CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Synthesis and Characterization of [(NHC)$_2$Cu]X Complexes: Catalytic and Mechanistic Studies of Hydrosilylation Reactions

Silvia Díez-González,[a,b] Edwin D. Stevens,[b] Natalie M. Scott,[b] Jeffrey L. Petersen,[c] and Steven P. Nolan*[a,b]

[a] *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona (Spain)*
[b] *Department of Chemistry, University of New Orleas, New Orleans, Louisiana 70148 (USA)*
[c] *C. Eugene bennet Department of Chemistry, West Virginia university, Morgantown, West Virginia 26506-6045 (USA)*

Supporting Information

General Considerations

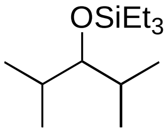
All ketones were used as received. Solid reagents were stored under argon in a glovebox containing less than 1 ppm oxygen. Tetrakis(acetonitrile)copper(I) hexafluorophosphate and tetrafluoroborate,[1] NHC salts and free IPr were synthesized according to literature procedures.[2] Solvents were distilled from appropriate drying agents. Flash column chromatography was performed on silica gel 60 (320-400 mesh). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ (USA). All reported yields are isolated yields and are average of at least two runs.

Catalytic Studies: Hydrosilylation of Ketones

General Procedure

In a vial fitted with a septum screw cap, **5b** (18 mg, 0.03 mmol, 3 mol %) and sodium *tert*-butoxide (12 mg, 12 mol %) were charged inside a glove box and stirred in dry THF (2 mL) at 55°C outside of the glove box for 10 minutes before adding triethylsilane (0.33 mL, 2 mmol, 2 equiv) through the septum using a syringe. After 10 more minutes of stirring, the ketone (1 mmol) was added. When the starting material was a solid, it was added as a solution in THF. The reaction was monitored by GC, after consumption of the starting material or no further conversion, the reaction mixture was opened to air and filtered through a plug of active charcoal and celite using ethyl acetate as solvent. The organic phase was concentrated in vacuo and the purity of the residue established by GC and ^{1}H NMR analyses. Flash chromatography was then performed unless crude product was estimated to be greater than 95% pure.

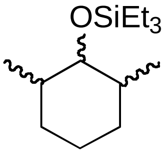
(1-Isopropyl-2-methylpropoxy)triethylsilane (Table 7, entry 1)



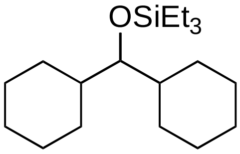
Using the general procedure, 2,4-dimethylpentanone (0.142 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.228 g (99% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[3]

(2,6-Dimethylcyclohexyloxy)triethylsilane (Table 7, entry 2)

Using the general procedure, 2,6-dimethylcyclohexanone (0.140 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product presented a mixture of diastereisomers *meso trans/trans : cis/trans : meso cis/cis* = 39 : 9 : 52, determined by ^{1}H NMR. Purification by flash chromatography on silica gel (pentane) afforded three fractions of the title compound. First, 0.087 g of the *meso trans/trans* isomer, then 0.0646 g of a mixture 32 : 68 of isomers *cis/trans* and *meso cis/cis*, and finally 0.080 g of the *meso cis/cis* isomer (96% yield) as colorless oils. Spectroscopic data were consistent with previously reported data for this compound.[4]



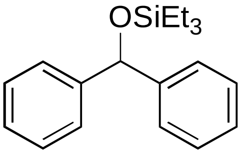
(Dicyclohexylmethoxy)triethylsilane (Table 7, entry 3)



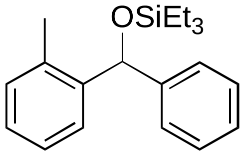
Using the general procedure, dicyclohexyl ketone (0.200 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.305 g, 98% yield). Spectroscopic data were consistent with previously reported data for this compound.[5]

(Diphenylmethoxy)triethylsilane (Table 7, entry 4)

Using the general procedure, benzophenone (0.182 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 98:2) to afford 0.282 g (95% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[5]

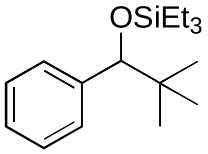


(Phenyl-*o*-tolylmethoxy)triethylsilane (Table 7, entry 5)



