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Symmetric Bridgehead-to-Bridgehead Coupling of Bicyclo[1.1.1]pentanes and [*n*]Staffanes

Ctibor Mazal,[†] Alex J. Paraskos,[‡] and Josef Michl*,[‡]

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, and Department of Organic Chemistry, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic

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Symmetrical bridgehead-to-bridgehead coupling of bicyclo[1.1.1]pentane cages has been effected in 48−70% yields by the cuprate oxidation method.

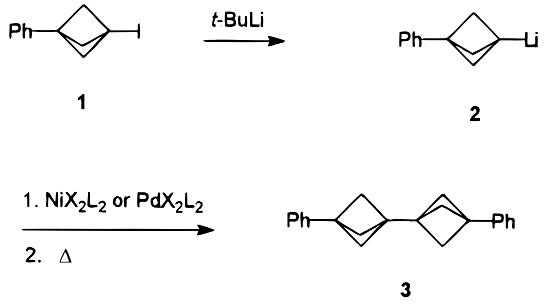
Introduction

For some time, we have worked with axially functionalized [*n*]staffanes (oligomers of [1.1.1]propellane), which are of interest for use as rigid rods in a molecular-size "Tinkertoy"[1] construction kit.[2,3] So far, the only synthetic access to these structures is the oligomerization of [1.1.1]propellane, followed by separation of rods of different lengths. Although this was quite adequate initially, when rods of all lengths were desired, it provides only poor yields of rods of any particular length, except the shortest. Clearly, procedures for symmetrical and unsymmetrical bridgehead-to-bridgehead coupling of shorter [*n*]staffanes into longer ones would offer a much better synthetic route to the longer members of the series. Presently, we report that the cuprate oxidation procedure[4] can be used for symmetrical coupling, permitting a doubling of rod length.

Results and Discussion

Only a few examples of coupling involving bond formation between two tertiary carbon atoms have been reported so far,[5,6] and bridgehead positions appear to be particularly demanding since the structure prevents a backside attack. The instability of bridgehead carbocations in the bicyclo[1.1.1]pentane cage[7] precludes the use of methods based on nucleophilic substitution.[8]

Scheme 1



We have chosen the readily accessible[2] 1-iodo-3-phenylbicyclo[1.1.1]pentane (**1**) as a model substrate for the development of a coupling procedure. In view of the above, the failure of our initial attempts to couple **1** with various organometallics, including (3-phenylbicyclo[1.1.1]pentyl)zinc chloride, in the presence of nickel(0) or palladium(0) catalysts was not surprising. We also tried the radical pathway via a dimethyl boronate that was followed in certain related reactions,[9] but again failed.

On the positive side, the relative stability of bridgehead carbanions permitted an in situ preparation of bis(bicyclo[1.1.1]pentyl)palladium(II) and nickel(II) phosphine complexes from (3-phenylbicyclo[1.1.1]pentyl)lithium (**2**) and the corresponding dihalides, $PdCl_2(PPh_3)_2$, $NiBr_2[P(n\text{-}Bu)_3]_2$, and $NiCl_2$dppp, at low temperature. The decomposition of these complexes gave 20−40% of the desired coupling product, 3,3′-diphenyl[2]staffane (**3**), in analogy to reductive elimination from other dialkyl- or diarylpalladium and -nickel complexes[10] (Scheme 1).

The success of the reductive coupling on Pd and Ni next turned our attention to the preparatively more convenient oxidative coupling of dialkyl cuprates.[4] We first tried Lipshutz's "higher-order" cyanocuprate method which had been successfully used for preparations of various biaryls in good or excellent yields,[11] and has also been tested for dialkylcyanocuprates.[12] Such a procedure

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[†] Masaryk University.

[‡] University of Colorado.

(1) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862, and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors.

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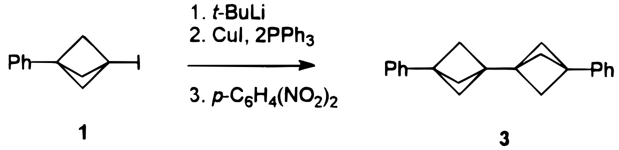
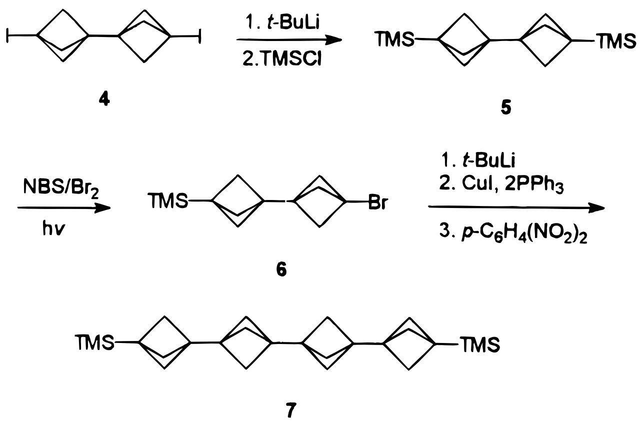
S0022-3263(97)01419-9 CCC: $15.00

