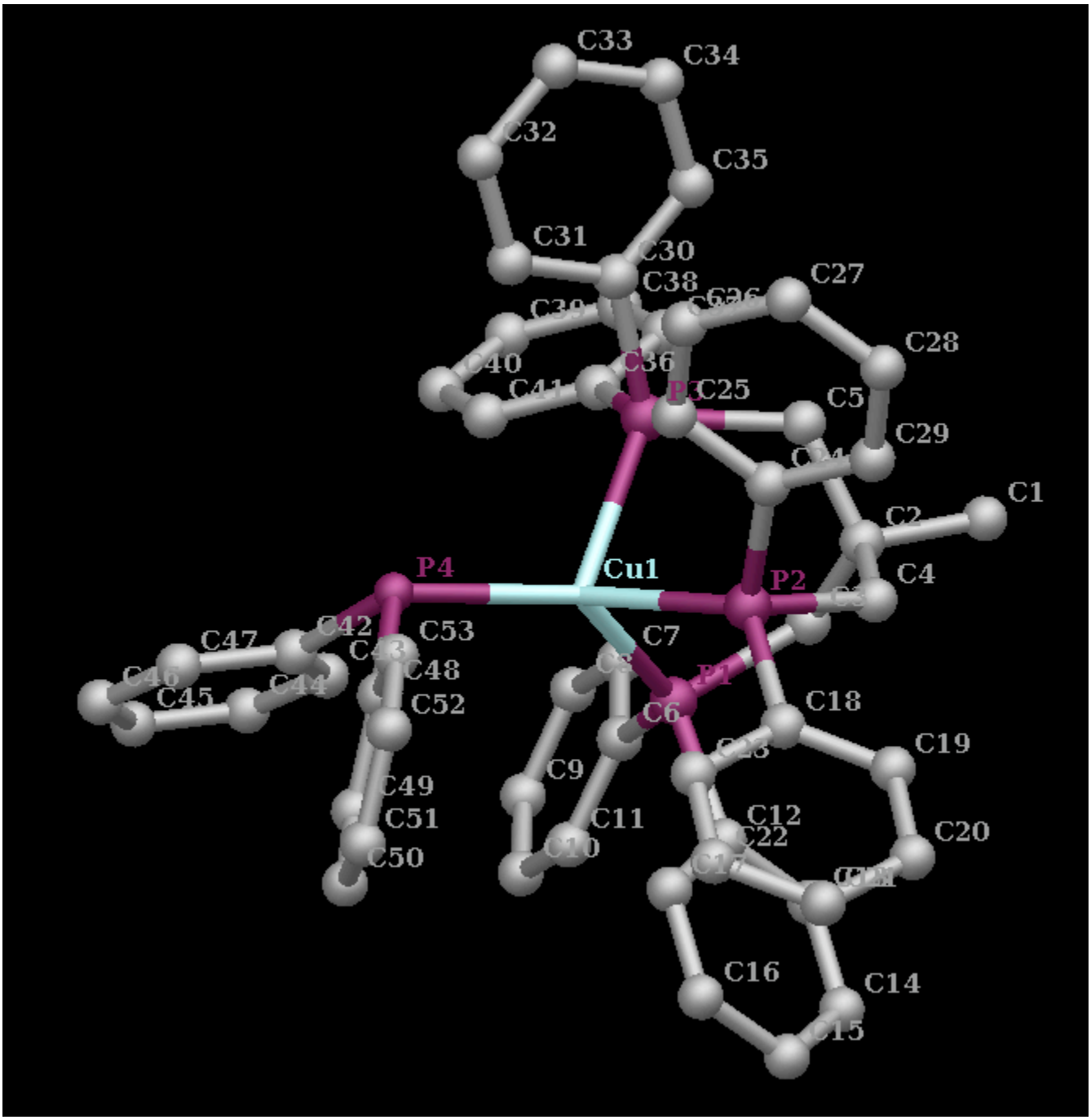

Figure S3. Atom labeling for Cu(triphosPh_6)(PPh_2). All H atoms are omitted for clarity.

```
|  Jaguar version 7.6, release 211                                    |
  |                                                                     |
  |  Copyright (c) 2009 Schrodinger,  LLC.                              |
  |  All Rights Reserved.                                               |
  |                                                                     |
  |  Use of this program should be acknowledged in publications as:     |
  |  Jaguar, version 7.6, Schrodinger, LLC, New York, NY, 2009.         |
  +---------------------------------------------------------------------+

  basis set:              lacv3p**++
  net molecular charge:    0
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multiplicity: 1

This run will use ECP on 1 atom
number of basis functions.... 1665

Final geometry:

atom	x	y	z
	angstroms		
Cu1	2.0999446756	2.2860190511	5.9462557479
P1	2.3857522553	1.1107633225	3.8181414485
P2	3.8005034007	0.9412533575	6.9711321525
P3	3.7488901249	3.9409689463	5.2382390210
P4	0.2306728170	3.1666354488	7.0389113952
C1	6.6322701073	1.1834876250	3.8315392630
H1A	6.7104928823	0.1141755529	3.6140208937
H1B	7.4481724977	1.4511559686	4.5096117822
H1C	6.7778906213	1.7293882229	2.8944834413
C2	5.2574560117	1.5217804088	4.4631367637
C3	4.2027303791	1.2517014814	3.3486626773
H3A	4.4816255392	0.3331231723	2.8259211822
H3B	4.2750608720	2.0525822375	2.6102063220
C4	5.1010211888	0.5550733031	5.6749813545
H4A	6.0706865431	0.4666188868	6.1718105013
H4B	4.8566765306	-0.4354074206	5.2823220354
C5	5.3435035726	3.0227772546	4.8881679929
H5A	5.9195916168	3.5590217117	4.1304629782
H5B	5.9268353466	3.0814905725	5.8113494165
C6	1.5509044066	1.4092222994	2.1849818506
C7	1.9607845179	2.4264011763	1.3124576792
H7A	2.8144974240	3.0492151819	1.5449237065
C8	1.2661547222	2.6744068924	0.1302807498
H8A	1.6072121574	3.4639590939	-0.5296107771
C9	0.1396155648	1.9246156173	-0.1961314936
H9A	-0.4005949622	2.1200131789	-1.1155053734
C10	-0.2910674241	0.9254084735	0.6741683810
H10A	-1.1724989653	0.3396405217	0.4384638036
C11	0.4055436942	0.6703753300	1.8517894614
H11A	0.0534297654	-0.1119345778	2.5125331708
C12	2.1137210579	-0.7090127414	4.0128943474
C13	2.6190861006	-1.6588681188	3.1139420210
H13A	3.2124187274	-1.3466038715	2.2617090303
C14	2.3422021607	-3.0110542183	3.2859249912
H14A	2.7372568207	-3.7360430178	2.5828216197
C15	1.5474538226	-3.4320955786	4.3535678638
H15A	1.3313799382	-4.4863834292	4.4853950347
C16	1.0324980455	-2.4965325905	5.2446957902
H16A	0.4192191905	-2.8144614310	6.0791079440
C17	1.3147657715	-1.1408493102	5.0755978968
H17A	0.9132712706	-0.4120252899	5.7706762663
C18	3.5116263831	-0.7092472838	7.7587307036
C19	4.3991658375	-1.7886188008	7.6684961641
H19A	5.3100458168	-1.7116399586	7.0873119770
C20	4.1244457577	-2.9874149351	8.3233344611
H20A	4.8191876339	-3.8159947643	8.2396791785
C21	2.9648424180	-3.1205556530	9.0839640871
H21A	2.7534207486	-4.0535192278	9.5944932997
C22	2.0777019524	-2.0508693592	9.1815347243
H22A	1.1690242045	-2.1399791591	9.7653138669
C23	2.3447087763	-0.8555833878	8.5185764619
H23A	1.6355453313	-0.0396255885	8.5920798446

C24	4.7568085054	1.8035699317	8.3063957022
C25	4.1946902461	2.9392309447	8.8957330818
H25A	3.2374008722	3.3055621114	8.5455065369
C26	4.8585056649	3.6057050580	9.9256438856
H26A	4.4143605848	4.4928977775	10.3613501393
C27	6.0883997597	3.1411581955	10.3796316859
H27A	6.6066303947	3.6603051798	11.1780585366
C28	6.6530137917	2.0010559926	9.8059704071
H28A	7.6060680261	1.6269575559	10.1635238211
C29	5.9901992644	1.3356220765	8.7799495074
H29A	6.4344823535	0.4379824284	8.3646609323
C30	4.2879149084	5.3408593152	6.3245160807
C31	3.3088050989	5.9318627598	7.1333783777
H31A	2.3015877966	5.5270881408	7.1508518978
C32	3.6252347168	7.0280591688	7.9333849862
H32A	2.8566774204	7.4771412702	8.5524987179
C33	4.9217597922	7.5379197761	7.9452059298
H33A	5.1680547360	8.3878538736	8.5718285158
C34	5.9026827348	6.9498706124	7.1487139775
H34A	6.9141696328	7.3411164715	7.1534138188
C35	5.5866303351	5.8619138508	6.3383257042
H35A	6.3628210210	5.4285252662	5.7184425450
C36	3.3777282244	4.8934076398	3.6862327339
C37	4.3402563191	5.2949962658	2.7518982671
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C38	3.9832427993	6.0766067668	1.6548080934
H38A	4.7416385416	6.3776808076	0.9403177459
C39	2.6602335415	6.4813271448	1.4833389480
H39A	2.3848141228	7.0946379261	0.6327170413