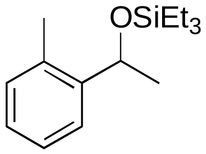
Using the general procedure, 2-methylbenzophenone (0.18 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 99:1) to afford 0.302 g (97% yield) of the title compound as a colorless oil.[5]

(2,2-Dimethyl-1-phenylpropoxy)triethylsilane (Table 7, entry 6)



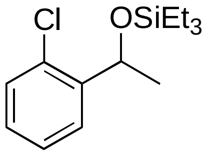
Using the general procedure, 2,2-dimethylpropiophenone (0.170 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.261 g (94% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[5]

Triethyl-(1-*o*-tolylethoxy)silane (Table 7, entry 7)



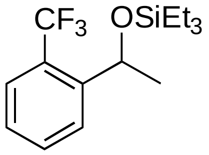
Using the general procedure, 2'-methylacetophenone (0.132 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.238 g (95% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[5]

[1-(2-Chlorophenyl)ethoxy]triethylsilane (Table 7, entry 8)



Using the general procedure, 2'-chloroacetophenone (0.130 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 98:2) to afford 0.250 g (92% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[5]

[1-(2-(Trifluoromethyl)phenylethoxy]triethylsilane (Table 7, entry 9)



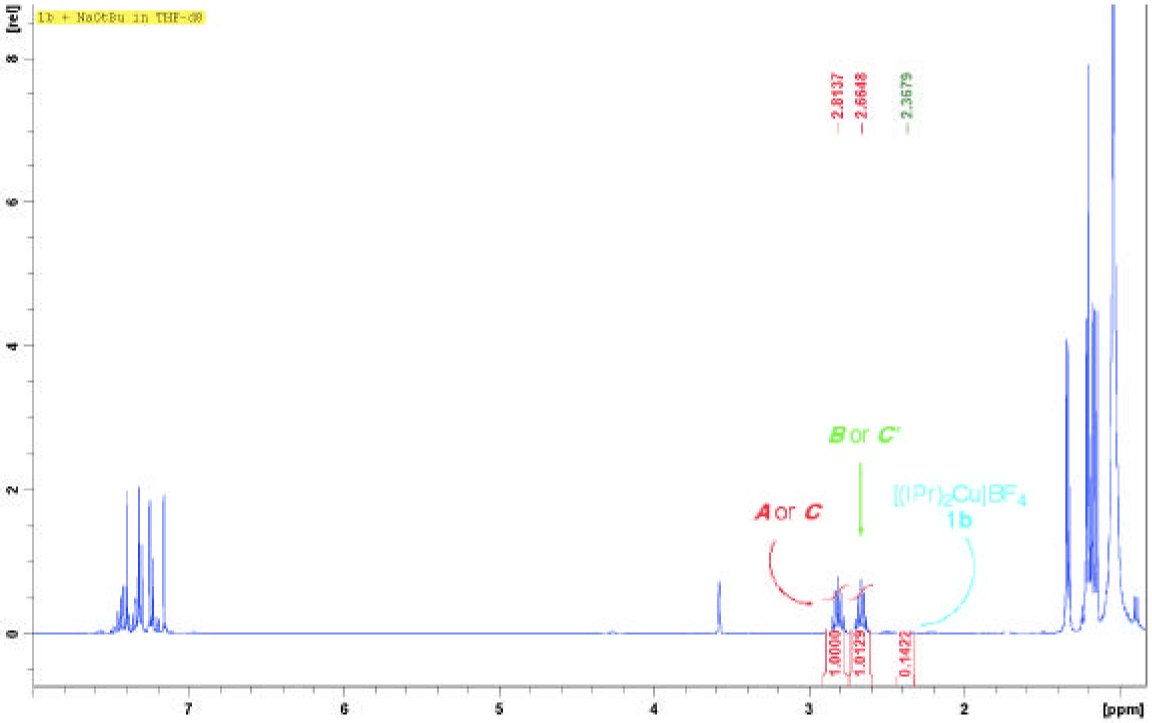
Using the general procedure, 2'-(trifluoromethyl)acetophenone (0.150 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.251 g (82%

yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[5]