Scheme 2



Scheme 3

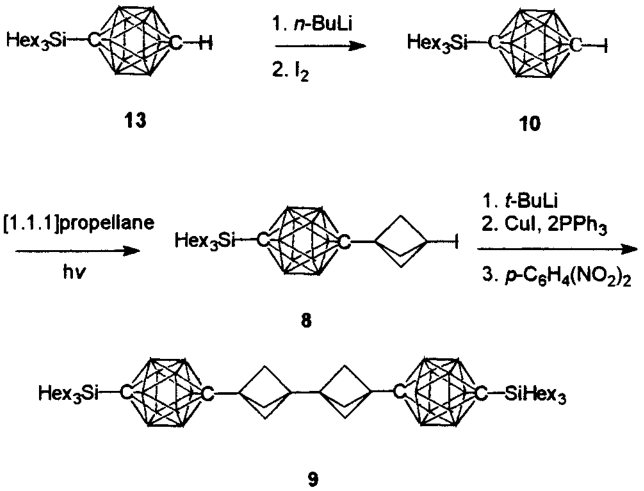


would offer the possibility of asymmetric coupling. However, a complex mixture of products was formed when the lithium derivative **2** was used for the preparation of the cyanocuprate which was then oxidized by oxygen. Besides the desired coupling product **3**, we detected 1-phenylbicyclo[1.1.1]pentane,[13] 1-cyano-3-phenylbicyclo[1.1.1]pentane,[14] and a compound whose spectral properties suggested the 1-hydroxy-3-phenylbicyclo[1.1.1]pentane structure. When CuCl$_2$ was used for the cuprate oxidation instead of oxygen, about 50% of the original iodo derivative **1** was reformed.

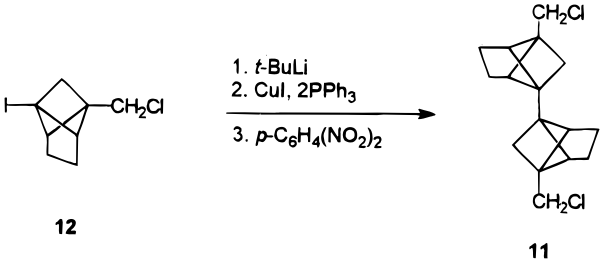
Phosphine stabilized cuprates seemed to be a useful alternative for a symmetric version of the coupling reaction. Szeimies et al.[6] provided an inspiring example with their synthesis of 1,1′-bi(homocubane). Indeed, **3** was obtained from **1** in 60 ± 10% yield in repeated runs following a slightly modified protocol, in that a homogeneous solution of PPh$_3$ and CuI (2:1) in THF was used in the cuprate preparation instead of the more hazardous [CuI·P(*n*-Bu)$_3$]$_4$ (Scheme 2).

We next tested the generality of this procedure. The synthesis of a [4]staffane derivative started with 3,3′-diiodo[2]staffane (**4**), easily and specifically accessible by the insertion of [1.1.1]propellane into a C−I bond of 1,3-diiodobicyclo[1.1.1]pentane, in which higher staffanes are not formed.[2] Lithiation and silylation of **4** gave 3,3′-bis(trimethylsilyl)[2]staffane (**5**), which was transformed in about 50% yield to 3-bromo-3′-(trimethylsilyl)[2]staffane (**6**) by reaction with NBS and bromine in dichloromethane under irradiation. The bromo derivative **6** is somewhat unstable under the reaction conditions, and this is most likely responsible for the low yield. No 3,3′-dibromo[2]staffane was detected. Lithiation of **6** by *t*-BuLi in ether at −40 °C followed by oxidative cuprate coupling at −60 °C gave 3,3‴-bis(trimethylsilyl)[4]staffane (**7**) in 40 ± 10% yield in repeated runs (Scheme 3).

