Supporting Information

for

Angew. Chem. Int. Ed. Z53469

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69451 Weinheim, Germany
Highly Active Nickel Catalysts for the Isomerization of Unactivated Vinyl Cyclopropanes to Cyclopentenes**

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General information. N-Heterocyclic carbene ligands and their corresponding salts (e.g., IMes and IMesBF₄, IPr and IPrBF₄) were prepared as previously reported or under slightly modified procedures and handled in a N₂ filled drybox or using standard Schlenk techniques. Solvents were dried over alumina columns. The VCPs (3-cyclopropyl-3-butenyl)-benzene (1), (1-cyclopropyl-vinyl)-benzene (3), 1-(2-methoxyethoxy)-1-vinylcyclopropane (5), and (1-bicyclo[3.1.0]hex-1-ylvinyl)-trimethylsilane (11) were prepared using literature procedures. All other materials were purchased from commercial sources and used without further purification.

¹H and ¹³C NMR spectra were recorded on a GE-300 NMR and referenced to residual protiated solvent (resonances downfield to the standard are reported as positive). All ¹³C
NMR spectra were proton decoupled. Low-resolution mass spectra were obtained on a Hewlett Packard 5890 series II gas chromatograph interfaced with a Hewlett Packard 5989A mass spectrometer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. High-resolution mass spectra (HR-MS) (EI) were provided by the University of Utah Mass Spectrometry Facility.

**(1-Methyl-tridec-1-enyl)-cyclopropane (7).** A solution of BuLi (2 mL, 2.5 M in hexane) was added to a solution of dodecyltriphenylphosphonium bromide (2.56 g, 5 mmol) in THF (25 mL) at -78 °C. After being stirred at 0 °C for 30 min, cyclopropyl methyl ketone (0.42 g, 5 mmol) was added. The mixture was stirred at room temperature overnight. Excess water was added and the mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO₄, concentrated, and then chromatographed with hexane to give 7 (0.98 g, 83%, Z:E = 3:4) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, ppm): (Z) δ 5.21 (m, 1H), 1.98 (t, 6.9 Hz, 2H), 1.67 (m, 1H), 1.49 (s, 3H), 1.26 (m, 18H), 0.88 (t, 0.66 Hz, 3H), 0.51 (m, 2H), 0.42 (m, 2H); (E) δ 5.21 (m, 1H), 2.12 (t, 6.9 Hz, 2H), 1.40 (s, 3H), 1.26 (m, 19H), 0.88 (t, 0.66 Hz, 3H), 0.49-0.62 (m, 4H); ¹³C (¹H) NMR (75 MHz, CDCl₃, ppm): δ 135.2, 134.3, 126.2, 123.5, 31.9, 30.0, 29.9, 29.68, 29.66,
29.64, 29.60, 29.43, 29.36, 29.34, 27.9, 27.5, 22.7, 18.8, 14.1, 12.3, 4.1, 3.8.

(2-Cyclopropylvinyl)-benzene (9a). A solution of BuLi (2 mL, 2.5 M in hexane) was added to a solution of benzyltriphenylphosphonium bromide (2.17 g, 5 mmol) in THF (25 mL) at -78 ºC. After being stirred at 0 ºC for 30 min, cyclopropanecarboxaldehyde (0.35 g, 5 mmol) was added. The mixture was stirred at room temperature overnight. Excess water was added and the mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO₄, concentrated, and then chromatographed with hexane to give 9a (0.56 g, 78%, Z:E = 1:2) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, ppm): (Z) δ 7.17-7.45 (m, 5H), 6.35 (d, 10.5 Hz, 1H), 5.07 (t, 10.5 Hz, 1H), 1.91 (m, 1H), 0.82 (m, 2H), 0.51 (m, 2H); (E) δ 7.17-7.45 (m, 5H), 6.47 (d, 15.6 Hz, 1H), 5.73 (dd, 15.6, 9.0 Hz, 1H), 1.60 (m, 1H), 0.82 (m, 2H), 0.51 (m, 2H); ¹³C {¹H} NMR (75 MHz, CDCl₃, ppm): δ 144.1, 136.7, 134.8, 128.7, 128.6, 128.4, 128.1, 127.4, 126.5, 126.3, 125.6, 125.5, 14.5, 11.0, 8.0, 7.2.