Mechanistic Studies: NMR Data

Reaction 1:

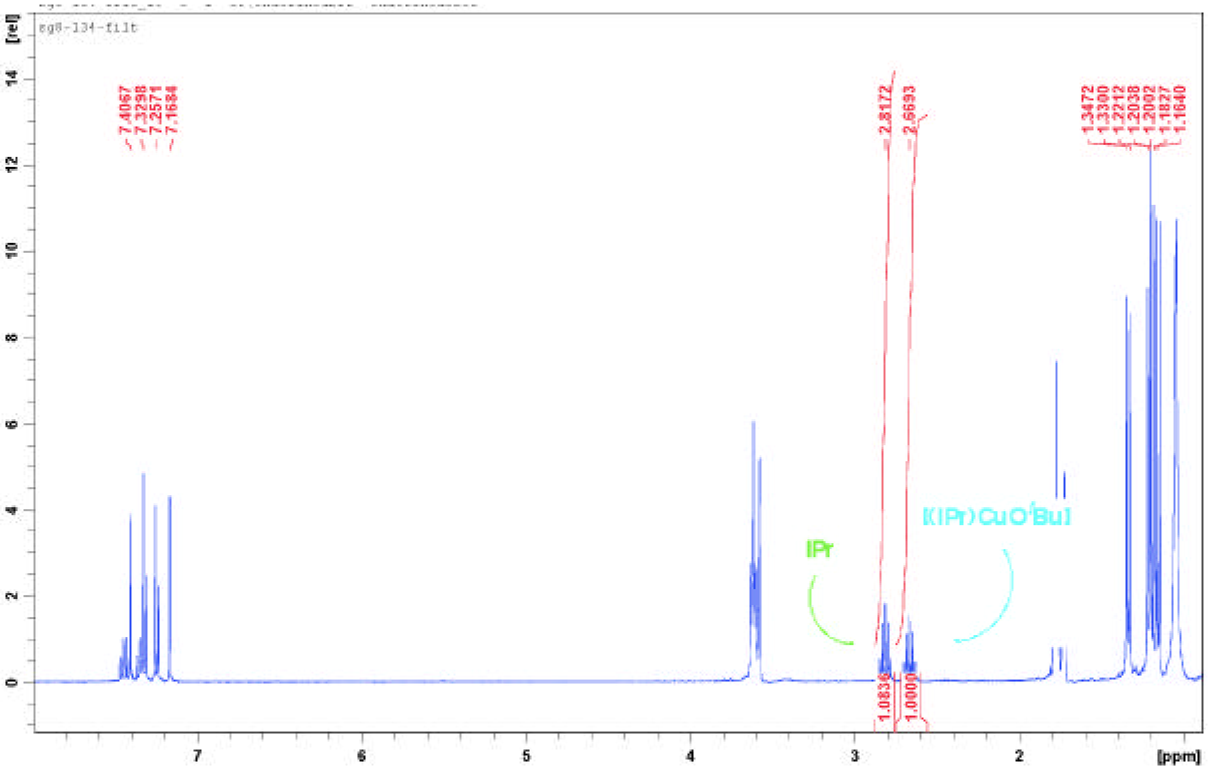
In a J-Young NMR tube, **1b** (56 mg, 0.06 mmol), sodium *tert*-butoxide (22 mg, 0.23 mmol) and [D$_8$]THF (1 mL) were charged inside a glove box. The reaction was allowed to evolve at room temperature. No changes in the ^{1}H NMR were observed from 10 minutes to 19 h. At first and according to the appearance of two new septuplets corresponding to the CH of isopropyl groups on the ligands, it was proposed: i) the formation of two new species (***A*** and ***B***) or ii) one compound where both IPr ligands on the copper center would not be equivalent (***C*** and ***C'***).