Scheme 4



Scheme 5



The next test case involved the coupling of 1-(12-(trihexylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-iodobicyclo[1.1.1]pentane (**8**) to yield 3,3′-bis(12-(trihexylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)[2]staffane (**9**), a new type of structure in which the [*n*]staffane[2] and 12-vertex *p*-carborane[15,16] rod motifs are mixed. In repeated runs, the yield was 75 ± 10%. The starting **8** was obtained by the photochemical insertion of [1.1.1]propellane into the C−I bond of 1-(trihexylsilyl)-12-iodo-1,12-dicarba-*closo*-dodecaborane (**10**), analogous to its insertion into other C−I bonds, particularly those in 1,3-diiodobicyclo[1.1.1]pentane[2] and 1,4-diiodocubane[17] (Scheme 4).

Finally, 3,3′-bis(chloromethyl)-2,4:2′,4′-bisethano[2]staffane (**11**) was prepared in 70% yield by the oxidative cuprate coupling of the bridgehead lithium compound derived from 1-(chloromethyl)-3-iodo-2,4-ethanobicyclo[1.1.1]pentane (**12**), which was isolated as a byproduct in the synthesis of 2,4-ethano[1.1.1]propellane,[18] where it probably forms as an adduct of chloroiodomethane on the propellane (Scheme 5).

Conclusion

We conclude that the oxidation of bridgehead cuprates represents a suitable procedure for symmetric coupling of bridgehead bromides and iodides of the bicyclo[1.1.1]pentane and [*n*]staffane series.

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Experimental Section

General Methods. 1-Iodo-3-phenylbicyclo[1.1.1]pentane (**1**) and 3,3′-diiodo[2]staffane (**4**) were prepared by literature methods.[2] [1.1.1]Propellane was prepared solvent-free[19] and dissolved in pentane. 1-(Trihexylsilyl)-1,12-dicarba-*closo*-dodecaborane (**13**) was prepared as described for 1-(triethylsilyl)-1,10-dicarba-*closo*-decaborane[15] and used for further synthesis without a full characterization (^{1}H NMR δ 0.39 (m, 6 H), 0.84 (*t*, 9 H), 1.10−1.33 (m, 24 H), 1.30−3.10 (m, 10 H), 2.80 (s, 1H); ^{13}C NMR δ 12.60, 14.09, 22.60, 23.42, 31.36, 33.43, carborane carbons not observed). All the reactions were carried out under an argon atmosphere unless specified otherwise. Melting points were determined on a Mel-TempII (Laboratory Devices) apparatus with a microscope attachment and are uncorrected. ^{1}H, ^{13}C, and ^{11}B NMR spectra were measured on a Varian VXR-300S spectrometer and referred to TMS and B(OMe)$_3$, respectively. IR spectra were recorded on a Perkin-Elmer 1600 Series spectrometer. MS spectra were taken on a VG 7070EQ-HF Hybrid tandem mass spectrometer. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

3,3′-Bis(trimethylsilyl)[2]staffane (5). A solution of **4**[2] (1.860 g, 4.8 mmol) in THF (50 mL) was added dropwise to a well-stirred solution of *t*-BuLi (12 mL, 1.7 M in pentane, 20.4 mmol) in THF (20 mL) at −65 °C. The addition was accomplished within 20 min. Chlorotrimethylsilane (2.5 mL, 20 mmol) was added to the mixture after 15 min of additional stirring at −65 °C. Stirring was continued for 1 h at −65 °C. Then, the mixture was slowly allowed to warm to room temperature. Washing of the reaction mixture with a saturated solution of NH$_4$Cl (2 × 20 mL), drying over MgSO$_4$, and evaporation of the solvent gave a crude product that was chromatographed on an alumina column with hexanes. Pure **5** (1.23 g, 92%) was isolated as a white crystalline solid after removing the solvent: mp 124 °C; ^{1}H NMR δ −0.12 (s, 18 H), 1.46 (s, 12 H); ^{13}C NMR δ −3.47, 27.83, 46.18, 48.32; IR (KBr) 2958, 2902, 2857, 1243, 1218, 1176, 917, 833, 743 cm^{-1}; CI$^+$MS, *m/z* 277 (M − H, 100). Anal. Calcd for $C_{16}H_{30}Si_2$: C, 69.07; H, 10.79. Found: C, 69.10; H, 10.92.

