Supporting Information

NHC-Coordinated Diphosphene-Stabilized Gold(I) Hydride and Its Reversible Conversion to Gold(I) Formate with CO$_2$

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Experimental Details

General considerations: All experiments were carried out under argon or nitrogen using standard Schlenk techniques, PL-HE-2GB Innovative Technology, and MBraun Unilab GloveBox. Hexane, diethylene, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. Benzene was refluxed over sodium/benzophenone, then distilled and stored under argon or nitrogen. Compounds 1[S1] and \text{NHC}_{Me}^{4}[S2] and \text{NHC}_{Pr_2Me_2}^{2}[S3] were prepared according to the reported literature procedures. AuCl·SMe₂ was purchased from Sigma Aldrich or TCI Chemicals and used as received. C₆D₆, THF-d₈ and toluene-d₈ were dried and distilled over potassium under argon or nitrogen. NMR spectra were recorded with a Bruker NanoBay 300 MHz NMR spectrometer. \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (\textsuperscript{1}H) or the deuterated solvent itself \textsuperscript{13}C{\textsuperscript{1}H}. \textsuperscript{31}P{\textsuperscript{1}H} and \textsuperscript{31}P spectra were referenced to the peaks of H₃PO₄. UV/vis spectra were acquired using a Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. IR spectra were recorded Bruker-Alpha spectrometer. Elemental analysis was performed on a Leco CHN-900 analyzer. Melting points were determined in closed NMR tubes under argon atmosphere and are reported without correction.

Synthesis of 2:

\[
\begin{align*}
\text{P=)} \quad \text{Ar} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qa
changes to light yellow. Subsequently, all volatiles are removed in vacuum and the resulting residue is extracted with 10 mL of toluene. Light yellow crystals of 2 are obtained after keeping the toluene extract overnight at −20 °C. After collecting the first crop of crystals, the mother liquor is concentrated to about 5 mL and kept at −20 °C for another 2 days yielding a second crop of crystals. Total isolated yield = 0.102 g (50 %). M.P.: 120 °C (dec.). \(^1\)H NMR (300 MHz, CD\(_6\)D\(_6\), 298 K): \(\delta = 1.02\) (s, 3H, CH\(_3\) of Mes), 1.18 (s, 3H, CH\(_3\) of C-CCH\(_3\), NHC\(_{Me}\)), 1.21 (s, 3H, CH\(_3\) of Mes), 1.35 (s, 3H, CH\(_3\) of C-CCH\(_3\), NHC\(_{Me}\)), 1.39 (s, 3H, CH\(_3\) of C-CCH\(_3\)), 1.93 (s, 3H, N-CH\(_3\), NHC\(_{Me}\)), 1.95 (s, 3H, CH\(_3\) of Mes), 2.05 (s, 3H, CH\(_3\) of Mes), 2.08 (s, 3H, CH\(_3\) of Mes), 2.31 (s, 3H, CH\(_3\) of Mes), 2.35 (s, 3H, CH\(_3\) of Mes), 2.45 (s, 3H, CH\(_3\) of Mes), 2.52 (s, 6H, CH\(_3\) of Mes), 2.78 (s, 3H, CH\(_3\) of Mes), 3.36 (s, 3H, N-CH\(_3\), NHC\(_{Me}\)), 6.22 (1H, Ar-H), 6.65 (br, 1H, Ar-H), 6.77 (s, 3H, Ar-H), 6.81-6.83 (m, 2H, Ar-H), 6.90-6.95 (m, 3H, Ar-H), 7.05 (s, 4H, Ar-H) ppm. \(^1\)H NMR (300 MHz, THF-d\(_8\), 298 K): \(\delta = 0.94\) (s, 3H, CH\(_3\) of Mes), 1.26 (s, 3H, CH\(_3\) of Mes), 1.43 (s, 3H, CH\(_3\) of Mes), 1.50 (s, 3H, CH\(_3\) of Mes), 1.72 (s, 3H, CH\(_3\) of Mes), 1.97 (s, 3H, CH\(_3\)-C-CCH\(_3\), NHC\(_{Me}\)), 1.98 (s, 6H, CH\(_3\) of Mes), 2.04 (s, 3H, CH\(_3\)-C-CCH\(_3\), NHC\(_{Me}\)), 2.20 (s, 3H, CH\(_3\) of Mes), 2.30 (s, 6H, CH\(_3\) of Mes), 2.39 (s, 3H, CH\(_3\) of Mes), 2.40 (s, 3H, N-CH\(_3\), NHC\(_{Me}\)), 2.47 (s, 3H, CH\(_3\) of Mes), 3.55 (s, 3H, N-CH\(_3\), NHC\(_{Me}\)), 6.55 (3H, br, Ar-H), 6.60 (1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.79 (s, 2H, Ar-H) 6.91-6.97 (m, 4H, Ar-H), 7.08-7.21 (m, 2H, Ar-H), 7.3 (t, \(^2\)J\(_{HH}\) = 7 Hz, 1H, Ar-H) ppm. \(^1\)H NMR (300 MHz, THF-d\(_8\), 298 K): \(\delta = 8.7\) (1C, CH\(_3\), CH\(_3\)-C-CCH\(_3\), NHC\(_{Me}\)), 8.9 (1C, CH\(_3\), CH\(_3\)-C-CCH\(_3\), NHC\(_{Me}\)), 20.1 (1C, CH\(_3\)-Mes), 20.4 (1C, CH\(_3\)-Mes), 21.08 (1C, CH\(_3\)-Mes), 21.5 (1C, CH\(_3\)-Mes), 21.7 (1C, CH\(_3\)-Mes), 22.0 (1C, CH\(_3\)-Mes), 22.1 (1C, CH\(_3\)-Mes), 22.6 (1C, CH\(_3\)-Mes), 22.8 (1C, CH\(_3\)-Mes), 23.4 (1C, CH\(_3\)-Mes), 23.6 (1C, CH\(_3\)-Mes), 33.2 (1C, CH\(_3\)-Mes), 33.4 (1C, N-CH\(_3\)), 37.2 (1C, N-CH\(_3\)), 126.2 (1C, Ar-CH), 126.3 (1C, A-CH), 126.4 (1C, Ar-CH), 126.98 (2C, Ar-C\(_{quat}\)), 127.8 (1C, Ar-CH), 128.3 (1C, Ar-CH), 128.6 (1C, Ar-CH), 129.1 (1C, Ar-CH), 129.4 (1C, Ar-CH), 129.7 (2C, Ar-C\(_{quat}\)), 129.8 (1C, Ar-CH), 129.9 (1C, Ar-CH), 130.34 (1C, Ar-CH), 130.5 (1C, Ar-CH), 132.3 (1C, Ar-CH), 132.75 (1C, Ar-CH), 136.1 (1C, Ar-C\(_{quat}\)), 136.5 (2C, Ar-C\(_{quat}\), 136.7 (1C, Ar-C\(_{quat}\) 137.0 (1C, Ar-CH), 137.2 (1C, Ar-C\(_{quat}\), 137.6 (1C, Ar-C\(_{quat}\), 137.8 (1C, Ar-C\(_{quat}\), 138.8 (dd, \(^1\)J\(_{C,C}\) = 68 Hz, \(^2\)J\(_{C,C}\) = 5 Hz, 1C, Ar-C\(_{quat}\)), 138.6 (1C, Ar-C\(_{quat}\)), 138.9 (1C, Ar-C\(_{quat}\), 140.2 (1C, Ar-C\(_{quat}\)), 140.3 (1C, Ar-C\(_{quat}\), 142.8 (2C, Ar-C\(_{quat}\)), 143.9 (dd, \(^1\)J\(_{C,P}\) = 49 Hz, \(^2\)J\(_{C,P}\) = 8 1C, Ar-C\(_{quat}\)), 144.9 (1C, Ar-C\(_{quat}\), 145.1 (1C, Ar-C\(_{quat}\), 148.5 (1C, Ar-C\(_{quat}\), 149.5 (1C, Ar-C\(_{quat}\)), 154.7 (dd, \(^1\)J\(_{C,P}\) = 99 Hz, \(^2\)J\(_{C,P}\) = 4 Hz, 1C, N-C-N) ppm. \(^3\)P NMR (121.5 MHz, THF-d\(_8\), 298 K): \(\delta = -0.3\) (d, \(^1\)J\(_{P,P}\) = 466 Hz), -32.5 (d, \(^1\)J\(_{P,P}\) = 466 Hz) ppm. \(^3\)P NMR (121.5 MHz, CD\(_6\)D\(_6\), 298 K): \(\delta = 1.3\) (d, \(^1\)J\(_{P,P}\) = 462), -31.7 (d, \(^1\)J\(_{P,P}\) =
462) ppm. UV/vis (THF): $\lambda_{\text{max}}(\varepsilon) = 402$ (4360), 332 (9046), 252 (34110) nm (Lmol$^{-1}$cm$^{-1}$). Elemental Analysis (%) calcd. for C$_{55}$H$_{62}$AuCl$_2$: C 63.19, H 6.07, N 2.68; found: C 63.28, H 6.23, N 2.44.