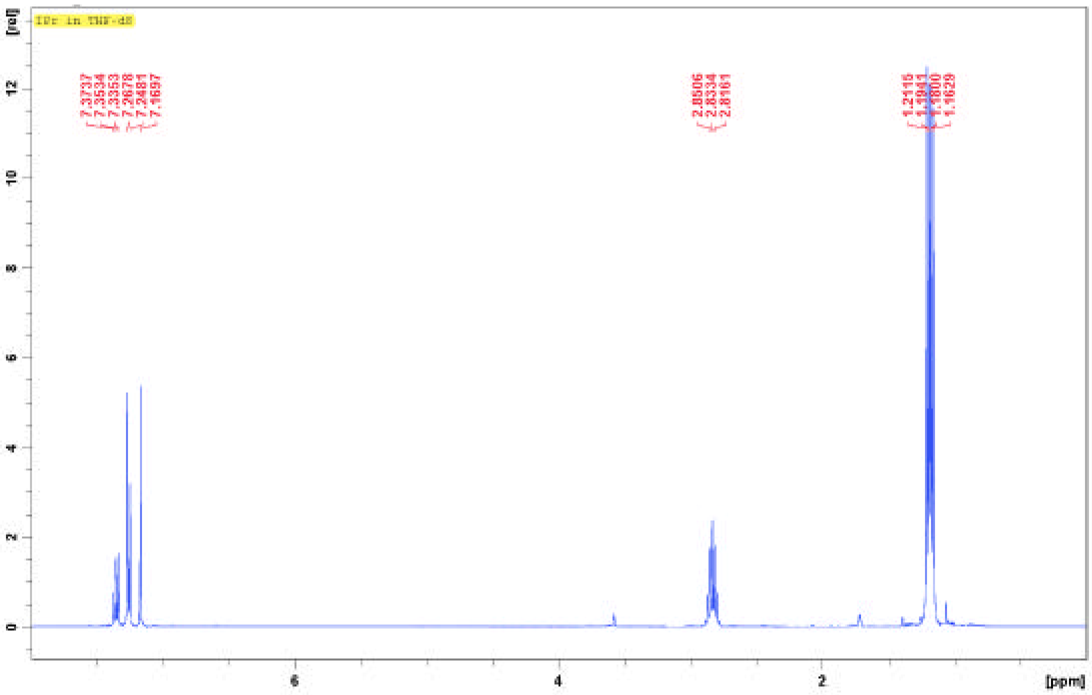
Reaction 2

In an vial fitted with a screw cap, **1b** (0.133 g, 0.144 mmol) and NaO*t*Bu (0.066 g, 0.69 mmol), were loaded and stirred in dry THF (3 mL) for 2 h inside a glovebox. After filtering the reaction mixture through a plug of celite (THF), the filtrate was mixed with pentane to form a precipitate. The white powder formed was filtered off and identified as a mixture of the starting complex **1b** with some unidentified by-products. After concentration of the filtrate, an equimolar mixture of free IPr and [(IPr)CuO*t*Bu][5] was observed in ^{1}H and ^{13}C NMR.

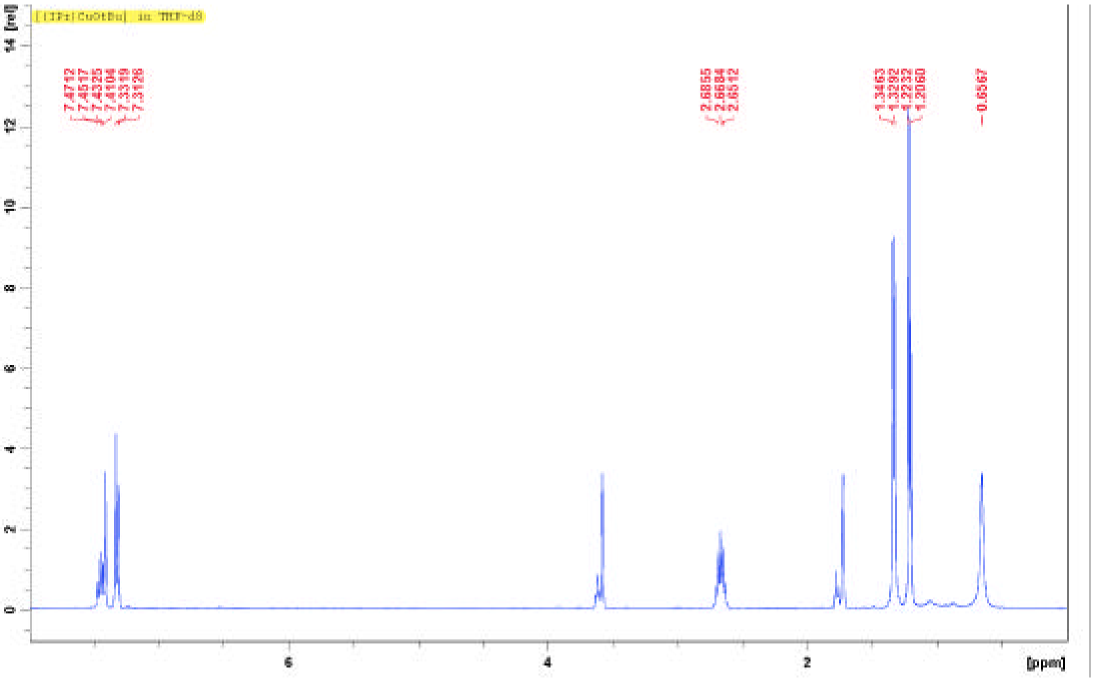
^{1}H NMR of isolated products in [D$_8$]THF