C40	1.6962096702	6.0930927640	2.4100586640
H40A	0.6629033396	6.3954180341	2.2850532359
C41	2.0505802276	5.2996556568	3.4989275181
H41A	1.2858387515	4.9916165720	4.2015751345
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C43	-1.0366237407	3.2845806836	4.4722275017
H43A	-0.0949880474	2.9362592626	4.0678786623
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H44A	-1.9331267034	3.4822346171	2.5298884001
C45	-3.3157029456	3.9994080745	4.0985707586
H45A	-4.1342646376	4.2283765246	3.4249287620
C46	-3.4858624134	4.1105600408	5.4809499229
H46A	-4.4402594271	4.4324562331	5.8852687365
C47	-2.4338938773	3.8266770321	6.3448820679
H47A	-2.5774924834	3.9401888797	7.4140418293
C48	-0.4562080019	1.9007675799	8.2006459756
C49	-1.3957112529	0.9175195951	7.8375513759
H49A	-1.7630247060	0.8850995155	6.8182738037
C50	-1.8688355400	-0.0098923135	8.7621893486
H50A	-2.5998843845	-0.7497053908	8.4507246406
C51	-1.4095919085	0.0027804600	10.0806605020
H51A	-1.7836490600	-0.7162058276	10.8012052498
C52	-0.4754582200	0.9663942159	10.4601600382
H52A	-0.1155502269	1.0009923465	11.4835520971
C53	-0.0164327936	1.9042226178	9.5373013980
H53A	0.6842377669	2.6681231147	9.8591196400

bond lengths (angstroms):

Cu1	-P1	:	2.447812	Cu1	-P2	:	2.398055
Cu1	-P3	:	2.441141	Cu1	-P4	:	2.337426

P1	-C3	:	1.881936	P1	-C6	:	1.858295
P1	-C12	:	1.850274	P2	-C4	:	1.876296
P2	-C18	:	1.851463	P2	-C24	:	1.855004
P3	-C5	:	1.873077	P3	-C30	:	1.852090
P3	-C36	:	1.858393	P4	-C42	:	1.852921
P4	-C48	:	1.850366	C1	-H1A	:	1.094012
C1	-H1B	:	1.094132	C1	-H1C	:	1.094206
C1	-C2	:	1.550313	C2	-C3	:	1.558025
C2	-C4	:	1.558063	C2	-C5	:	1.562385
C3	-H3A	:	1.093082	C3	-H3B	:	1.091769
C4	-H4A	:	1.093121	C4	-H4B	:	1.093132
C5	-H5A	:	1.092498	C5	-H5B	:	1.093612
C6	-C7	:	1.401411	C6	-C11	:	1.403126
C7	-H7A	:	1.082018	C7	-C8	:	1.393399
C8	-H8A	:	1.084052	C8	-C9	:	1.392057
C9	-H9A	:	1.084092	C9	-C10	:	1.393314
C10	-H10A	:	1.084252	C10	-C11	:	1.391798
C11	-H11A	:	1.082855	C12	-C13	:	1.402046
C12	-C17	:	1.397910	C13	-H13A	:	1.084368
C13	-C14	:	1.390917	C14	-H14A	:	1.084450
C14	-C15	:	1.395981	C15	-H15A	:	1.084246
C15	-C16	:	1.390887	C16	-H16A	:	1.083251
C16	-C17	:	1.395043	C17	-H17A	:	1.084212
C18	-C19	:	1.400325	C18	-C23	:	1.400170
C19	-H19A	:	1.083237	C19	-C20	:	1.393340
C20	-H20A	:	1.084532	C20	-C21	:	1.393185
C21	-H21A	:	1.084325	C21	-C22	:	1.393114
C22	-H22A	:	1.083713	C22	-C23	:	1.392665
C23	-H23A	:	1.083560	C24	-C25	:	1.397505
C24	-C29	:	1.401600	C25	-H25A	:	1.083171
C25	-C26	:	1.394832	C26	-H26A	:	1.083612
C26	-C27	:	1.390880	C27	-H27A	:	1.084233
C27	-C28	:	1.395604	C28	-H28A	:	1.084484
C28	-C29	:	1.390987	C29	-H29A	:	1.084255
C30	-C31	:	1.400785	C30	-C35	:	1.399411
C31	-H31A	:	1.085649	C31	-C32	:	1.393479
C32	-H32A	:	1.084277	C32	-C33	:	1.393225
C33	-H33A	:	1.084299	C33	-C34	:	1.393704
C34	-H34A	:	1.084528	C34	-C35	:	1.392935
C35	-H35A	:	1.083768	C36	-C37	:	1.400255
C36	-C41	:	1.400515	C37	-H37A	:	1.083482
C37	-C38	:	1.393550	C38	-H38A	:	1.084576
C38	-C39	:	1.394114	C39	-H39A	:	1.084234
C39	-C40	:	1.392436	C40	-H40A	:	1.083858
C40	-C41	:	1.393110	C41	-H41A	:	1.083250
C42	-C43	:	1.402528	C42	-C47	:	1.408181
C43	-H43A	:	1.082360	C43	-C44	:	1.396011
C44	-H44A	:	1.085231	C44	-C45	:	1.391994
C45	-H45A	:	1.084557	C45	-C46	:	1.397241
C46	-H46A	:	1.085341	C46	-C47	:	1.390542
C47	-H47A	:	1.084716	C48	-C49	:	1.407580
C48	-C53	:	1.407147	C49	-H49A	:	1.083927
C49	-C50	:	1.392442	C50	-H50A	:	1.085710
C50	-C51	:	1.396220	C51	-H51A	:	1.084456
C51	-C52	:	1.394696	C52	-H52A	:	1.085386
C52	-C53	:	1.393519	C53	-H53A	:	1.085380

bond angles:

P2	-Cu1	-P1	:	91.118444	P3	-Cu1	-P1	:	89.683268
P3	-Cu1	-P2	:	91.439115	P4	-Cu1	-P1	:	132.895899

P4	-Cu1	-P2	: 125.351888	P4	-Cu1	-P3	: 114.857339
C3	-P1	-Cu1	: 107.077081	C6	-P1	-Cu1	: 129.382804
C6	-P1	-C3	: 101.681868	C12	-P1	-Cu1	: 111.317486
C12	-P1	-C3	: 103.996393	C12	-P1	-C6	: 100.627066
C4	-P2	-Cu1	: 108.162407	C18	-P2	-Cu1	: 124.824510
C18	-P2	-C4	: 102.622640	C24	-P2	-Cu1	: 114.364161
C24	-P2	-C4	: 103.627098	C24	-P2	-C18	: 100.873064
C5	-P3	-Cu1	: 107.273692	C30	-P3	-Cu1	: 122.608590
C30	-P3	-C5	: 103.436458	C36	-P3	-Cu1	: 117.049429
C36	-P3	-C5	: 105.377650	C36	-P3	-C30	: 99.239929
C42	-P4	-Cu1	: 111.109565	C48	-P4	-Cu1	: 109.427686
C48	-P4	-C42	: 101.626094	H1B	-C1	-H1A	: 108.000039
H1C	-C1	-H1A	: 107.929770	H1C	-C1	-H1B	: 108.025283
C2	-C1	-H1A	: 110.958487	C2	-C1	-H1B	: 110.819713
C2	-C1	-H1C	: 110.980006	C3	-C2	-C1	: 105.728865
C4	-C2	-C1	: 105.695197	C4	-C2	-C3	: 112.385639
C5	-C2	-C1	: 105.760969	C5	-C2	-C3	: 113.478997
C5	-C2	-C4	: 112.955477	C2	-C3	-P1	: 119.217935