Synthesis of 3:

0.3 mL of Na-selectride solution (1.0 N in THF) is added to a Schlenk flask containing 0.290g (0.277 mmol) of 2 in toluene (15 mL) at −78 °C. After the addition, the flask is covered with aluminum foil immediately in order to protect from light. The reaction mixture is slowly brought to room temperature with continuous stirring. Subsequently, all the volatiles are removed and the resulting residue is extracted with 7 mL of THF. Light yellow crystals of 3 are obtained after storing the THF extract overnight at −20 °C. After collecting the first crop of crystals, the mother liquor is concentrated to about 5 mL and kept at −20 °C for another 2 days resulting in second crop of crystals. Total isolated yield: 0.250g (90 %). M.P.: 100 °C (dec., black residue melts at 180 °C). $^1$H NMR (300 MHz, THF-$d_8$, 298 K): $\delta$ = 0.87 (s, br, 6H, CH$_3$ of Mes), 0.98 (s, 3H, CH$_3$ of Mes), 1.29 (s, 6H, CH$_3$ of Mes), 1.45 (s, br, 6H, CH$_3$ of Mes), 1.77 (s, 3H, CH$_3$ of Mes), 1.97 (s, 6H, 3H from CH$_3$ of C-CCH$_3$, NHC$_{Me^4}$), 3H, CH$_3$ of Mes), 2.06 (s, 3H, C-CCH$_3$, NHC$_{Me^4}$), 2.27 (s, br, 9H, CH$_3$ of M), 2.40 (s, 3H, N-CH$_3$, NHC$_{Me^4}$), 3.61 (s, 3H, N-CH$_3$, NHC$_{Me^4}$), 4.60 (d, 1H, $^2$J$_{H,H}$= 138 Hz, Ar-H), 6.55 (br, 6H, Ar-H), 6.76 (s, 3H, Ar-H), 6.89 (m, 4H, Ar-H), 7.23 (t, $^3$J$_{H,H}$= 7.53 Hz, Ar-H) ppm. $^{13}$C($^1$H) NMR (75.43 MHz, THF-$d_8$, 298 K): $\delta$ = 8.5 (1C, CH$_3$, CH$_3$C–CCH$_3$, NHC$_{Me^4}$), 8.6 (1C, CH$_3$, CH$_3$C–CCH$_3$, NHC$_{Me^4}$), 20.0 (1C, CH$_3$-Mes), 20.7 (1C, CH$_3$-Mes), 21.0 (2C, CH$_3$-Mes), 22.1 (1C, CH$_3$-Mes), 23.1 (2C, CH$_3$-Mes), 25.4 (1C, CH$_3$-Mes), 25.7 (1C, CH$_3$-Mes s), 26.2 (1C, CH$_3$-Mes), 32.6 (2C, CH$_3$-Mes), 32.8 (1C, N-CH$_3$, NHC$_{Me^4}$), 36.89 (1C, N-CH$_3$, NHC$_{Me^4}$), 125.0 (1C, Ar-CH), 125.1 (1C, Ar-CH), 126.15 (2C, Ar-C$_{quat}$), 127.2 (1C, Ar-C$_{quat}$), 127.2 (1C, Ar-C$_{quat}$), 127.8 (2C, Ar-CH), 127.9 (2C, Ar-CH), 128.2 (1C, Ar-C$_{quat}$), 128.2 (1C, Ar-C$_{quat}$), 128.6 (1C, Ar-CH), 128.6 (2C, Ar-CH), 129.2 (2C, Ar-CH), 129.4 (1C, Ar-C$_{quat}$), 129.5 (1C, Ar-CH), 129.9 (1C, Ar-CH), 130.0 (1C, Ar-C$_{quat}$), 132.2 (C, Ar-CH), 135.5 (1C, Ar-C$_{quat}$), 136.6 (4C, Ar-C$_{quat}$), 136.9 (1C, Ar-C$_{quat}$), 137.5 (1C, Ar-C$_{quat}$), 139.4 (1C, Ar-C$_{quat}$), 141.6 (1C, Ar-C$_{quat}$), 143.3 (1C, Ar-C$_{quat}$), 144.6 (1C, Ar-C$_{quat}$), 148.6 (1C, Ar-C$_{quat}$), 149.6 (1C, Ar-C$_{quat}$), 149.7 (1C, Ar-C$_{quat}$), 154.0 (1C, Ar-C$_{quat}$), 156.1 (1C, Ar-C$_{quat}$), 157.7 (1C, N-C-N). ppm.
$^{31}$P$^1$H NMR (121.5 MHz, THF-$d_8$, 298 K): $\delta = -14.5$ (d, $^{1}J_{(H, P)} = 470$ Hz, $P$-Au), 1.6 (d, $^{1}J_{(H, P)} = 470$ Hz, $P$-$NHC^{Me_2}$) ppm. $^{31}$P NMR (121.5 MHz, THF-$d_8$, 298 K): $\delta = -14.5$ (dd, $^{1}J_{(P, H)} = 470$ Hz, $^{2}J_{(P, P)} = 138$ Hz, P-Au), 1.6 (d, br, $^{1}J_{(P, p)} = 470$ Hz, P-$NHC^{Me_2}$) ppm. FT-IR (KBr, cm$^{-1}$): $\tilde{\nu}$ (cm$^{-1}$) = 1893 (vs, Au-H), 1640(s), 1607(s), 1552(w), 1475 (s), 1430(s), 1395(w), 1370(s), 1177(s), 1070(vs), 1026(s), 916(w), 846(vs), 805(vs), 750(s), 661(br, w), 593(w), 550(w). UV/vis (THF): $\lambda_{\text{max}}(\%) = 420 (4973)$ nm (Lmol$^{-1}$cm$^{-1}$), two solider at 350 nm, 300 nm. Elemental Analysis (%) calcd for C$_{55}$H$_{63}$AuN$_{2}$P$_{2}$: C 65.27, H 6.37, N 2.77; found: C 65.12, H 6.21, N 2.48.