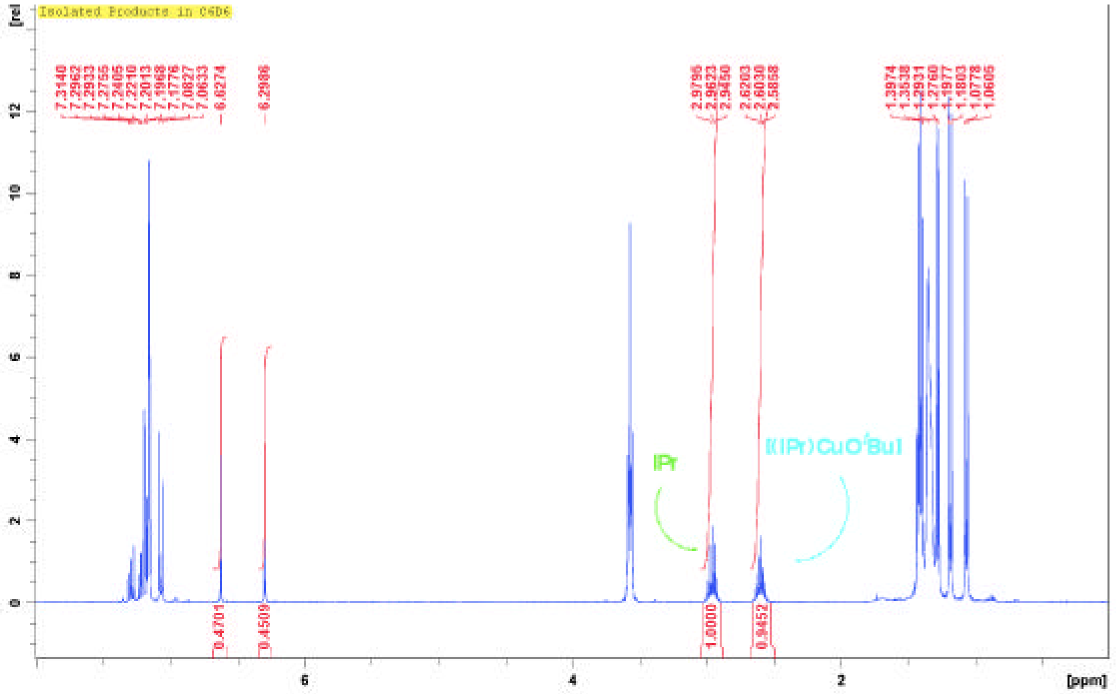
^{1}H NMR of IPr in [D$_8$]THF



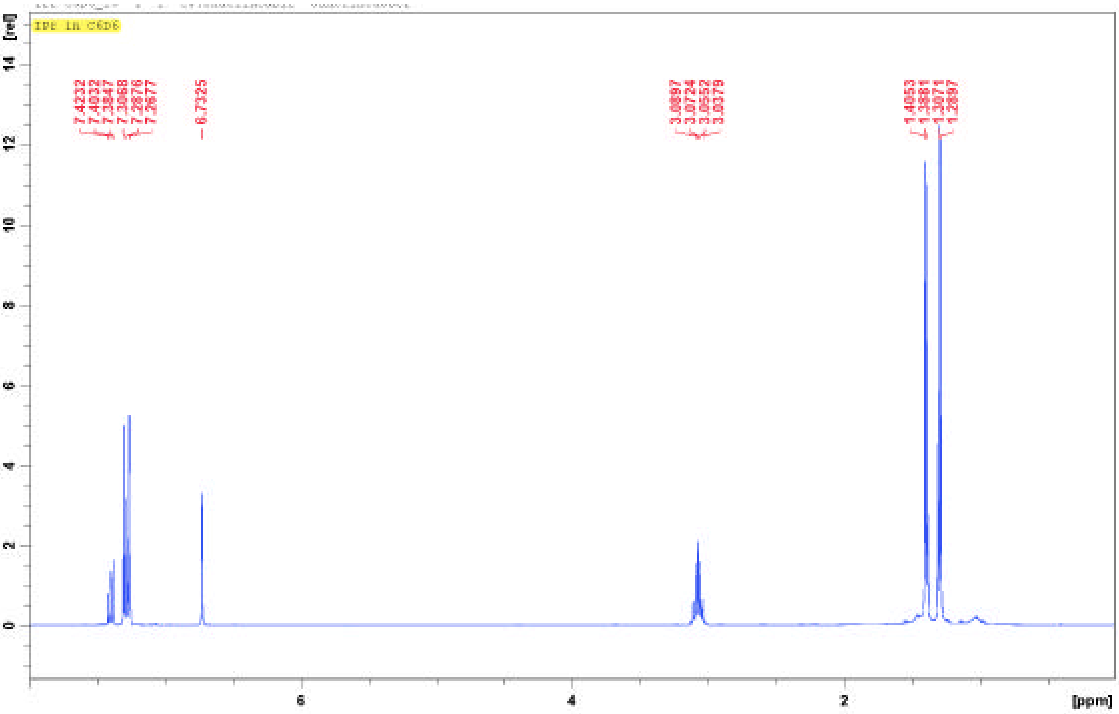