H3A	-C3	-P1	: 107.620213	H3A	-C3	-C2	: 108.362673
H3B	-C3	-P1	: 106.716448	H3B	-C3	-C2	: 108.168728
H3B	-C3	-H3A	: 106.026659	C2	-C4	-P2	: 118.632464
H4A	-C4	-P2	: 108.513633	H4A	-C4	-C2	: 108.339788
H4B	-C4	-P2	: 106.242277	H4B	-C4	-C2	: 107.773004
H4B	-C4	-H4A	: 106.751579	C2	-C5	-P3	: 118.352880
H5A	-C5	-P3	: 109.750679	H5A	-C5	-C2	: 108.175214
H5B	-C5	-P3	: 105.665030	H5B	-C5	-C2	: 108.095364
H5B	-C5	-H5A	: 106.131799	C7	-C6	-P1	: 122.164516
C11	-C6	-P1	: 119.396206	C11	-C6	-C7	: 118.235659
H7A	-C7	-C6	: 120.983329	C8	-C7	-C6	: 120.770992
C8	-C7	-H7A	: 118.239348	H8A	-C8	-C7	: 119.290986
C9	-C8	-C7	: 120.430946	C9	-C8	-H8A	: 120.275968
H9A	-C9	-C8	: 120.333605	C10	-C9	-C8	: 119.337562
C10	-C9	-H9A	: 120.327887	H10A	-C10	-C9	: 120.194442
C11	-C10	-C9	: 120.344845	C11	-C10	-H10A	: 119.460709
C10	-C11	-C6	: 120.863655	H11A	-C11	-C6	: 120.063541
H11A	-C11	-C10	: 119.072628	C13	-C12	-P1	: 123.081386
C17	-C12	-P1	: 117.896071	C17	-C12	-C13	: 118.956780
H13A	-C13	-C12	: 120.400879	C14	-C13	-C12	: 120.502842
C14	-C13	-H13A	: 119.081318	H14A	-C14	-C13	: 119.816998
C15	-C14	-C13	: 120.073253	C15	-C14	-H14A	: 120.106980
H15A	-C15	-C14	: 119.981395	C16	-C15	-C14	: 119.861425
C16	-C15	-H15A	: 120.157074	H16A	-C16	-C15	: 120.378223
C17	-C16	-C15	: 120.071969	C17	-C16	-H16A	: 119.546842
C16	-C17	-C12	: 120.530032	H17A	-C17	-C12	: 119.429369
H17A	-C17	-C16	: 120.040586	C19	-C18	-P2	: 124.113457
C23	-C18	-P2	: 117.004189	C23	-C18	-C19	: 118.857613
H19A	-C19	-C18	: 120.847767	C20	-C19	-C18	: 120.525883
C20	-C19	-H19A	: 118.626049	H20A	-C20	-C19	: 119.654607
C21	-C20	-C19	: 120.193579	C21	-C20	-H20A	: 120.151681
H21A	-C21	-C20	: 120.103935	C22	-C21	-C20	: 119.662921
C22	-C21	-H21A	: 120.232875	H22A	-C22	-C21	: 120.566799
C23	-C22	-C21	: 120.237377	C23	-C22	-H22A	: 119.193670
C22	-C23	-C18	: 120.518797	H23A	-C23	-C18	: 120.235678
H23A	-C23	-C22	: 119.244549	C25	-C24	-P2	: 118.291161
C29	-C24	-P2	: 122.796635	C29	-C24	-C25	: 118.867685
H25A	-C25	-C24	: 119.601645	C26	-C25	-C24	: 120.546887
C26	-C25	-H25A	: 119.850989	H26A	-C26	-C25	: 119.540180
C27	-C26	-C25	: 120.148772	C27	-C26	-H26A	: 120.307802
H27A	-C27	-C26	: 120.204532	C28	-C27	-C26	: 119.763483
C28	-C27	-H27A	: 120.031788	H28A	-C28	-C27	: 120.120219
C29	-C28	-C27	: 120.081271	C29	-C28	-H28A	: 119.796967

C28	-C29	-C24	: 120.585205	H29A	-C29	-C24	: 120.502628
H29A	-C29	-C28	: 118.902532	C31	-C30	-P3	: 117.009912
C35	-C30	-P3	: 123.870090	C35	-C30	-C31	: 119.070546
H31A	-C31	-C30	: 120.030720	C32	-C31	-C30	: 120.310582
C32	-C31	-H31A	: 119.652146	H32A	-C32	-C31	: 119.516185
C33	-C32	-C31	: 120.269862	C33	-C32	-H32A	: 120.212428
H33A	-C33	-C32	: 120.208090	C34	-C33	-C32	: 119.716969
C34	-C33	-H33A	: 120.074906	H34A	-C34	-C33	: 120.114741
C35	-C34	-C33	: 120.155083	C35	-C34	-H34A	: 119.729346
C34	-C35	-C30	: 120.472696	H35A	-C35	-C30	: 120.672036
H35A	-C35	-C34	: 118.855149	C37	-C36	-P3	: 124.537724
C41	-C36	-P3	: 116.718881	C41	-C36	-C37	: 118.617126
H37A	-C37	-C36	: 120.838741	C38	-C37	-C36	: 120.668053
C38	-C37	-H37A	: 118.489341	H38A	-C38	-C37	: 119.681834
C39	-C38	-C37	: 120.184048	C39	-C38	-H38A	: 120.130878
H39A	-C39	-C38	: 120.117559	C40	-C39	-C38	: 119.618175
C40	-C39	-H39A	: 120.264265	H40A	-C40	-C39	: 120.365065
C41	-C40	-C39	: 120.190693	C41	-C40	-H40A	: 119.440583
C40	-C41	-C36	: 120.716369	H41A	-C41	-C36	: 119.983477
H41A	-C41	-C40	: 119.299046	C43	-C42	-P4	: 122.693379
C47	-C42	-P4	: 119.894954	C47	-C42	-C43	: 117.158581
H43A	-C43	-C42	: 119.125080	C44	-C43	-C42	: 121.621307
C44	-C43	-H43A	: 119.245505	H44A	-C44	-C43	: 119.431686
C45	-C44	-C43	: 120.256792	C45	-C44	-H44A	: 120.301356
H45A	-C45	-C44	: 120.532166	C46	-C45	-C44	: 119.082751
C46	-C45	-H45A	: 120.384901	H46A	-C46	-C45	: 119.950275
C47	-C46	-C45	: 120.418516	C47	-C46	-H46A	: 119.626625
C46	-C47	-C42	: 121.450733	H47A	-C47	-C42	: 119.151173
H47A	-C47	-C46	: 119.397614	C49	-C48	-P4	: 124.311838
C53	-C48	-P4	: 118.600117	C53	-C48	-C49	: 117.087493
H49A	-C49	-C48	: 119.317489	C50	-C49	-C48	: 121.382252
C50	-C49	-H49A	: 119.299289	H50A	-C50	-C49	: 119.480678
C51	-C50	-C49	: 120.614394	C51	-C50	-H50A	: 119.904773
H51A	-C51	-C50	: 120.528051	C52	-C51	-C50	: 118.915747
C52	-C51	-H51A	: 120.550712	H52A	-C52	-C51	: 120.044880
C53	-C52	-C51	: 120.358195	C53	-C52	-H52A	: 119.587038
C52	-C53	-C48	: 121.632922	H53A	-C53	-C48	: 119.021125
H53A	-C53	-C52	: 119.336957				

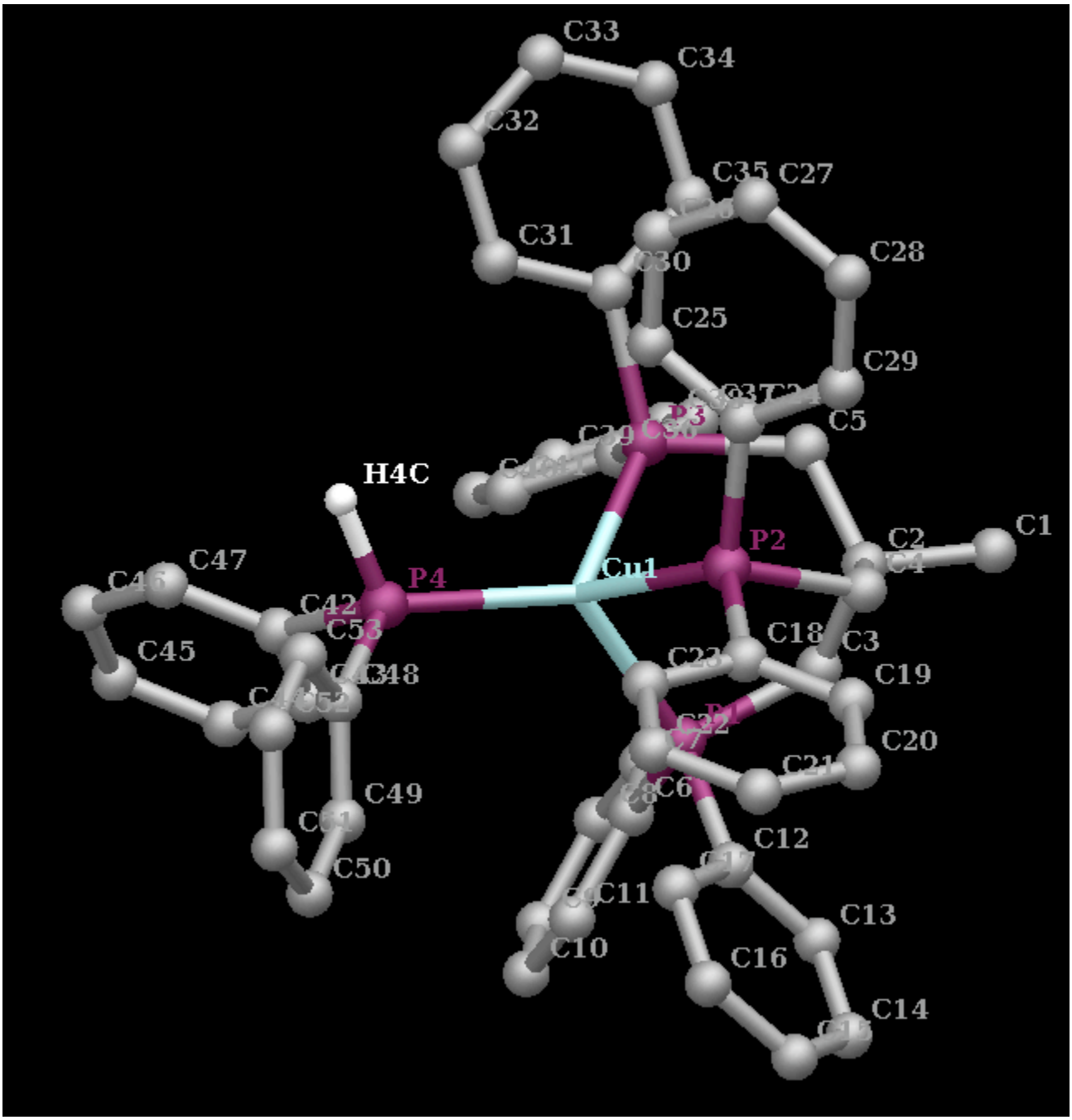

Figure S4. Atom labeling for $[Cu(triphosPh_6)(PHPh_2)]^+$ cation. All H atoms except for the P-H are omitted for clarity.