**Synthesis of 4:**

A closed cap NMR tube containing 0.030g (0.03 mmol) of 3 in 1 mL of toluene and 2 drops of C$_{6}$D$_{6}$ is heated in 70 °C oil bath for 1 hr. $^{31}$P NMR measurement shows full conversion of 3 and formation of compound 4 (94 %) along with free diphosphene 1 (6 %). The reaction mixture is transferred into a Schlenk flask, evaporated to dryness and extracted with warm n-hexane (7 ml of n-hexane $\times$ 2) to obtain compound 4 as white crystals. Total isolated yield: 0.020 g (66%).

**M.P.:** 170 °C (dec.). $^1$H NMR (300 MHz, C$_{6}$D$_{6}$, 298 K): $\delta = 1.30$ (s, 6H, CH$_3$C-CCH$_3$, NHC$^{Me_2}$), 2.18 (s, 6H, CH$_3$ of Mes ), 2.22 (s, 6H, CH$_3$ of Mes), 2.25(s, 12H, CH$_3$ of Mes), 2.34 (s, 6H, CH$_3$ of Mes), 2.44 (s, 6H, CH$_3$ of Mes), 2.91(s, 6H, CH$_3$ of Mes), 4.19 (dd, $^{1}J_{(p, H)} = 214$ Hz, $^{2}J_{(p, H)} = 9$ Hz, P-H), 6.64 (s, 2H, Ar–H), 6.85-6.92(m, 4H, Ar-H), 6.95-6.99(m, 6H, Ar-H), 7.01-7.07 (m, 2H, Ar-H) ppm. $^{13}$C($^1$H) NMR (75.43 MHz, C$_{6}$D$_{6}$, 298 K): $\delta = 8.6$ (2C, CH$_3$C-CCH$_3$, NHC$^{Me_2}$), 21.7 (2C, CH$_3$-Mes), 22.0 (2C, CH$_3$-Mes), 22.4 (1C, CH$_3$-Mes), 22.5 (1C, CH$_3$-Mes), 22.80 (1C, CH$_3$-Mes), 22.86 (1C, CH$_3$-Mes), 22.91 (1C, CH$_3$-Mes), 22.95 (1C, CH$_3$-Mes), 23.0 (2C, CH$_3$-Mes), 34.5 (2C, N-CH$_3$, NHC$^{Me_2}$), 124.2 (2C, CH$_3$C-CCH$_3$, NHC$^{Me_2}$), 125.0 (1C, Ar-CH), 127.0 (1C, Ar-CH), 128.1 (2C, Ar-CH), 128.2 (2C, Ar-CH), 128.5 (2C, Ar-CH), 128.6 (1C, Ar-CH), 128.7 (1C, Ar-CH), 128.9 (2C, Ar-CH), 129.5 (2C, Ar-CH), 135.3 (2C, Ar-C$_{quat}$), 135.9(2C, Ar-C$_{quat}$), 136.0 (2C, Ar-C$_{quat}$), 136.6 (1C, Ar-C$_{quat}$), 136.7 (1C, Ar-C$_{quat}$), 137.2 (2C, Ar-C$_{quat}$), 138.02 (2C, Ar-C$_{quat}$), 138.09 (2C, Ar-C$_{quat}$), 139.9 (1C, Ar-C$_{quat}$), 141.6 (2C, Ar-C$_{quat}$), 142.0 (3C, Ar-C$_{quat}$), 147.0 (1C, dd, $^{1}J_{(C, p)} = 14.9$ Hz, $^{2}J_{(C, p)} = 4.66$ Hz, P-Ar-C$_{quat}$ ), 147.2 (1C, dd, $^{1}J_{(C, p)} = 12.24$ Hz, $^{2}J_{(C, p)} = 3$ Hz, P-Ar-C$_{quat}$), 193.6 (1C, S5
\[ d, J_{(C, P)} = 53.54 \text{ Hz, N-C-N of NHC}_{Me}^{+} \text{ ppm.} \]

\[ ^{31}P\{^1H\} \text{ NMR (121.5 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta = -95.1 \text{ (d, } J_{(P, H)} = 295 \text{ Hz, } P-H, -76.5 \text{ (d, } J_{(P, H)} = 295 \text{ Hz, } P) \text{ ppm.} \]

\[ ^{31}P \text{ NMR (121.5 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta = -95.1 \text{ (dd, } J_{(P, H)} = 295 \text{ Hz, } J_{(P, H)} = 214 \text{ Hz, } P-H, -76.5 \text{ (d, } J_{(P, H)} = 295 \text{ Hz, } J_{(P, H)} = 9 \text{ Hz, } P) \text{ ppm.} \]