^{1}H NMR of [(IPr)CuOtBu] in [D$_8$]THF



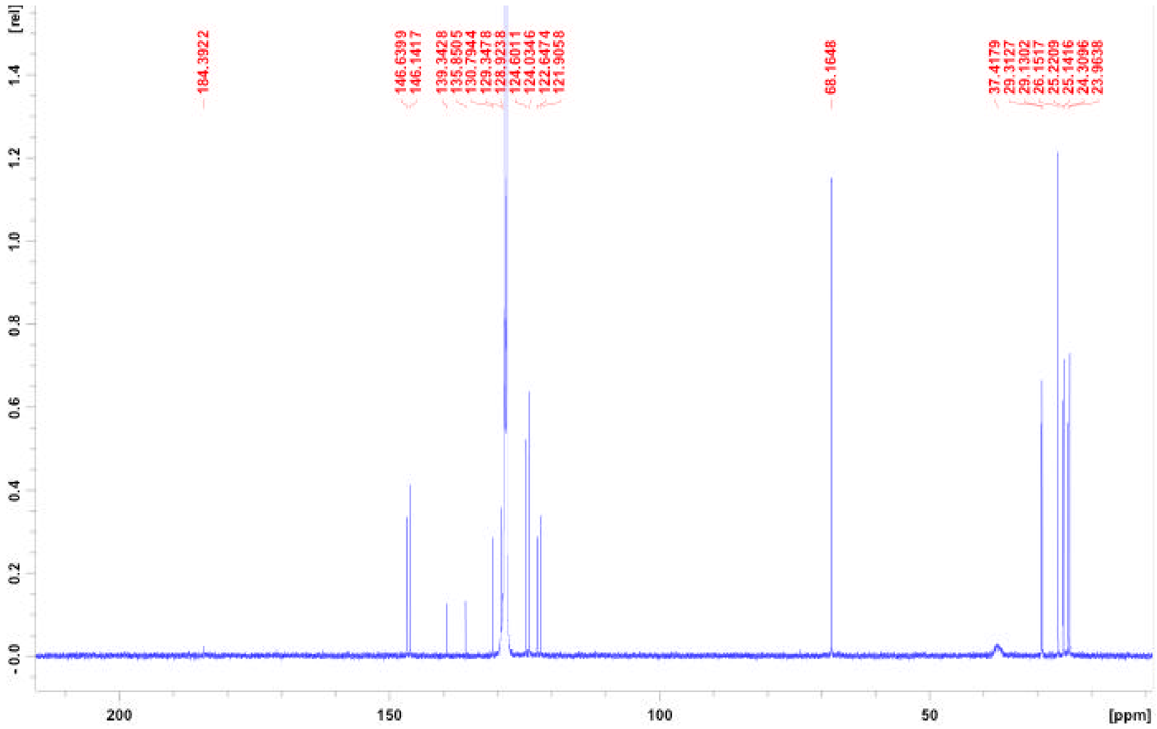
^{1}H NMR of isolated products in C$_6$D$_6$