```
+-------------------------------------------------------------------+
|  Jaguar version 7.6, release 211                                  |
|                                                                   |
|  Copyright (c) 2009 Schrodinger,  LLC.                            |
|  All Rights Reserved.                                             |
|                                                                   |
|  Use of this program should be acknowledged in publications as:   |
|  Jaguar, version 7.6, Schrodinger, LLC, New York, NY, 2009.       |
+-------------------------------------------------------------------+
```

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  basis set:              lacv3p**++
  net molecular charge:    1
  multiplicity:            1

  This run will use ECP on 1 atom
  number of basis functions....         1672
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Final geometry:

atom	x	y	z
		angstroms	
Cu1	2.2263350000	2.2420460000	5.9445480000
P1	2.4110100000	0.9831140000	3.9201390000
P2	3.9374090000	1.0044230000	7.0675500000
P3	3.7026380000	3.9700640000	5.2022780000
P4	0.2111760000	2.7923550000	6.9762700000
C1	6.6333260000	1.2567790000	3.8197330000
H1A	6.7406840000	0.1890740000	3.6096140000
H1B	7.4554320000	1.5558660000	4.4760460000
H1C	6.7404750000	1.7975360000	2.8750410000
C2	5.2631160000	1.5573520000	4.4788170000
C3	4.1922390000	1.2390930000	3.3899020000
H3A	4.5002290000	0.3394940000	2.8520420000
H3B	4.1980120000	2.0481010000	2.6570950000
C4	5.1694580000	0.6057920000	5.7126370000
H4A	6.1592200000	0.5378950000	6.1703760000
H4B	4.9207510000	-0.3949080000	5.3507320000
C5	5.3083650000	3.0668320000	4.8812240000
H5A	5.8709930000	3.6082080000	4.1182440000
H5B	5.8862850000	3.1561200000	5.8047080000
C6	1.4363640000	1.3009890000	2.3774550000
C7	1.7785460000	2.2966650000	1.4544590000
H7A	2.6667430000	2.9000060000	1.5855350000
C8	0.9723280000	2.5410630000	0.3438750000
H8A	1.2627020000	3.3090870000	-0.3632400000
C9	-0.1945390000	1.8093690000	0.1442380000
H9A	-0.8170560000	1.9990040000	-0.7223420000
C10	-0.5532060000	0.8265000000	1.0650010000
H10A	-1.4573590000	0.2466540000	0.9188410000
C11	0.2539190000	0.5733930000	2.1701530000
H11A	-0.0316370000	-0.2096640000	2.8623730000
C12	2.2463610000	-0.8485700000	4.0837250000
C13	2.6898660000	-1.7243390000	3.0814540000
H13A	3.1550210000	-1.3387780000	2.1810440000
C14	2.5117430000	-3.0968200000	3.2161030000
H14A	2.8554900000	-3.7637000000	2.4338450000
C15	1.8810420000	-3.6136770000	4.3492240000
H15A	1.7415880000	-4.6837520000	4.4503020000
C16	1.4298400000	-2.7530660000	5.3442160000
H16A	0.9447650000	-3.1464320000	6.2292850000
C17	1.6112110000	-1.3763710000	5.2109480000
H17A	1.2600370000	-0.7134930000	5.9914680000
C18	3.6580290000	-0.6206760000	7.8999240000
C19	4.5203110000	-1.7165470000	7.7808350000
H19A	5.3965240000	-1.6693070000	7.1461350000
C20	4.2633510000	-2.8961080000	8.4770000000
H20A	4.9383450000	-3.7377300000	8.3724240000
C21	3.1478290000	-2.9940720000	9.3048940000
H21A	2.9517840000	-3.9118250000	9.8470220000
C22	2.2848500000	-1.9072960000	9.4314890000
H22A	1.4119250000	-1.9745400000	10.0703600000

C23	2.5361700000	-0.7309910000	8.7310120000
H23A	1.8472960000	0.1002060000	8.8284420000
C24	4.9315400000	1.9072350000	8.3390650000
C25	4.4235590000	3.0934560000	8.8747270000
H25A	3.4822490000	3.4855000000	8.5109640000
C26	5.1223430000	3.7837290000	9.8643510000
H26A	4.7191160000	4.7081320000	10.2602880000
C27	6.3356860000	3.2896950000	10.3317190000
H27A	6.8811020000	3.8233210000	11.1013170000
C28	6.8480580000	2.1007330000	9.8104690000
H28A	7.7878400000	1.7063040000	10.1793930000
C29	6.1499190000	1.4118960000	8.8243820000
H29A	6.5526720000	0.4767200000	8.4522410000
C30	4.2042940000	5.4033740000	6.2571540000
C31	3.2094270000	6.0314800000	7.0157210000
H31A	2.1961830000	5.6457350000	7.0038740000
C32	3.5055800000	7.1534000000	7.7854450000
H32A	2.7238500000	7.6327250000	8.3635690000
C33	4.8044450000	7.6569370000	7.8131450000
H33A	5.0380110000	8.5278170000	8.4143070000
C34	5.8011190000	7.0386970000	7.0617440000
H34A	6.8125410000	7.4280800000	7.0759990000
C35	5.5029980000	5.9228400000	6.2829240000
H35A	6.2933360000	5.4689420000	5.6978540000
C36	3.2839990000	4.8527700000	3.6287970000
C37	4.2332220000	5.2565810000	2.6819540000
H37A	5.2810190000	5.0098060000	2.8022630000
C38	3.8503170000	6.0022440000	1.5689910000
H38A	4.5969790000	6.3063680000	0.8444140000
C39	2.5172140000	6.3709260000	1.3962820000
H39A	2.2237440000	6.9602230000	0.5353340000
C40	1.5669460000	5.9809790000	2.3362990000
H40A	0.5275350000	6.2606270000	2.2103990000
C41	1.9465670000	5.2206530000	3.4396200000
H41A	1.1931150000	4.9113540000	4.1536300000
C42	-1.0673030000	3.6926410000	6.0097760000
C43	-1.1898970000	3.4500220000	4.6372780000
H43A	-0.5107600000	2.7674760000	4.1397720000
C44	-2.1845460000	4.0876320000	3.8970050000
H44A	-2.2758790000	3.8847170000	2.8363330000
C45	-3.0506510000	4.9838300000	4.5178130000
H45A	-3.8205770000	5.4837170000	3.9417050000
C46	-2.9270170000	5.2387140000	5.8835580000
H46A	-3.5989730000	5.9365780000	6.3694150000
C47	-1.9458970000	4.5920870000	6.6286390000
H47A	-1.8708690000	4.7851160000	7.6929290000
C48	-0.7332030000	1.4892960000	7.8710940000
C49	-1.3753750000	0.4755540000	7.1497430000
H49A	-1.3441030000	0.4717830000	6.0656480000
C50	-2.0781980000	-0.5237420000	7.8162830000
H50A	-2.5831990000	-1.2959390000	7.2476090000
C51	-2.1375440000	-0.5298180000	9.2095200000
H51A	-2.6887500000	-1.3065150000	9.7264290000
C52	-1.4951810000	0.4710730000	9.9337780000
H52A	-1.5450840000	0.4777920000	11.0165340000
C53	-0.7984160000	1.4793350000	9.2689050000
H53A	-0.3155380000	2.2608010000	9.8454260000
H4C	0.3744600000	3.6947650000	8.0533560000

bond lengths (angstroms):

Cu1	-P1	:	2.391076	Cu1	-P2	:	2.391781
Cu1	-P3	:	2.390916	Cu1	-P4	:	2.329840
P1	-C3	:	1.876021	P1	-C6	:	1.852256
P1	-C12	:	1.846330	P2	-C4	:	1.874204
P2	-C18	:	1.847118	P2	-C24	:	1.849356
P3	-C5	:	1.870097	P3	-C30	:	1.849000
P3	-C36	:	1.852099	P4	-C42	:	1.838242
P4	-C48	:	1.841338	P4	-H4C	:	1.414609
C1	-H1A	:	1.093467	C1	-H1B	:	1.093644
C1	-H1C	:	1.093774	C1	-C2	:	1.549907
C2	-C3	:	1.560065	C2	-C4	:	1.560945
C2	-C5	:	1.562853	C3	-H3A	:	1.092442
C3	-H3B	:	1.091574	C4	-H4A	:	1.092595
C4	-H4B	:	1.092809	C5	-H5A	:	1.091685
C5	-H5B	:	1.093063	C6	-C7	:	1.400136
C6	-C11	:	1.403761	C7	-H7A	:	1.081709
C7	-C8	:	1.393956	C8	-H8A	:	1.083600
C8	-C9	:	1.391693	C9	-H9A	:	1.083720
C9	-C10	:	1.393728	C10	-H10A	:	1.084010
C10	-C11	:	1.391717	C11	-H11A	:	1.083462
C12	-C13	:	1.402931	C12	-C17	:	1.397362
C13	-H13A	:	1.084327	C13	-C14	:	1.390526
C14	-H14A	:	1.083890	C14	-C15	:	1.396026
C15	-H15A	:	1.083847	C15	-C16	:	1.390771
C16	-H16A	:	1.083227	C16	-C17	:	1.394971
C17	-H17A	:	1.082563	C18	-C19	:	1.399516
C18	-C23	:	1.400516	C19	-H19A	:	1.082970
C19	-C20	:	1.393570	C20	-H20A	:	1.083919
C20	-C21	:	1.392622	C21	-H21A	:	1.083793
C21	-C22	:	1.393500	C22	-H22A	:	1.083825
C22	-C23	:	1.391949	C23	-H23A	:	1.083941
C24	-C25	:	1.397175	C24	-C29	:	1.401906
C25	-H25A	:	1.082629	C25	-C26	:	1.394321
C26	-H26A	:	1.083457	C26	-C27	:	1.390936
C27	-H27A	:	1.083751	C27	-C28	:	1.395657
C28	-H28A	:	1.083914	C28	-C29	:	1.390777
C29	-H29A	:	1.084091	C30	-C31	:	1.399893
C30	-C35	:	1.398979	C31	-H31A	:	1.084252
C31	-C32	:	1.392439	C32	-H32A	:	1.084012
C32	-C33	:	1.393329	C33	-H33A	:	1.083689
C33	-C34	:	1.392905	C34	-H34A	:	1.083880
C34	-C35	:	1.393045	C35	-H35A	:	1.083035
C36	-C37	:	1.400214	C36	-C41	:	1.399946
C37	-H37A	:	1.083167	C37	-C38	:	1.393311
C38	-H38A	:	1.083978	C38	-C39	:	1.393886
C39	-H39A	:	1.083802	C39	-C40	:	1.392372
C40	-H40A	:	1.083711	C40	-C41	:	1.392668
C41	-H41A	:	1.083128	C42	-C43	:	1.399158
C42	-C47	:	1.401400	C43	-H43A	:	1.083793
C43	-C44	:	1.394230	C44	-H44A	:	1.083763
C44	-C45	:	1.392376	C45	-H45A	:	1.083777
C45	-C46	:	1.394816	C46	-H46A	:	1.083788
C46	-C47	:	1.391355	C47	-H47A	:	1.084252
C48	-C49	:	1.400145	C48	-C53	:	1.399367
C49	-H49A	:	1.084553	C49	-C50	:	1.391700
C50	-H50A	:	1.083838	C50	-C51	:	1.394514
C51	-H51A	:	1.083643	C51	-C52	:	1.392466
C52	-H52A	:	1.083926	C52	-C53	:	1.394321
C53	-H53A	:	1.084544				

bond angles:

P2	-Cu1	-P1	: 94.004088	P3	-Cu1	-P1	: 94.013810
P3	-Cu1	-P2	: 94.474569	P4	-Cu1	-P1	: 124.477884
P4	-Cu1	-P2	: 122.213354	P4	-Cu1	-P3	: 120.055016
C3	-P1	-Cu1	: 103.933054	C6	-P1	-Cu1	: 125.040168
C6	-P1	-C3	: 103.933105	C12	-P1	-Cu1	: 116.131613
C12	-P1	-C3	: 104.186438	C12	-P1	-C6	: 101.368721
C4	-P2	-Cu1	: 103.940097	C18	-P2	-Cu1	: 123.961173
C18	-P2	-C4	: 103.773005	C24	-P2	-Cu1	: 117.050736
C24	-P2	-C4	: 104.329806	C24	-P2	-C18	: 101.593926
C5	-P3	-Cu1	: 103.556088	C30	-P3	-Cu1	: 123.412601
C30	-P3	-C5	: 103.850476	C36	-P3	-Cu1	: 117.946101
C36	-P3	-C5	: 106.165911	C36	-P3	-C30	: 100.169686
C42	-P4	-Cu1	: 118.973588	C48	-P4	-Cu1	: 119.449221
C48	-P4	-C42	: 104.204830	H4C	-P4	-Cu1	: 112.830839
H4C	-P4	-C42	: 99.681813	H4C	-P4	-C48	: 98.083942
H1B	-C1	-H1A	: 107.971721	H1C	-C1	-H1A	: 107.888301
H1C	-C1	-H1B	: 108.027514	C2	-C1	-H1A	: 110.969603
C2	-C1	-H1B	: 110.874939	C2	-C1	-H1C	: 110.977862
C3	-C2	-C1	: 105.692126	C4	-C2	-C1	: 105.720663
C4	-C2	-C3	: 112.716256	C5	-C2	-C1	: 105.735858
C5	-C2	-C3	: 113.367791	C5	-C2	-C4	: 112.768054
C2	-C3	-P1	: 118.835900	H3A	-C3	-P1	: 107.126222
H3A	-C3	-C2	: 108.549418	H3B	-C3	-P1	: 107.211075
H3B	-C3	-C2	: 108.285911	H3B	-C3	-H3A	: 106.158254
C2	-C4	-P2	: 118.764336	H4A	-C4	-P2	: 107.809354
H4A	-C4	-C2	: 108.341346	H4B	-C4	-P2	: 106.533135
H4B	-C4	-C2	: 108.065991	H4B	-C4	-H4A	: 106.738408
C2	-C5	-P3	: 119.067287	H5A	-C5	-P3	: 108.843666
H5A	-C5	-C2	: 108.296816	H5B	-C5	-P3	: 105.633110
H5B	-C5	-C2	: 108.164152	H5B	-C5	-H5A	: 106.109658
C7	-C6	-P1	: 122.852937	C11	-C6	-P1	: 118.507756
C11	-C6	-C7	: 118.496263	H7A	-C7	-C6	: 121.160283
C8	-C7	-C6	: 120.566644	C8	-C7	-H7A	: 118.271492
H8A	-C8	-C7	: 119.287008	C9	-C8	-C7	: 120.466906
C9	-C8	-H8A	: 120.246009	H9A	-C9	-C8	: 120.287221
C10	-C9	-C8	: 119.456987	C10	-C9	-H9A	: 120.255220
H10A	-C10	-C9	: 120.184815	C11	-C10	-C9	: 120.239999
C11	-C10	-H10A	: 119.571740	C10	-C11	-C6	: 120.765013
H11A	-C11	-C6	: 120.149926	H11A	-C11	-C10	: 119.073691
C13	-C12	-P1	: 121.857067	C17	-C12	-P1	: 119.125364
C17	-C12	-C13	: 118.960620	H13A	-C13	-C12	: 120.456542
C14	-C13	-C12	: 120.428828	C14	-C13	-H13A	: 119.099144
H14A	-C14	-C13	: 119.786531	C15	-C14	-C13	: 120.125750
C15	-C14	-H14A	: 120.085009	H15A	-C15	-C14	: 119.957325
C16	-C15	-C14	: 119.878460	C16	-C15	-H15A	: 120.163981
H16A	-C16	-C15	: 120.339067	C17	-C16	-C15	: 120.010933
C17	-C16	-H16A	: 119.647701	C16	-C17	-C12	: 120.592392
H17A	-C17	-C12	: 119.852920	H17A	-C17	-C16	: 119.554039
C19	-C18	-P2	: 123.874811	C23	-C18	-P2	: 117.249785
C23	-C18	-C19	: 118.839457	H19A	-C19	-C18	: 120.944887
C20	-C19	-C18	: 120.442215	C20	-C19	-H19A	: 118.612562
H20A	-C20	-C19	: 119.616929	C21	-C20	-C19	: 120.279657
C21	-C20	-H20A	: 120.103284	H21A	-C21	-C20	: 120.121369
C22	-C21	-C20	: 119.683638	C22	-C21	-H21A	: 120.194958
H22A	-C22	-C21	: 120.261425	C23	-C22	-C21	: 120.101654
C23	-C22	-H22A	: 119.635924	C22	-C23	-C18	: 120.651862
H23A	-C23	-C18	: 120.133474	H23A	-C23	-C22	: 119.212508
C25	-C24	-P2	: 118.856859	C29	-C24	-P2	: 122.188794