**FT-IR (KBr, cm\(^{-1}\)):** \( \tilde{\nu} \) (cm\(^{-1}\)) = 2731 (vw), 2327 (w), 1646 (w), 1611 (s), 1562 (w), 1480 (w), 1434 (vs), 3191 (vs), 1368 (w), 1256 (w), 1226 (w), 1180 (w), 1091 (w), 1028 (s), 877 (vw), 851 (vs), 800 (s), 744 (s), 693 (s), 593 (s), 453 (vs).

**Elemental Analysis (%) calcd for C\(_{53}\)H\(_{63}\)AuN\(_2\)P\(_2\):** C 65.27, H 6.37, N 2.77; found: C 63.03, H 6.15, N 2.58 (deviations in the values of CHN analysis are likely due to the sensitivity of the compound).

### Synthesis of 5:

The Ar gas of a Schlenk flask with a toluene solution of 3 (0.050g, 0.05 mmol, in 10 mL of toluene) is exchanged for CO\(_2\) using standard Schlenk line technique and stirred for 30 mins. The \(^{31}P\) NMR spectrum of an aliquot from the reaction mixture with 2 drops of C\(_6\)D\(_6\) shows complete conversion of 3 into 5. The reaction mixture is evaporated to dryness (2.3\times10^{-1} torr pressure for 2 hrs.) to obtain compounds 5 and 3 in an approximate 95:5 ratio (total amount of isolated compounds = 0.050 g). Overnight exposure to vacuum (2.3\times10^{-1} torr) gives a mixture of 5 and 3 in an approximate 1:1 ratio. The NMR data was recorded on a freshly prepared sample of 5 with about 5 % of 3. **\(^1H\) NMR (300 MHz, C\(_6\)D\(_6\), 298 K):** \( \delta = 1.11 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.19 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.25 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.36 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.83 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.89 \text{ (s, } 3H, CH_3 \text{ of Mes), 1.97 \text{ (s, } 3H, C-CH_3, NHC}_{Me}^{+} \text{), 2.06 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.08 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.10 \text{ (s, } 6H, CH_3 \text{ of 2 molecule of toluene), 2.29 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.30 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.34 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.41 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.53 \text{ (s, } 3H, CH_3 \text{ of Mes), 2.60 \text{ (s, } 3H, CH_3 \text{ of Mes), 3.51 \text{ (s, } 3H, C-CH_3, NHC}_{Me}^{+} \text{), 6.25 \text{ (s, } 1H, Ar-H), 6.50-6.51 \text{ (m, } 1H, Ar-H), 6.65 \text{ (s, } 1H, Ar-H), 6.67-6.79 \text{ (m, } 3H, Ar-H), 6.83-6.87 \text{ (m, } 3H, Ar-H), 6.89(m, 3H, Ar-H), 6.91-6.94 \text{ (m, } 3H, Ar-H), 6.97-6.99 \text{ (m, } 4H, Ar-H), 7.01-7.05 \text{ (m, } 6H, Ar-H), 7.10 \text{ (s, } 1H, Ar-H) 7.12 \text{ (s, } 1H, Ar-H), 9.50 \text{ (1H, d, } J_{(H, P)} = 6.57 \text{ Hz) ppm.} \]

**\(^{13}C\{^1H\} \text{ NMR (75.43 MHz, C}_6\text{D}_6, 298 K):** \( \delta = 8.6 \text{ (1C, } CH_3, CH_3C-CH_3, NHC}_{Me}^{+} \text{), 9.4 \text{ (1C, } CH_3, CH_3C-CH_3, NHC}_{Me}^{+} \text{), 20.1 \text{ (2C, } CH_3\text{-Mes}} \]
Reaction of 5 with NHC^{Pr2Me2} at variable temperatures:

\[ \text{NHC}^{\text{Pr2Me2}} + \text{5} \rightarrow \text{3} + \text{6} + \text{7} \]
In a NMR tube, 0.012 g (0.01mmol) of compound 5 (with about 5% of 3) and 0.002 g of NHC\textsubscript{iPr\textsubscript{2}Me\textsubscript{2}} (0.01mmol, a 200 µL aliquot of a solution prepared from 0.5 ml toluene-\textsubscript{d\textsubscript{8}} and 5 mg NHC\textsubscript{iPr\textsubscript{2}Me\textsubscript{2}}) were mixed at −78 °C. The sample was transferred to the spectrometer and monitored by variable temperature $^{31}$P NMR. Only 5 is present at −70 °C, while at −10 °C new peaks at δ = −35.2 and 0.9 ppm ($^{1}J_{(P, P)} = 465$ Hz) appear, which we tentatively attribute to intermediate 7. At room temperature (25 °C) the intermediate has disappeared completely and only the resonances of compound 3 remain.