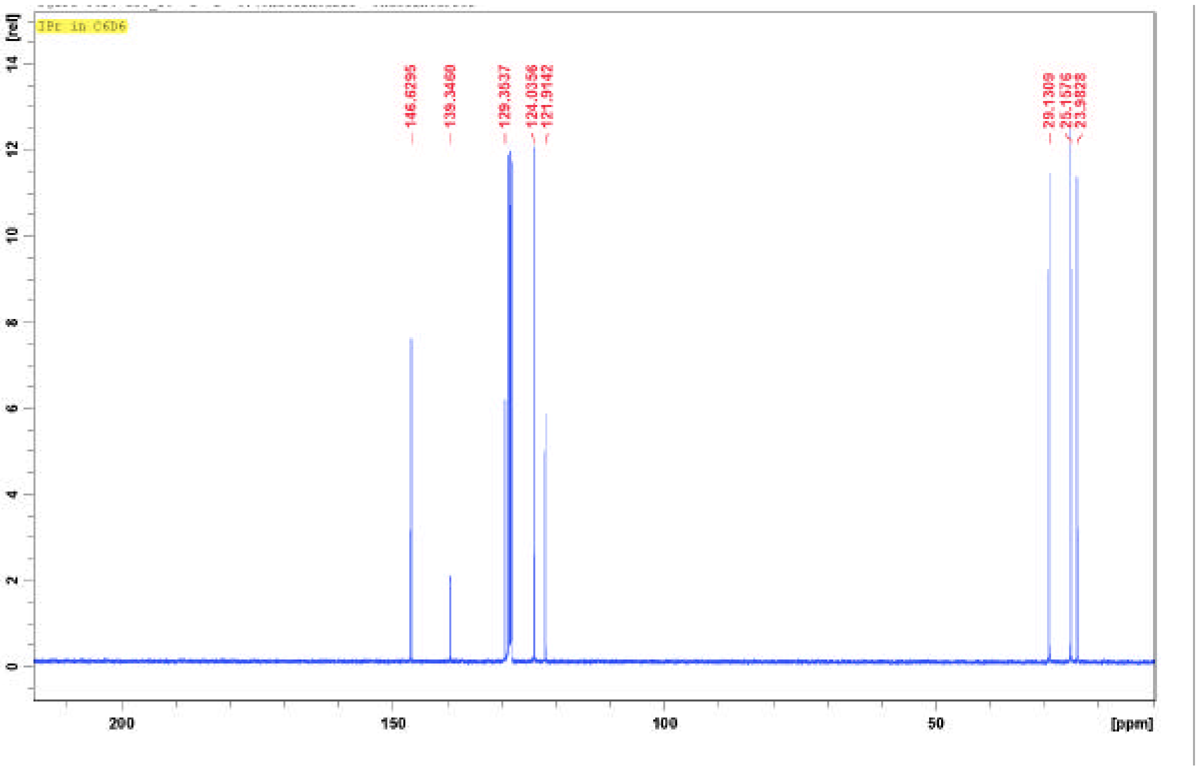
^{1}H NMR of IPr in C_6D_6



^{13}C NMR of isolated products in C_6D_6

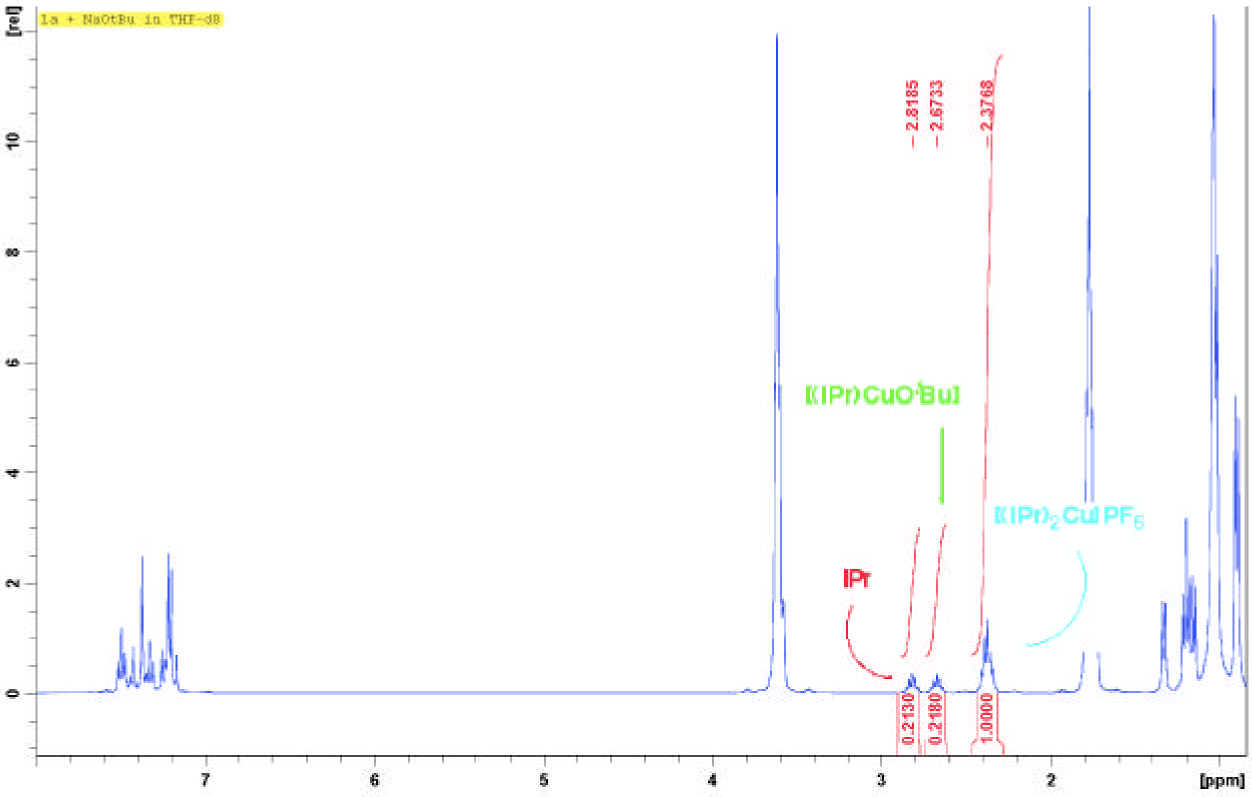


^{13}C of IPr in C_6D_6



Reaction 3:

In a J-Young NMR tube, **1a** (59 mg, 0.06 mmol), sodium *tert*-butoxide (22 mg, 0.23 mmol) and [D_8]THF (1 mL) were charged inside a glove box. The reaction was allowed to evolve at room temperature. No changes in the ^{1}H NMR were observed from 10 minutes to 19 h.



References

[1] G. J. Kubas, *Inorg. Synth*. **1979**, *19*, 90–92.

[2] a) J. Huang, S. P. Nolan, *J. Am. Chem. Soc*. **1999**, *121*, 9889–9890; b) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; c) L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49–54.

[3] J. Barden, J. Fleming, *Chem. Commun.* **2001**, *22*, 2366-2367.

[4] S. Díez-González, H. Kaur, F. Z. Kauer, E. D. Stevens, S. P. Nolan, *J. Org. Chem.* **2005**, *70*, 4784–4796.

[5] For spectroscopic data of [(IPr)CuO*t*Bu] in C_6D_6 see: N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369–3371.