Benzoic acid 3-cyclopropylallyl ester (9b). A solution of triethylamine (0.70 mL, 5mmol) in ethyl ether (5 mL) was added to a solution of 3-cyclopropyl-2-propen-1-ol (0.49 g, 5 mmol) and benzoyl chloride (0.58 mL, 5 mmol) in ether (25
mL). After stirring at room temperature overnight, excess water was added. The organic layer was washed with brine, dried over MgSO₄, concentrated, and then chromatographed with 9:1 hexane / ethyl acetate to give 9b (0.71 g, 71%) as a colorless oil. \( ^1H \text{NMR (300 MHz, CDCl}_3, \text{ppm): } \delta 7.39-8.07 \) (m, 5H), 5.77 (dt, 6.6 Hz, 15.3 Hz, 1H), 5.36 (dd, 6.0 Hz, 15.3 Hz, 1H), 4.74 (d, 6.6 Hz, 2H), 1.44 (m, 1H), 0.75 (m, 1H), 0.44 (m, 1H); \( ^{13}C \\{^1H\} \text{NMR (75 MHz, CDCl}_3, \text{ppm): } \delta 166.4, 140.7, 132.8, 130.4, 129.6, 128.3, 121.3, 65.7, 13.6, 6.9. \\

(2-Cyclopropylvinyl)-trimethylsilane (9c). A solution of DIBAL (12 mL, 1 M in THF) was added to a solution of 2-cyclopropylethynyltrimethylsilane (1.38 g, 10 mmol) in hexane (25 mL). After being stirred at room temperature overnight, excess water was added. The organic layer was washed with brine, dried over MgSO₄, concentrated, and then chromatographed with hexane to give 9c (1.30 g, 93%) as a colorless oil. \( ^1H \text{NMR (300 MHz, CDCl}_3, \text{ppm): } \delta 5.60 \) (dd, 10.2 Hz, 14.1 Hz, 1H), 5.35 (d, 14.1 Hz, 1H), 1.54 (m, 1H), 0.78 (m, 2H), 0.40 (m, 2H), 0.15 (s, 9H); \( ^{13}C \\{^1H\} \text{NMR (75 MHz, CDCl}_3, \text{ppm): } \delta 152.7, 125.7, 14.6, 7.44, 0.13. \\

(4-Cyclopropyl-3-butenyl)-benzene (9d). A solution of (4-cyclopropyl-3-butynyl)-benzene (0.85 g, 5 mmol) and \('BuOH (0.74 g 10 mmol) in THF (5 mL) was added to a solution of
lithium (0.35 g, 50 mmol) in liquid ammonia (15 mL) at -40 °C. The mixture was stirred at -40 °C for 1 hour and then allowed to warm to room temperature. Excess water was added and the mixture was extracted with ether. The organic extracts were washed with brine, dried over MgSO₄, concentrated, and then chromatographed with hexane to give 9d (0.78 g, 91%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.20-7.36 (m, 5H), 5.60 (dt, 6.6 Hz, 15.3 Hz, 1H), 5.05 (dd, 5.4 Hz, 15.3 Hz, 1H), 2.72 (m, 2H), 2.34 (m, 2H), 1.40 (m, 1H), 0.72 (m, 2H), 0.37 (m, 2H); ¹³C {¹H} NMR (75 MHz, CDCl₃, ppm): δ 142.2, 134.5, 128.5, 128.3, 127.2, 125.8, 36.2, 24.5, 13.5, 6.4.