**Reaction of 5 with NHC\textsubscript{iPr\textsubscript{2}Me\textsubscript{2}}:**

At −78 °C, 5 mL of THF is added to a Schlenk flask with 0.030 g (0.028 mmol) of 5 (having around 5% of 3) and 0.005 g of NHC\textsubscript{iPr\textsubscript{2}Me\textsubscript{2}}. The mixture is allowed to warm to room temperature slowly and subsequently all volatiles are removed under vacuum. The $^{1}$H and $^{31}$P{$^{1}$H} NMR measurement of the crude reaction mixture shows the formation of 3 and 6.\textsuperscript{S3} $^{1}$H NMR (300 MHz, THF-\textsubscript{d\textsubscript{8}}, 298 K) for 6 from the crude reaction mixture, δ = 1.54 (br-d, 12H, CH(CH\textsubscript{3})\textsubscript{2}), 2.24 (s, 6H, CH\textsubscript{3}-C=C-CH\textsubscript{3}), 4.83 (br-sept, 2H, CH(CH\textsubscript{3})\textsubscript{2}) ppm.\textsuperscript{S3}
Synthesis of 6:

In a NMR tube, 0.006 g (0.033 mmol) of NHC$_{iPr}^{Pr2Me_2}$ were dissolved in 0.5 mL THF-d$_8$. The Ar gas in NMR tube was exchange with CO$_2$ and a white precipitate of 6 was formed immediately. $^1$H NMR (300 MHz, THF-d$_8$, 298 K): $\delta = 1.54$ (d, $^3J = 7$ Hz, 12H, CH(CH$_3$)$_2$), 2.24 (s, 6H, CH$_3$-C=C-CH$_3$), 4.83 (sep, $^3J = 7$ Hz, 2H, CH(CH$_3$)$_2$) ppm.$^{53}$

Reaction of 3 with HCO$_2$H:

In a NMR tube, 0.016 g (0.0158 mmol) of compound 3 and 0.75 mg of HCO$_2$H (0.016 mmol, 5.5 µL solution from stock solution of containing 1mL C$_6$D$_6$ and 100 µL HCO$_2$H) were mixed at room temperature. Immediately, evolution of gas bubbles was observed and the subsequent measurement of $^1$H and $^{31}$P NMR showed the quantitative transformation of 3 into 5.
**NMR Spectra**

**Figure S1.** $^1$H NMR spectrum of 2 in C$_6$D$_6$ at RT.

**Figure S2.** $^{31}$P($^1$H) NMR spectrum of 2 in C$_6$D$_6$ at RT.
Figure S3. $^1$H NMR spectrum of 2 in THF- $d_8$ at RT.

Figure S4. $^{13}$C($^1$H) NMR spectrum of 2 in THF- $d_8$ at RT.
**Figure S5.** $^{31}\text{P}^{(1}\text{H})$ NMR spectrum of 2 in THF-d$_8$ at RT.

**Figure S6.** $^1\text{H}$ NMR spectrum of 3 in THF- d$_8$ at RT.
Figure S7. $^{13}$C($^1$H) NMR spectrum of 3 in THF-d$_8$ at RT (crystalline sample of 3 is not enough soluble in THF-d$_8$ to get better $^{13}$C($^1$H) NMR spectrum).

Figure S8. $^{31}$P($^1$H) NMR spectrum of 3 in THF-d$_8$ at RT.
Figure S9. $^{31}$P NMR spectrum of 3 in THF-d$_8$ at RT.

Figure S10. $^1$H NMR spectrum of 4 in C$_6$D$_6$ at RT.
**Figure S11.** $^{13}$C($^1$H) NMR spectrum of 4 in C$_6$D$_6$ at RT.

**Figure S12.** $^{31}$P($^1$H) NMR spectrum of 4 in C$_6$D$_6$ at RT.
Figure S13. $^{31}$P NMR spectrum of 4 in C$_6$D$_6$ at RT.

Figure S14. $^{31}$P NMR spectrum of 4 (crude) in C$_6$D$_6$ at RT.
Figure S15. $^1$H NMR spectrum of 5 in C$_6$D$_6$ at RT.