```
 C29     -C24     -C25     : 118.897317  H25A    -C25     -C24     : 119.653010
 C26     -C25     -C24     : 120.678009  C26     -C25     -H25A    : 119.666459
 H26A    -C26     -C25     : 119.685489  C27     -C26     -C25     : 119.988368
 C27     -C26     -H26A    : 120.324569  H27A    -C27     -C26     : 120.180919
 C28     -C27     -C26     : 119.823633  C28     -C27     -H27A    : 119.995011
 H28A    -C28     -C27     : 120.078387  C29     -C28     -C27     : 120.162652
 C29     -C28     -H28A    : 119.756758  C28     -C29     -C24     : 120.445013
 H29A    -C29     -C24     : 120.586453  H29A    -C29     -C28     : 118.956909
 C31     -C30     -P3      : 117.654646  C35     -C30     -P3      : 123.381644
 C35     -C30     -C31     : 118.891295  H31A    -C31     -C30     : 119.906276
 C32     -C31     -C30     : 120.657454  C32     -C31     -H31A    : 119.435934
 H32A    -C32     -C31     : 119.848391  C33     -C32     -C31     : 120.028964
 C33     -C32     -H32A    : 120.122593  H33A    -C33     -C32     : 120.156793
 C34     -C33     -C32     : 119.728914  C34     -C33     -H33A    : 120.114025
 H34A    -C34     -C33     : 120.076438  C35     -C34     -C33     : 120.264767
 C35     -C34     -H34A    : 119.657806  C34     -C35     -C30     : 120.424279
 H35A    -C35     -C30     : 120.788350  H35A    -C35     -C34     : 118.787159
 C37     -C36     -P3      : 123.966149  C41     -C36     -P3      : 117.128432
 C41     -C36     -C37     : 118.716634  H37A    -C37     -C36     : 120.995077
 C38     -C37     -C36     : 120.543369  C38     -C37     -H37A    : 118.456574
 H38A    -C38     -C37     : 119.656361  C39     -C38     -C37     : 120.222511
 C39     -C38     -H38A    : 120.115696  H39A    -C39     -C38     : 120.080353
 C40     -C39     -C38     : 119.669387  C40     -C39     -H39A    : 120.250095
 H40A    -C40     -C39     : 120.257210  C41     -C40     -C39     : 120.113661
 C41     -C40     -H40A    : 119.627616  C40     -C41     -C36     : 120.726169
 H41A    -C41     -C36     : 120.029244  H41A    -C41     -C40     : 119.244310
 C43     -C42     -P4      : 119.456731  C47     -C42     -P4      : 121.210386
 C47     -C42     -C43     : 119.311025  H43A    -C43     -C42     : 120.304441
 C44     -C43     -C42     : 120.267974  C44     -C43     -H43A    : 119.427296
 H44A    -C44     -C43     : 119.612965  C45     -C44     -C43     : 120.091431
 C45     -C44     -H44A    : 120.295028  H45A    -C45     -C44     : 120.117090
 C46     -C45     -C44     : 119.937268  C46     -C45     -H45A    : 119.945641
 H46A    -C46     -C45     : 120.110019  C47     -C46     -C45     : 120.127368
 C47     -C46     -H46A    : 119.761503  C46     -C47     -C42     : 120.257758
 H47A    -C47     -C42     : 120.288413  H47A    -C47     -C46     : 119.452702
 C49     -C48     -P4      : 119.817140  C53     -C48     -P4      : 120.954827
 C53     -C48     -C49     : 119.215589  H49A    -C49     -C48     : 120.283103
 C50     -C49     -C48     : 120.314964  C50     -C49     -H49A    : 119.393329
 H50A    -C50     -C49     : 119.708631  C51     -C50     -C49     : 120.206715
 C51     -C50     -H50A    : 120.084199  H51A    -C51     -C50     : 120.088945
 C52     -C51     -C50     : 119.794195  C52     -C51     -H51A    : 120.114940
 H52A    -C52     -C51     : 120.184204  C53     -C52     -C51     : 120.150885
 C53     -C52     -H52A    : 119.660056  C52     -C53     -C48     : 120.314663
 H53A    -C53     -C48     : 120.338662  H53A    -C53     -C52     : 119.344163
```

Cu(triphos)_PH_2 [Here and elsewhere in this section, triphos is $MeC(CH_2PH_2)_3$, while triphosPh_6 is $MeC(CH_2PPh_2)_3$]