General procedure for generating and handling IPr.¹ In a drybox, IPrBF₄ (1 eq) and KO-t-Bu (1.1 eq) are weighed into an oven-dried screw cap vial equipped with a magnetic stir bar. THF is added and the reaction is stirred for approximately 2 hours. The reaction mixture is filtered through a frit containing Celite, concentrated in vacuo, and recrystallized with pentane to afford IPr. The free NHC is stored under inert atmosphere (N₂).

General procedure for the VCP isomerization reaction. In a drybox, VCP was weighed directly into an oven-dried screw cap vial equipped with a magnetic stir bar and subsequently dissolved in solvent (0.1 M). A solution of Ni(COD)₂ and IPr
was then added and the vial was sealed with a PTFE lined cap. The vial was then removed from the drybox and the dark greenish-black reaction was stirred. The reaction was monitored by GC and after complete consumption of substrate, the products were purified by chromatography on silica gel.

**General procedure for the VCP isomerization reaction using a Schlenk-line.** An oven dried two-neck round-bottomed flask equipped with a magnetic stir bar and gas-line adapter was evacuated and filled with N₂. The flask was sealed by placing a septum over the open neck on the flask. A (dry and degassed) pentane solution of diyne was added via syringe. To the stirring solution, a solution of Ni(COD)₂ and IPr (in dry and degassed pentane) was added. The dark greenish-black reaction mixture was stirred for 10 hours until complete consumption of starting material was observed by GC. The contents of the reaction vessel were then concentrated and purified by silica gel column chromatography.

(2-Cyclopent-1-enylethyl)-benzene (2). The general procedure was used with (3-cyclopentyl-3-butenyl)-benzene (1, 200 mg, 1.2 mmol), Ni(COD)₂ (3 mg, 0.01 mmol), IPr (8 mg, 0.02 mmol), and 2 mL of pentane. The reaction mixture was purified by column chromatography on silica gel (pentane) to afford the desired product 2 (192 mg, 96%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.19-7.32 (m, 5H), 5.39
(m, 1H), 2.78 (t, 8.1 Hz, 2H), 2.26-2.41 (m, 6H), 1.88 (pent, 7.5 Hz, 2H); \(^{13}\text{C}\) \(^{1}\text{H}\) NMR (75 MHz, CDCl₃, ppm): δ 144.3, 142.5, 128.3, 128.2, 125.7, 123.7, 35.3, 34.4, 33.1, 32.5, 23.5; IR (neat): 3027, 2929, 2845, 1650, 1604, 1496, 1454, 1031, 749, 699; HR-MS calcd. for C\(_{13}\)H\(_{16}\) (M⁺): 172.1252, found 172.1220.

Cyclopent-1-enyl-benzene (4). The general procedure was used with (1-cyclopropylvinyl)-benzene (3, 200 mg, 1.4 mmol), Ni(COD)\(_2\) (3 mg, 0.01 mmol), IPr (8 mg, 0.02 mmol), and 2 mL of pentane. The reaction mixture was purified by column chromatography on silica gel (pentane) to afford the desired product 4 (192 mg, 96%) as a colorless oil. \(^{1}\text{H}\) NMR (300 MHz, CDCl₃, ppm): δ 7.21-7.48 (m, 5H), 6.21 (m, 1H), 2.74 (m, 2H), 2.55 (m, 6H), 2.04 (pent, 7.5 Hz, 2H); \(^{13}\text{C}\) \(^{1}\text{H}\) NMR (75 MHz, CDCl₃, ppm): δ 142.5, 136.8, 128.3, 126.8, 126.1, 125.6, 33.4, 33.2, 23.4; IR (neat): 3055, 2952, 2844, 1598, 1494, 1446, 1037, 751, 691; HR-MS calcd. for C\(_{11}\)H\(_{12}\) (M⁺): 144.0939, found 144.0940.