3-Bromo-3′-(trimethylsilyl)[2]staffane (6). Bromine (25 μL, 0.49 mmol) was added to a solution of **5** (135 mg, 0.49 mmol) and *N*-bromosuccinimide (90 mg, 0.50 mmol) in dry dichloromethane (30 mL). The solution was stirred under incandescent irradiation at −20 °C until the starting **5** was fully consumed (monitored by GC or ^{1}H NMR). Then, solvent was removed under reduced pressure and the residue was sublimed at 30−40 °C/0.1 Torr. The sublimate was dissolved in pentane and filtered. Evaporation of pentane gave **6** (72 mg, 52%) as a crystalline solid: mp 66−68 °C; ^{1}H NMR δ −0.11 (s, 9 H), 1.54 (s, 6 H), 2.03 (s, 6 H); ^{13}C NMR δ −3.50, 28.96, 38.13, 41.64, 43.98, 49.35, 57.34; IR (KBr) 2955, 1384, 1197, 831 cm^{-1}; CI$^+$MS (NH$_3$), *m/z* 302 (M + NH$_4^+$, 45), 287 (M + H, 87) 285 (100). Anal. Calcd for $C_{13}H_{21}SiBr$: C, 54.73; H, 7.42. Found: C, 54.77; H, 7.40.

1-(12-(Trihexylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-iodobicyclo[1.1.1]pentane (8). Carborane **13** (353 mg, 1.1 mmol) was lithiated by overnight stirring with *n*-BuLi (0.6 mL, 2.5 M in pentane, 1.5 mmol) in 30 mL of ether at room temperature. After the addition of iodine (400 mg, 16 mmol), the mixture was stirred for 30 min. The crude reaction mixture was washed with 3 × 10 mL of saturated NH$_4$Cl solution, filtered through a silica gel pad, and concentrated under reduced pressure. The material obtained (3.54 g, 80% of **10** by GC analysis; ^{1}H NMR δ 0.37 (m, 6 H), 0.84 (t, 9 H), 1.10−1.33 (m, 24 H), 1.30−3.10 (m, 10 H); ^{13}C NMR δ 12.70, 14.08, 22.59, 23.35, 31.31, 33.36, carborane carbons not observed) was irradiated in a stirred pentane solution of [1.1.1]-propellane (60 mL, 2 mol %) by an incandescent lamp for 36 h. A resulting mixture was chromatographed on silica gel by hexane, and 2.8 g (88%) of pure **8** was obtained as a viscous oil: ^{1}H NMR δ 0.39 (m, 6 H), 0.86 (t, J = 6.6 Hz, 9 H), 1.10−1.33 (m, 24 H), 2.01 (s, 6 H), 1.2−3.1 (m, 10 H); ^{13}C NMR δ 2.34, 12.78, 14.09, 22.58, 23.39, 31.32, 33.38, 48.96, 60.86, 68.06, 86.45; ^{11}B NMR δ −13.9 (br); IR (neat) 2956, 2926, 2856, 2605, 1190, 1100 cm^{-1}; EIMS, *m/z* 492 (41), 407 (21), 341 (47), 257 (22), 173 (18), 43 (100); HRMS calcd for $C_{25}B_{10}H_{54}ISi$ (M − H) 619.3970, found 619.3982.

1-(Chloromethyl)-3-iodo-2,4-ethanobicyclo[1.1.1]pentane (12) was formed as a byproduct in the synthesis of 2,4-ethano[1.1.1]propellane, which followed the procedure of Szeimies et al.[18] It was isolated by a Kugelrohr distillation of the residue left after propellane distillation. An analytically pure sample was prepared by extraction with hexanes followed by Kugelrohr distillation (0.1 Torr, oven temperature 75−100 °C): ^{1}H NMR δ 1.64 (m, 4 H), 2.53 (s, 2 H), 2.85 (s, 2 H), 3.40 (s, 2 H); ^{13}C NMR δ 19.12, 24.81, 41.36, 48.12, 50.21, 69.20; IR (neat) 2973, 2944, 2866, 1463, 1288, 1262, 1208, 1187, 1138, 944, 862 cm^{-1}; EIMS, *m/z* 268 (M, 6.5), 254 (3), 233 (M − Cl, 20), 219 (15), 205 (28), 141 (75), 105 (100). Anal. Calcd for $C_8H_{10}ICl$: C, 35.78; H, 3.75. Found: C, 35.86; H, 3.73.