```
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  +-------------------------------------------------------------------+
  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1
```

```
  This run will use ECP on 1 atom
  number of basis functions....          349
final geometry:
                                  angstroms
  atom              x                  y                  z
  Cu1          2.0917410000       2.3877870000       6.0200780000
  P1           2.3574080000       1.2289350000       3.8781920000
  P2           3.8386810000       0.9438760000       6.8847690000
  P3           3.8253300000       3.9038440000       5.2650760000
  P4           0.1326480000       2.9345310000       7.1200850000
  H6           6.1767310000       1.2293050000       3.8777000000
  C2           5.2295210000       1.4915650000       4.3653560000
  C3           4.1522060000       1.2088820000       3.2869270000
  H3A          4.3646040000       0.2495770000       2.8091010000
  H3B          4.2325770000       1.9686920000       2.5034440000
  C4           5.1584510000       0.5470420000       5.5930980000
  H4A          6.1357910000       0.5163880000       6.0803420000
  H4B          4.9573590000      -0.4694990000       5.2414650000
  C5           5.3891710000       2.9911300000       4.7268240000
  H5A          5.8355570000       3.5190330000       3.8808560000
  H5B          6.1003350000       3.0779340000       5.5541590000
  H17          1.7225730000       1.3930970000       2.6190270000
  H18          2.1191820000      -0.1653790000       3.9757360000
  H19          3.7790380000      -0.3229930000       7.5216620000
  H20          4.6438660000       1.5631860000       7.8736070000
  H21          4.4416960000       5.0222020000       5.8851290000
  H22          3.5052360000       4.5693890000       4.0548590000
  H23         -0.5116250000       3.6016950000       6.0311830000
  H24         -0.5609770000       1.7073120000       6.8762650000
```

Li(triphos)_PH_2

```
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  +-------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1
  number of basis functions....          335

 final geometry:
                                  angstroms
  atom              x                  y                  z
  Li1          1.8691871534       2.4175288659       6.0972317645
  P1           2.4173364553       1.2107784388       3.7841943186
  P2           3.9136884424       0.8755743683       6.8651070493
  P3           3.9105514393       3.9254947887       5.2579313214
  P4          -0.1417439094       2.9849195581       7.2700906061
  H6           6.2421163207       1.2371194280       3.8516005461
  C2           5.2922127879       1.4924073093       4.3383711778
  C3           4.2278569418       1.2393045328       3.2427253335
  H3A          4.4556588617       0.3010339827       2.7322942652
```

H3B	4.3070018820	2.0279273617	2.4880716556
C4	5.2129736426	0.5196529504	5.5406269538
H4A	6.1925210446	0.4637438559	6.0202409610
H4B	4.9959937912	-0.4850867255	5.1649985557
C5	5.4602727151	2.9804691092	4.7325596851
H5A	5.9309775793	3.5180071105	3.9066183079
H5B	6.1541879502	3.0437450305	5.5764820914
H17	1.8333743714	1.2406892221	2.4918372424
H18	2.2541775011	-0.1864169575	3.9699750349
H19	4.0220847794	-0.3516313546	7.5684205352
H20	4.7089099405	1.6188319236	7.7751901521
H21	4.5596954400	5.0867854228	5.7506923854
H22	3.5545001694	4.4948429808	4.0079397655
H23	-0.7038062767	3.7787373839	6.2187807584
H24	-0.8723541241	1.8154629924	6.8827937828

Na(triphos)_PH_2

```
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  +--------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

final geometry:
                                angstroms
  atom              x                y                z
  Na1           1.5065030783     2.4208227692     6.3275392597
  P1            2.5438770489     1.1416248461     3.6773853063
  P2            4.1175976638     0.7397314418     6.8135515978
  P3            4.0615229308     3.9118849687     5.2666626945
  P4           -0.8018805124     3.1531431024     7.5354129475
  H6            6.3713491562     1.2546308533     3.7567563636
  C2            5.4242841258     1.4856492885     4.2616265647
  C3            4.3600966176     1.2400439664     3.1655488237
  H3A           4.6122969652     0.3231845776     2.6284248766
  H3B           4.4184894723     2.0517030472     2.4336076679
  C4            5.3862653378     0.4800434963     5.4371119946
  H4A           6.3772879474     0.4353459587     5.8939241657
  H4B           5.1868897153    -0.5187527248     5.0362483198
  C5            5.5888694630     2.9654011733     4.6822636037
  H5A           6.0375200470     3.5191649131     3.8546658572
  H5B           6.3035071622     3.0158823875     5.5097977687
  H17           2.0088372036     1.0291030438     2.3666474413
  H18           2.4703384340    -0.2499760649     3.9525703404
  H19           4.4256953989    -0.4410162935     7.5407423985
  H20           4.8779755577     1.5951916373     7.6544579812
  H21           4.7377510085     5.1115440426     5.6146661692
  H22           3.6092644496     4.3939179760     4.0096210080
  H23          -1.1097129304     4.1140106509     6.5172452527
  H24          -1.5626962960     2.1262425398     6.8869111719
```

K(triphos)_PH_2

```
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  +-------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  This run will use ECP on 1 atom
  number of basis functions....          329
final geometry:
                                 angstroms
  atom              x                 y                 z
  K1           1.1798267407      2.4847308184      6.3270314823
  P1           2.9192570117      1.1054359211      3.4398589517
  P2           4.3400561379      0.7369910916      6.6905480669
  P3           4.2877951272      3.9388107105      5.1192872961
  P4          -1.4914869505      3.1002331554      7.9762955368
  H6           6.7359356313      1.3220414039      3.7537510097
  C2           5.7565362941      1.5277221771      4.2057576422
  C3           4.7650407857      1.2394670377      3.0542726805
  H3A          5.0705716089      0.3192454041      2.5517673356
  H3B          4.8513333718      2.0392267196      2.3118482141
  C4           5.6910347066      0.5294748150      5.3852306260
  H4A          6.6560884799      0.5285557330      5.8964460704
  H4B          5.5553751111     -0.4789140730      4.9814124433
  C5           5.8588047234      3.0149247008      4.6180338970
  H5A          6.3323428798      3.5712430857      3.8062325487
  H5B          6.5314154468      3.0925890399      5.4781514775
  H17          2.5069093584      0.8731029340      2.0992891955
  H18          2.8778280524     -0.2680561049      3.8026398362
  H19          4.7161788904     -0.3893140629      7.4719471957
  H20          4.9986458979      1.6747739269      7.5309457060
  H21          4.9288565733      5.1753858506      5.4031556313
  H22          3.8549069319      4.3379118304      3.8257633468
  H23         -1.4998694529      4.4926255072      7.6324044136
  H24         -2.3756703961      2.7655429796      6.8983816244
```

Cu_PPh_2

```
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  +-------------------------------------------------------------------+
  basis set:             lacv3p**++
  net molecular charge:    0
```