Figure S16. $^{13}$C($^1$H) NMR spectrum of 5 in C$_6$D$_6$ at RT.
**Figure S17.** $^{31}$P NMR spectrum of 5 in C$_6$D$_6$ at RT.

**Figure S18.** $^1$H NMR spectrum of 5 after 15 hrs. vacuum in C$_6$D$_6$ at RT.
Figure S19. $^{31}$P($^1$H) NMR spectrum of 5 after 15 hrs. vacuum in C$_6$D$_6$ at RT.

Figure S20. Variable temperature $^{31}$P-NMR spectra of 5.
**Figure S21.** Variable temperature $^{31}$P-NMR spectra for the reaction of 5 and NHC$^{\text{ipr}_2\text{Me}_2}$.

**Figure S22.** $^1$H NMR of Reaction of 5 with NHC$^{\text{ipr}_2\text{Me}_2}$ (1:1 molar ratio) in THF-$d_8$ at RT.
Figure S23. $^{31}$P($^1$H) NMR from the 1:1 reaction of 5 with NHC$_{^2}$Pr$_2$Me$_2$ in THF-d$_8$ at RT.

Figure S24. $^1$H NMR spectrum of 6 (reaction NHC$_{^2}$Pr$_2$Me$_2$ with CO$_2$) in THF-d$_8$ at RT.
Figure S25. $^1$H NMR spectrum of 1:1 mixture of 3 and HCO$_2$H in C$_6$D$_6$ at RT.

Figure S26. $^{31}$P NMR spectrum of 1:1 mixture of 3 and HCO$_2$H in C$_6$D$_6$ at RT.
Figure S27. $^{13}$C$\textsuperscript{1}$H NMR spectrum of 1:1 mixture of 3 and HCO$_2$H in C$_6$D$_6$ at RT.
**UV/vis Spectra**

*Figure S28.* UV/vis spectrum of compound 2 in THF.

*Figure S29.* Linear regression of compound 2 at 402 nm.
Figure S30. Linear regression of compound 2 at 332 nm.

Figure S31. Linear regression of compound 2 at 252 nm.
Figure S32. UV/vis spectrum of compound 3 in THF.

Figure S33. Linear regression of compound 3 at 320 nm.
**Crystallographic Details**

Single crystal X-ray data of **2-toluene, 3-benzene, 4-n-hexane, and 5-toluene** were collected at 120 K using a Rigaku XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite-monochromated Mo Kα radiation, \( \lambda = 0.71073 \) Å. The unit cell parameters and the data reduction was obtained with the CrysAlisPro software from Rigaku Oxford Diffraction.\(^{[54]}\) A multi-scan absorption correction was applied to the collected reflections during data processing with SCALE3 ABSPACK also integrated in the CrysAlisPro software.\(^{[55]}\) The structure was solved by SHELXT\(^{[55]}\) structure solution program using Intrinsic phasing and refined by full matrix least-squares method based on \( F^2 \) using SHELXL\(^{[56]}\) refinement programme in the Olex-2 software.\(^{[57]}\) All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogens were placed in geometrically calculated positions or found in the Fourier difference map and include in the refinement process using riding model. The program Diamond (version 3.2k) is used for creating the crystallographic figures.\(^{[58]}\)
**Table S1.** Crystal data and structure refinement for 2-toluene (CCDC: 1870010)