General Procedure for Coupling Reaction via Cuprates. A CuI−PPh$_3$ complex was prepared in situ by stirring 1 equiv of CuI and 2.2 equiv of PPh$_3$ in THF at room temperature until CuI was fully dissolved (usually for 1.5 h). The solution was cooled in a dry ice/acetone bath and added dropwise via cannula to a well-stirred solution of 2 equiv of the lithium derivative prepared by lithiation of the corresponding iodo derivative with 2 molar excess of *t*-BuLi at the same temperature. The amount of *t*-BuLi should be as exact as possible to avoid an excessive formation of a *tert*-butyl cross-coupled product; appearance of yellowish color of an excess of *t*-BuLi helped to control the addition. 1,4-Dinitrobenzene (1 equiv) in THF was slowly added to the reaction mixture 10 min after the addition of *t*-BuLi was completed. The mixture turned in brown within minutes and was stirred for an additional 1 h at −65 °C before it was allowed to warm to room temperature. It was then diluted with ether, washed with aqueous NH$_4$Cl, and dried over MgSO$_4$ with 2 equiv of iodine to oxidize PPh$_3$. The residue left after the evaporation of solvents was extracted by ether. The extract was further purified by chromatography or crystallization.

3,3′-Diphenyl[2]staffane[20] (3). The general procedure for coupling was followed. The crude product obtained from **1**[2] (174 mg, 0.65 mmol) was chromatographed on a silica gel column with 2% Et$_2$O in petroleum ether, yielding 61 mg (66%) of white crystalline **3**. An analytical sample was prepared by crystallization from hexanes: mp 221.5−222.5 °C; ^{1}H NMR δ 1.91 (s, 12 H), 7.16−7.30 (m, 10 H); ^{13}C NMR δ 38.21, 40.70, 51.10, 126.02, 126.26, 128.09, 141.50; IR (neat) 3022, 2965, 2904, 2867, 1444, 1211, 745, 697 cm^{-1}; EIMS, *m/z* 286 (M, 31), 285 (M − H, 100), 272 (M − CH$_2$, 28), 271 (69), 258 (64), 243 (60), 229 (50), 215 (38). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.97.

3,3‴-Bis(trimethylsilyl)[4]staffane (7). Lithiation of **6** was accomplished by an addition of *t*-BuLi (0.45 mL, 1.7 M in pentane, 0.76 mmol) to a solution of **6** (100 mg, 0.35 mmol) in ether (10 mL) at −65 °C and by an additional 4 h of stirring at −40 °C. Then, the solution was cooled to −65 °C and the general coupling procedure was followed. The reaction was quenched with 10 mL of a saturated solution of NH$_4$Cl and, after an addition of CHCl$_3$ (25 mL), washed twice with water (10 mL). Combined organic extracts were dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was dissolved in acetone, yielding **7** (35 mg, 48%) as solid flakes that were filtered off and washed with acetone. Crystallization from chloroform gave **7** as colorless needles: mp >156 °C subl; ^{1}H NMR δ −0.10 (s, 18 H), 1.33 (s, 12 H), 1.49 (s, 12 H); ^{13}C NMR δ −3.54, 28.06, 37.97, 38.46, 45.74, 47.33, 48.70; IR (KBr) 2952, 2900, 2861, 1443, 1247, 1209, 1161, 992, 910, 836, 742, 692, 628, 542 cm^{-1}; CI$^+$MS(NH$_3$) *m/z* 411(M + H, 100). Anal. Calcd for $C_{26}H_{42}Si_2$: C, 76.02; H, 10.31. Found: C, 75.54; H, 10.95.

3,3′-Bis(12-(trihexylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)[2]staffane (9). Crude ethereal extract from the

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(20) Friedli, A. C. Ph.D. Dissertation, University of Texas, Austin, 1992.

reaction of 2.8 g (4.95 mmol) of **8** was filtered through a silica gel pad and crystallized from THF/methanol (1:1), yielding 65% of white crystals of **9**: mp 111−112 °C; ^{1}H NMR δ 0.38−0.48 (m, 12 H), 0.85 (t, $J = 6.6$ Hz, 18 H), 1.08−1.32 (m, 48 H), 1.23 (s, 12 H), 1.30−3.04 (m, 20 H); ^{13}C NMR δ 12.85, 14.10, 22.61, 23.44, 31.36, 33.43, 33.87, 40.79, 50.40, 51.28, 67.38; ^{11}B NMR δ −13.3, −14.0; IR (KBr) 2956, 2926, 2856, 2605, 1467, 1209, 1100, 771 cm^{-1}; EIMS *m/z* 984 (M, 3), 624 (33), 408 (100), 342 (64), 320 (57), 239 (52). Anal. Calcd for $C_{50}H_{110}B_{20}Si_2$: C, 61.04; H, 11.27. Found: C, 61.13; H, 11.05.