```
  multiplicity:            1
This run will use ECP on 1 atom
  number of basis functions....          400

final geometry:
                                  angstroms
  atom              x                  y                  z
  P1          -0.7692056205      3.3655954118      7.9107284178
  C2          -0.1997898860      3.9012339353      6.2239098491
  C3          -0.6948823266      3.3861471824      5.0150044519
  H4          -1.4585174502      2.6168828705      5.0376501461
  C5          -0.2234993681      3.8474634321      3.7894916496
  H6          -0.6265114748      3.4389678056      2.8692151025
  C7           0.7588509558      4.8348359384      3.7438534318
  H8           1.1247708624      5.1947828249      2.7886110573
  C9           1.2656229819      5.3563148002      4.9321902160
  H10          2.0339764025      6.1212098823      4.9065502947
  C11          0.7858863226      4.8971183240      6.1605284610
  H12          1.1840491172      5.3120088571      7.0804298931
  C13         -0.1823548653      1.6102328944      8.0029733240
  C14         -0.5132426367      0.8779963878      9.1572088776
  H15         -1.1485182831      1.3290286018      9.9136467689
  C16         -0.0409751116     -0.4142791749      9.3476132095
  H17         -0.3130429752     -0.9592735028     10.2451161201
  C18          0.7833729331     -1.0088094125      8.3901831419
  H19          1.1501737020     -2.0187297503      8.5346678368
  C20          1.1449455927     -0.2861660256      7.2572372432
  H21          1.7959994787     -0.7323975991      6.5131252455
  C22          0.6663090489      1.0098416957      7.0625788722
  H23          0.9572069143      1.5523407145      6.1717296160
  Cu24        -2.9805932506      3.0824980477      7.5906658170
```

Li_PPh_2

```
  +---------------------------------------------------------------------+
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  +---------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          386

final geometry:
                                  angstroms
  atom              x                  y                  z
  P4           0.5917272581      2.0292937270      6.2505304870
  C42         -0.5633380344      3.3052786134      5.5962422991
  C43         -0.0733287378      4.1211339126      4.5381238182
  H43A         0.8866027698      3.8751903339      4.0949517821
  C44         -0.7810003048      5.2090066418      4.0630516319
  H44A        -0.3675126608      5.7961678378      3.2494424993
  C45         -2.0259456325      5.5603482087      4.6114250089
  H45A        -2.5769904986      6.4111677379      4.2292244481
```

C46	-2.5427823980	4.7801897160	5.6334313632
H46A	-3.5163911495	5.0095395476	6.0550857165
C47	-1.8336038623	3.6710951429	6.1205276456
H47A	-2.3255074618	3.0359235348	6.8533235271
C48	-0.5006289895	1.2079636462	7.5241425569
C49	-1.7040885903	0.5440519929	7.2009591573
H49A	-2.0417790298	0.5405938934	6.1704859681
C50	-2.4499146813	-0.1187238590	8.1679795092
H50A	-3.3680727992	-0.6226455558	7.8847125925
C51	-2.0183398390	-0.1551786506	9.4979323835
H51A	-2.6009422792	-0.6778347377	10.2478806247
C52	-0.8304072645	0.4779101195	9.8448802453
H52A	-0.4746778267	0.4478173998	10.8692826817
C53	-0.0868931824	1.1534906251	8.8713586514
H53A	0.8604042874	1.6113252505	9.1503275687
Li24	-0.2749663166	3.5533432020	7.7718092555

Na_PPh$_2$

```
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  +---------------------------------------------------------------------+
  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          394

final geometry:
                                 angstroms
  atom              x                 y                 z
  P1           0.5361960144      2.2123740540      6.5697858340
  C2          -0.6423671137      3.3418999833      5.6861920657
  C3          -0.1629896410      3.9787904741      4.5165595777
  H4           0.8082391555      3.6899251238      4.1263615112
  C5          -0.9008366267      4.9540000121      3.8544619361
  H6          -0.4928309121      5.4145591483      2.9603731799
  C7          -2.1651128844      5.3297207589      4.3154380186
  H8          -2.7438196796      6.0822616562      3.7928945165
  C9          -2.6765111268      4.6983861099      5.4497392617
  H10         -3.6655992361      4.9580550372      5.8145011766
  C11         -1.9341795891      3.7278398111      6.1222789781
  H12         -2.3731190960      3.2433812981      6.9895426616
  C13         -0.5683782452      1.2122485036      7.6688730714
  C14         -1.7868433792      0.6471675178      7.2435668901
  H15         -2.1550934109      0.8627458375      6.2468542292
  C16         -2.5222143940     -0.1993176506      8.0684478754
  H17         -3.4588667107     -0.6136230271      7.7091962624
  C18         -2.0554654946     -0.5349208638      9.3401907024
  H19         -2.6265908243     -1.1994537877      9.9785221055
  C20         -0.8384348378     -0.0098582421      9.7722021285
  H21         -0.4531397999     -0.2678628825     10.7534790625
  C22         -0.1137687787      0.8531840048      8.9529082748
  H23          0.8332191001      1.2501844316      9.3081960291
  Na24         0.2303976892      4.4950161888      7.9281996076
```

K_PPh_2

```
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  +-------------------------------------------------------------------+
  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  This run will use ECP on 1 atom
  number of basis functions....          380

final geometry:
                                 angstroms
  atom               x                 y                 z
  P1            0.5297940709      2.1380783061      6.3527774393
  C2           -0.6178996969      3.3352095040      5.5654632785
  C3           -0.0392731352      4.1553675780      4.5584503750
  H4            0.9865168561      3.9602191816      4.2594762157
  C5           -0.7319403490      5.1927313335      3.9553984254
  H6           -0.2387936244      5.7863561193      3.1919370597
  C7           -2.0578732551      5.4777207315      4.3109691577
  H8           -2.6013644732      6.2836184862      3.8321745281
  C9           -2.6658011317      4.6769749347      5.2737701651
  H10          -3.7027233636      4.8519420153      5.5470599372
  C11          -1.9703291200      3.6290276747      5.8838164448
  H12          -2.5071986897      3.0108862789      6.5957763301
  C13          -0.5277923418      1.2171561310      7.5550875614
  C14          -1.8177857655      0.6998480406      7.2938738132
  H15          -2.2630642709      0.8550811994      6.3183149456
  C16          -2.5169778539     -0.0429672451      8.2412244877
  H17          -3.5048313131     -0.4212409540      7.9969824262
  C18          -1.9519875014     -0.3305536646      9.4858050689
  H19          -2.4968204061     -0.9156795858     10.2177318516
  C20          -0.6637076000      0.1306565415      9.7589129674
  H21          -0.1925154139     -0.1041874686     10.7083990961
  C22           0.0261477738      0.8930704424      8.8176955230
  H23           1.0362534480      1.2280951472      9.0436454384
  K24          -0.4753287754      4.2171423361      8.5212398115
```

PPh_2 anion

```
  +-------------------------------------------------------------------+
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  +-------------------------------------------------------------------+
  basis set:             lacv3p**++
  net molecular charge:   -1
  multiplicity:            1
```

```
  number of basis functions....          364

final geometry:
                                  angstroms
  atom              x                  y                  z
  P4            0.5466652735      2.4512783822      6.7121442609
  C42          -0.5820942913      3.4827585982      5.7180612284
  C43          -0.0480558679      4.0770261029      4.5440892473
  H43A          0.9630608625      3.8117731846      4.2471124687
  C44          -0.7710839846      4.9722714855      3.7665176993
  H44A         -0.3122629348      5.3967217891      2.8767450691
  C45          -2.0845482954      5.3181775771      4.1052948798
  H45A         -2.6567234525      6.0074325372      3.4927715337
  C46          -2.6377613709      4.7486583725      5.2563666650
  H46A         -3.6511557297      5.0091983183      5.5531803234
  C47          -1.9085198430      3.8642204886      6.0443020428
  H47A         -2.3628662090      3.4772306938      6.9487746324
  C48          -0.5161024879      1.3580406687      7.7129678919
  C49          -1.8179754234      0.8959903018      7.3913325078
  H49A         -2.2972790637      1.2533949854      6.4875188330
  C50          -2.4902753622     -0.0284879556      8.1836597903
  H50A         -3.4861382064     -0.3521490935      7.8895302790
  C51          -1.9011521333     -0.5601342613      9.3353760581
  H51A         -2.4290245434     -1.2815297015      9.9505864131
  C52          -0.6101355993     -0.1348845551      9.6692010039
  H52A         -0.1243177201     -0.5271346699     10.5595134458
  C53           0.0555141136      0.8001287437      8.8872045800
  H53A          1.0488962508      1.1272575935      9.1818866915
```

Cu_PH_2