1-(2-Methoxyethoxy)-cyclopentene (6). The general procedure was used with 1-(2-methoxyethoxy)-1-vinylcyclopropane (5, 200 mg, 1.4 mmol), Ni(COD)\(_2\) (3 mg, 0.01 mmol), IPr (8 mg, 0.02 mmol), and 2 mL of pentane. The reaction mixture was purified by column chromatography on silica gel (10% Et\(_2\)O in pentanes) to afford the desired product 6 (186 mg, 93%) as a colorless oil. \(^{1}\text{H}\) NMR (300 MHz, CDCl₃, ppm): δ 4.44 (m, 1H),
3.88 (m, 2H), 3.63 (m, 2H), 3.40 (s, 3H), 2.26-2.40 (m, 4H),
1.85 (m, 2H); $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$, ppm): δ 159.9, 93.9,
71.0, 68.4, 59.1, 31.9, 28.9, 21.3; IR (neat): 2941, 2879,
1736, 1644, 1593, 1454, 1347, 1244, 1197, 1128, 1064, 1035,
983, 852; HR-MS calcd. for C$_8$H$_{14}$O$_2$ (M+): 142.0994, found
142.0970.

1-Methyl-5-undecyl-cyclopentene (8). The general procedure
was used with (1-methyl-tridec-1-enyl)-cyclopropane (7, 200
mg, 0.85 mmol), Ni(COD)$_2$ (3 mg, 0.01 mmol), IPr (8 mg, 0.02
mmol), and 2 mL of hexane. The reaction mixture was purified
by column chromatography on silica gel (hexane) to afford the
desired product 8 (188 mg, 94%) as a colorless oil. $^1$H NMR
(300 MHz, CDCl$_3$, ppm): δ 5.31 (m, 1H), 2.40 (m, 1H), 2.22 (m,
2H), 2.04 (m, 1H), 1.67 (s, 3H), 1.07-1.61 (m, 23H), 0.89 (t,
6.9 Hz, 3H); $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$, ppm): δ 143.6, 124.2,
48.0, 33.6, 31.9, 30.9, 30.2, 29.72, 29.67, 29.39, 27.5,
22.7, 14.9, 14.1; IR (neat): 2924, 2853, 1603, 1464, 1153;
HR-MS calcd. for C$_{17}$H$_{32}$ (M+): 236.2504, found 236.2476.

Cyclopent-2-enyl-benzene (10a). The general procedure was
used with 2-cyclopropylvinylbenzene (9a, 200 mg, 1.4 mmol),
Ni(COD)$_2$ (3 mg, 0.01 mmol), IPr (8 mg, 0.02 mmol), and 2 mL
of hexane. The reaction mixture was purified by column
chromatography on silica gel (pentane) to afford the desired
product 10a (184 mg, 92%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 7.18-7.34 (m, 5H), 5.97 (m, 1H), 5.80 (m, 1H), 3.91 (m, 1H), 2.37-2.54 (m, 3H), 1.75 (m, 1H); $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$, ppm): $\delta$ 146.5, 134.3, 131.9, 128.4, 127.2, 126.0, 51.3, 33.8, 32.5; IR (neat): 3057, 2933, 1665, 1598, 1494, 1448, 1345, 1074, 1034, 757, 693.

(2,3,3a,4,5,6-hexahydro-1-pentalenyl)trimethylsilane (12). The general procedure was used with (1-bicyclo[3.1.0]hex-1-ylvinyl)-trimethylsilane (11, 200 mg, 1.1 mmol), Ni(COD)$_2$ (3 mg, 0.01 mmol), IPr (8 mg, 0.02 mmol), and 2 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (3% Et$_2$O in pentane) to afford the desired product 12 (182 mg, 91%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 2.84 (m, 1H), 2.60 (m, 2H), 2.17 (m, 2H), 2.06 (m, 2H), 1.88 (m, 2H), 1.25 (m, 1H), 1.00 (m, 1H), 0.06 (s, 9H); $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$, ppm): $\delta$ 165.4, 128.3, 55.6, 42.2, 32.4, 31.7, 29.3, 24.7, -1.1; IR (neat): 2955, 1699, 1248, 1040, 837, 754, 691.

References