3,3′-Bis(chloromethyl)-2,4:2′,4′-bisethano[2]staffane (11). The crude product obtained from 100 mg (0.37 mmol) of **12** was chromatographed on a silica gel column to give 35 mg (70%) of crystalline **11**; an analytical sample was obtained by sublimation at 60−80 °C /0.1 Torr: mp 91−92 °C; ^{1}H NMR δ 1.58−1.69 (m, 8 H), 1.79 (s, 4 H), 2.45 (s, 4 H), 3.32 (s, 4 H); ^{13}C NMR δ 25.74, 40.08, 41.36, 41.52, 43.91, 61.41; IR (KBr) 2962, 2867, 1384, 1259, 1221, 701 cm^{-1}; EIMS *m/z* 247 (M − Cl, 19), 235 (24), 233 (28), 219 (64), 205 (45), 169 (100), 167 (83), 155 (95). Anal. Calcd for $C_{16}H_{20}Cl_2$: C, 67.85; H, 7.12. Found: C, 67.92; H, 7.22.

3,3′-Diphenyl[2]staffane has also been obtained from **1** by Lipshutz higher-order cyanocuprate coupling and by stoichiometric reductive coupling of Pd(II) and/or Ni(II) complexes.

CuCN Coupling.[11] Copper cyanide (8 mg, 0.089 mmol) was placed in a dry three-necked round-bottom flask (50 mL) equipped with a gas dispersion tube and a rubber septum. The flask was again gently dried with a heat gun and allowed to cool to room temperature under argon. THF (10 mL) was added and the resulting suspension cooled to −65 °C. Lithiation of **1** (50 mg, 0.185 mmol) THF (10 mL) at −65 °C was effected with *t*-BuLi (0.22 mL, 1.7 M in pentane, 0.37 mmol). The solution was transferred through a cannula to the flask containing the CuCN suspension. The mixture was warmed to −40 °C and then recooled to −65 °C and stirred at this temperature for 0.5 h. Oxygen was then passed through the mixture for 0.5 h at the same temperature and for an additional 1.5 h at 0 °C. The reaction was quenched with a solution of methanol and concentrated $NaHSO_3$ (2 mL). The mixture was poured into concentrated NH_4Cl (10 mL) and extracted with ether. The ethereal extract was dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure. According to ^{1}H NMR, the resulting mixture contained **3** (50%), 1-phenylbicyclo[1.1.1]pentane[13] (14%), 1-cyano-3-phenylbicyclo[1.1.1]pentane[14] (11%), and 25% of an additional compound that was not fully characterized due to the small scale of the reaction, but is suspected to be 1-hydroxy-3-phenylbicyclo[1.1.1]pentane according to its spectra: ^{1}H NMR δ 2.19 (s, 6H), 2.20−2.43 (bs, 1H), 7.18−7.32 (m, 5H); EIMS *m/z* 159 (M − H, 95), 143 (M − OH, 60), 118 (100), 103 (80), 91 (48), 77 (63). When solid $CuCl_2$ (12 mg, 0.09 mmol) instead of oxygen was used to oxidize the cyanocuprate, a mixture of **3** (43%) and **1** (57%) was obtained.

Pd(II) Coupling. A solution of $PdCl_2(PPh_3)_2$ (63 mg, 0.09 mmol) in THF (10 mL) was slowly added to a dry ice-cooled stirred solution of **2**, prepared by lithiating **1** (50 mg, 0.185 mmol) with *t*-BuLi (0.22 mL, 1.7 M in pentane, 0.37 mmol) in THF (10 mL) at −65 °C. The resulting mixture was allowed to warm slowly to room temperature. Concentrated NH_4Cl (10 mL) was added, and the mixture was extracted by ether. The extract was dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure. ^{1}H NMR of the crude mixture showed 26% of **3** and 70% of 1-phenylbicyclo[1.1.1]-pentane.[13]

Ni(II) Coupling. When the above procedure was repeated with $NiBr_2[P(n\text{-}Bu)_3]_2$ (56 mg, 0.09 mmol) or $NiCl_2$dppp (50 mg, 0.09 mmol) catalyst instead of $PdCl_2(PPh_3)_2$, a similar mixture of products was obtained, containing 38% and 24% of **3**, respectively.

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