```
  +---------------------------------------------------------------------+
  |  Jaguar version 7.6, release 211                                    |
  |                                                                     |
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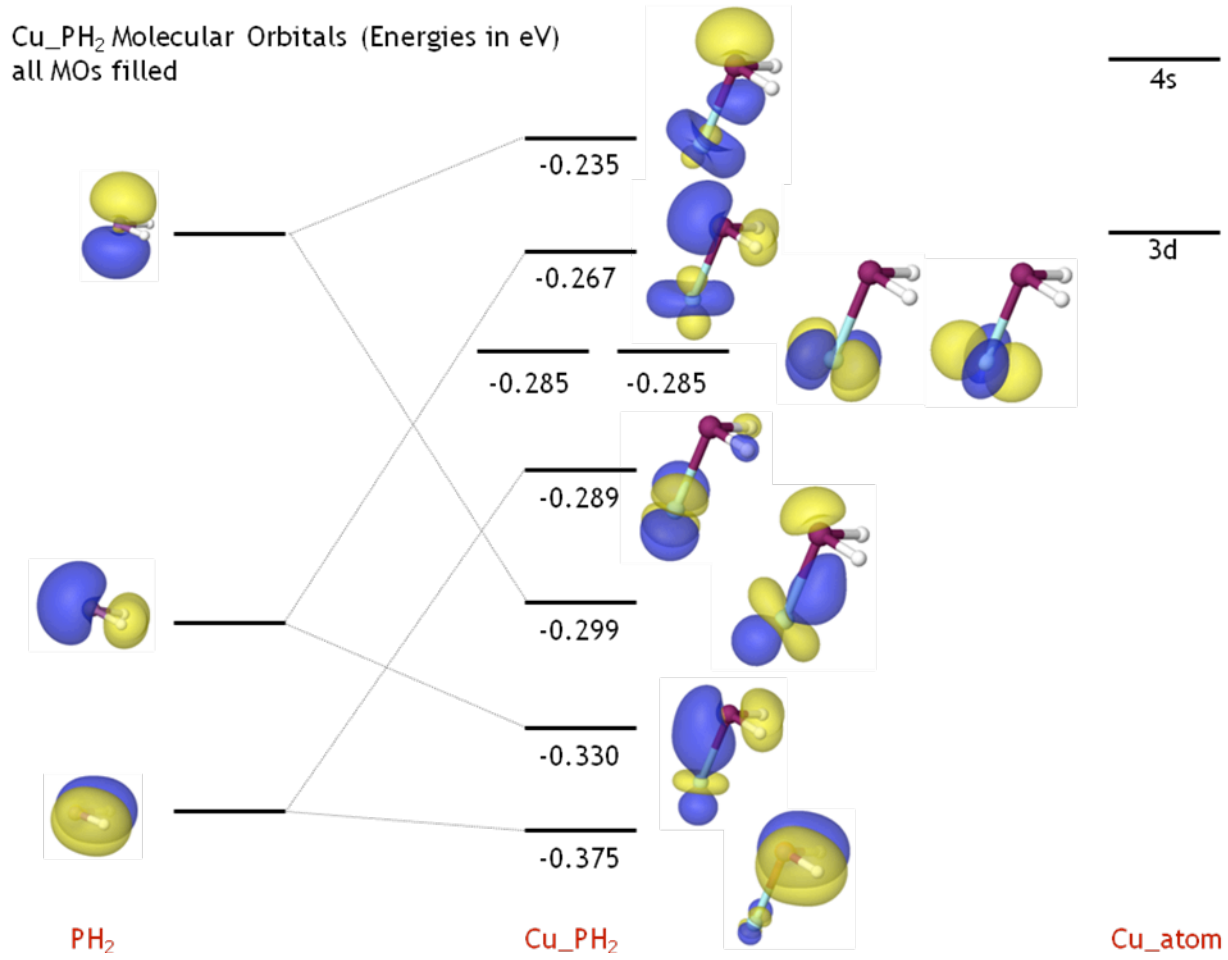
  +---------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  This run will use ECP on 1 atom
  number of basis functions....          80

final geometry:
                                  angstroms
  atom              x                  y                  z
  P1           -0.1149222593      0.7908623113     -0.0089827399
  H2           -0.4719279660      2.1706613528      0.0971485828
  H3           -1.2691738112      0.4820163648     -0.7931828120
  Cu4          -1.1115762630      0.2466154848      1.9182554149
```

Figure S5. Kohn-Sham Orbitals showing the Cu_P interactions in $CuPH_2$.



Li_PH_2

```
  +-------------------------------------------------------------------+
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  +-------------------------------------------------------------------+
  basis set:              lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          66

final geometry:
                                  angstroms
  atom              x                 y                 z
  P1          -0.2378880603      0.9408150263     -0.1828407832
  H2          -0.6370057847      2.3036724647      0.0004168068
  H3          -1.4373417678      0.6087091710     -0.8908860077
  Li4         -1.1756420976      0.3098670444      1.8573845826
```

Na_PH_2

```
  +-------------------------------------------------------------------+
  |  Jaguar version 7.6, release 211                                  |
  |                                                                   |
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  +-------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          74

final geometry:
                                angstroms
  atom              x                y                z
  P1          -0.1737017886     0.8386255158    -0.0462111047
  H2          -0.5751683862     2.2026042678     0.1266181152
  H3          -1.3715390508     0.5159176383    -0.7620889456
  Na4         -1.3215057135     0.1691732145     2.2531138286
```

K_PH_2

```
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  +-------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  This run will use ECP on 1 atom
  number of basis functions....          60

final geometry:
                                angstroms
  atom              x                y                z
  P1          -0.1399214818     0.8290468564    -0.0584027104
  H2          -0.5228394015     2.2027947472     0.0799945510
  H3          -1.3193322808     0.5157257535    -0.8092462353
  K4          -1.4087334321    -0.0321378692     2.7132237260
```

PH_2 anion

```
  +-------------------------------------------------------------------+
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  |                                                                   |
```

```
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  +--------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:   -1
  multiplicity:            1

  number of basis functions....          44

final geometry:
                                 angstroms
  atom              x                 y                 z
  P1          -0.3358428943      0.9125192456     -0.0409909995
  H2          -0.4812056239      2.3359888077     -0.2031574711
  H3          -1.2803524437      0.6452841510     -1.0946433478
```

PH_3

```
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  +--------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          51

final geometry:
                                 angstroms
  atom              x                 y                 z
  P1          -0.3150908903      0.9132709659     -0.0609824944
  H2          -0.6340767080      2.2994648796      0.0062277429
  H3          -1.4341430765      0.6054123974     -0.8860507628
  H4          -1.0073312807      0.6052508569      1.1447012638
```

PPh_2H

```
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  +--------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....         371
```

final geometry:

atom	x	y	z
	angstroms		
P4	0.5918585290	2.2156964250	6.4218960948
C42	-0.5671023343	3.5034098449	5.7448071113
C43	-0.3413223279	3.9462239296	4.4364946110
H43A	0.4724965704	3.5188527081	3.8600703063
C44	-1.1528628308	4.9267630224	3.8652739673
H44A	-0.9633196649	5.2600621026	2.8509653809
C45	-2.2084082744	5.4677356936	4.5940038559
H45A	-2.8442757383	6.2259667877	4.1508734529
C46	-2.4492292518	5.0256085827	5.8953917827
H46A	-3.2726894911	5.4411346537	6.4659153621
C47	-1.6348935409	4.0517467133	6.4670029881
H47A	-1.8361892905	3.7109706066	7.4762645276
C48	-0.4938033763	1.2504801426	7.5633179021
C49	-1.3623865301	0.2937816781	7.0182913836
H49A	-1.4128569958	0.1630076861	5.9421523335
C50	-2.1633133354	-0.4924092987	7.8413368460
H50A	-2.8347493751	-1.2215598091	7.4015567446
C51	-2.0944514176	-0.3522905974	9.2274610912
H51A	-2.7127359319	-0.9699001101	9.8689721414
C52	-1.2237204603	0.5820526839	9.7824907572
H52A	-1.1624698639	0.6963247584	10.8591943313
C53	-0.4327121388	1.3807485493	8.9567047083
H53A	0.2331509879	2.1117265315	9.4023627227
H4C	1.1973572289	3.0166499593	7.4302421421

$PPh_2(CH_2Ph)$

```
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+-------------------------------------------------------------------+

  basis set:             lacv3p**++
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          567
```

final geometry:

atom	x	y	z
	angstroms		
P4	0.4975697501	2.7061526745	6.8500953420
C42	-0.7309766183	3.8246234296	6.0270165837
C43	-1.2534359918	3.3959884557	4.7961172972
H43A	-0.9642325853	2.4279838715	4.3994600630
C44	-2.1389489057	4.1909114727	4.0767653688
H44A	-2.5355233415	3.8354668301	3.1320968684
C45	-2.5074832599	5.4460555541	4.5625853725
H45A	-3.1917943650	6.0703302088	3.9993088623
C46	-1.9851200597	5.8920124689	5.7724539972
H46A	-2.2621469915	6.8671970460	6.1580047497

C47	-1.1059036235	5.0879030291	6.5003791606
H47A	-0.7224694373	5.4597255380	7.4424023709
C48	-0.5990172291	1.3328970770	7.4502701655
C49	-0.0503089626	0.0466669139	7.5136548258
H49A	0.9731674145	-0.1131568538	7.1922029013
C50	-0.8040745934	-1.0279034106	7.9849454128
H50A	-0.3625333040	-2.0172578826	8.0305859951
C51	-2.1215895932	-0.8305011856	8.3895734556
H51A	-2.7116131686	-1.6656116916	8.7504974272
C52	-2.6826157634	0.4451786355	8.3219789038
H52A	-3.7107349886	0.6030721438	8.6294611789
C53	-1.9271753671	1.5185110105	7.8569179075
H53A	-2.3781949157	2.5030599715	7.7991298000
C24	0.8306825479	3.6137876488	8.4716395316
H26	1.2991638353	4.5626818813	8.1945419721
H27	-0.1105717634	3.8364584889	8.9801588136
C27	3.4599335132	1.3815786134	11.0737258271
C28	2.0928351689	1.4342176482	11.3348817457
C29	1.2457279733	2.1538143329	10.4938358197
C30	1.7484785206	2.8350207489	9.3805663198
C31	3.1240895213	2.7692363487	9.1251369597
C32	3.9728255270	2.0518387727	9.9636828078
H33	4.1205326589	0.8248739970	11.7287555046
H34	1.6830204640	0.9161767511	12.1949155558
H35	0.1821279789	2.1874863458	10.7039210119
H36	3.5312197155	3.2842383905	8.2610561723
H37	5.0358724921	2.0180135592	9.7519326634