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| **Empirical formula**           | C₆₂H₇₀AuClN₂P₂                             |
| **Formula weight**              | 1137.55                                    |
| **Temperature/K**               | 120(2)                                     |
| **Crystal system**              | monoclinic                                 |
| **Space group**                 | P₂₁/c                                      |
| a/Å                            | 14.3181(2)                                 |
| b/Å                            | 15.9475(2)                                 |
| c/Å                            | 23.9841(3)                                 |
| α/°                            | 90.0000(10)                                |
| β/°                            | 90.0000(10)                                |
| γ/°                            | 89.9980(10)                                |
| Volume/Å³                       | 5476.48(12)                                |
| Z                              | 4                                          |
| ρ<sub>calc</sub>/g/cm³          | 1.380                                      |
| μ/mm⁻¹                         | 2.833                                      |
| F(000)                         | 2328.0                                     |
| Crystal size/mm³               | 0.23 × 0.18 × 0.14                         |
| Radiation                      | MoKα (λ = 0.71073)                         |
| 2θ range for data collection/° | 5.108 to 52.998                            |
| Index ranges                   | -16 ≤ h ≤ 17, -15 ≤ k ≤ 20, -30 ≤ l ≤ 29 |
| Reflections collected          | 86138                                      |
| Independent reflections        | 11311 [R<sub>int</sub> = 0.0613, R<sub>σ</sub> = 0.0366] |
| Data/restraints/parameters      | 11311/0/629                                |
| Goodness-of-fit on F²          | 1.020                                      |
| Final R indexes [I>=2σ (I)]    | R<sub>1</sub> = 0.0255, wR<sub>2</sub> = 0.0729 |
| Final R indexes [all data]     | R<sub>1</sub> = 0.0348, wR<sub>2</sub> = 0.0913 |
| Largest diff. peak/hole / e Å⁻³ | 0.66/-0.96                                |
| **Identification code** | AJ0633 |
|------------------------|--------|
| **Empirical formula**  | C₆₁H₆₉AuN₂P₂ |
| **Formula weight**     | 1089.08 |
| **Temperature/K**      | 120.01(10) |
| **Crystal system**     | monoclinic |
| **Space group**        | P2₁/c |
| **a/Å**                | 13.8790(3) |
| **b/Å**                | 15.8269(3) |
| **c/Å**                | 24.1162(5) |
| **α/°**                | 90 |
| **β/°**                | 90.637(2) |
| **γ/°**                | 90 |
| **Volume/Å³**          | 5297.07(19) |
| **Z**                  | 4 |
| **ρ<sub>calc</sub>/g/cm³** | 1.366 |
| **μ/mm⁻¹**             | 2.877 |
| **F(000)**             | 2232.0 |
| **Crystal size/mm³**   | 0.13 × 0.12 × 0.11 |
| **Radiation**          | MoKα (λ = 0.71073) |
| **2θ range for data collection/°** | 5.142 to 58.09 |
| **Index ranges**       | -18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -32 ≤ l ≤ 32 |
| **Reflections collected** | 74584 |
| **Independent reflections** | 12757 [R<sub>int</sub> = 0.0572, R<sub>sigma</sub> = 0.0555] |
| **Data/restraints/parameters** | 12757/0/623 |
| **Goodness-of-fit on F²** | 1.027 |
| **Final R indexes [I>2σ (I)]** | R₁ = 0.0403, wR₂ = 0.0701 |
| **Final R indexes [all data]** | R₁ = 0.0667, wR₂ = 0.0757 |
| **Largest diff. peak/hole / e Å⁻³** | 1.49/-0.83 |
**Table S3.** Crystal data and structure refinement for 4-**n**-hexane (CCDC: 1904676)

| Property                           | Value                                      |
|------------------------------------|--------------------------------------------|
| Identification code                | AJ0770                                     |
| Empirical formula                  | C₅₈H₇₀AuN₂P₂                               |
| Formula weight                     | 1054.06                                    |
| Temperature/K                      | 120.00(10)                                 |
| Crystal system                     | monoclinic                                 |
| Space group                        | P2₁/c                                      |
| a/Å                                | 10.6030(4)                                 |
| b/Å                                | 19.5623(8)                                 |
| c/Å                                | 25.2437(9)                                 |
| α/°                                | 90                                         |
| β/°                                | 91.738(4)                                  |
| γ/°                                | 90                                         |
| Volume/Å³                          | 5233.6(3)                                  |
| Z                                  | 4                                          |
| \( \rho_{\text{calc}} \)/g/Å³     | 1.338                                      |
| \( \mu \)/μmol/Å²                  | 2.910                                      |
| F(000)                             | 2164.0                                     |
| Crystal size/mm³                   | 0.16 × 0.14 × 0.12                         |
| Radiation                          | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°     | 5.27 to 58.78                              |
| Index ranges                       | -12 ≤ h ≤ 13, -21 ≤ k ≤ 26, -27 ≤ l ≤ 34  |
| Reflections collected              | 20607                                      |
| Independent reflections            | 10378 [R_{int} = 0.0339, R_{sigma} = 0.0533] |
| Data/restraints/parameters         | 10378/0/589                                |
| Goodness-of-fit on \( F^2 \)       | 1.029                                      |
| Final R indexes [I>2σ(I)]          | \( R_1 = 0.0341, wR_2 = 0.0724 \)          |
| Final R indexes [all data]         | \( R_1 = 0.0481, wR_2 = 0.0766 \)          |
| Largest diff. peak/hole / e Å³     | 2.00/-0.69                                 |

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### Table S4. Crystal data and structure refinement for 5-toluene (CCDC 1904668)

| Property                        | Value                              |
|---------------------------------|------------------------------------|
| Identification code             | AJ0730                             |
| Empirical formula               | C$_{63}$H$_{71}$AuN$_2$O$_2$P$_2$   |
| Formula weight                  | 1147.12                            |
| Temperature/K                   | 120.00(10)                         |
| Crystal system                  | monoclinic                         |
| Space group                     | P2$_1$/c                            |
| a/Å                             | 14.3397(6)                         |
| b/Å                             | 16.2736(8)                         |
| c/Å                             | 23.7035(9)                         |
| α/°                             | 90                                 |
| β/°                             | 89.974(4)                          |
| γ/°                             | 90                                 |
| Volume/Å$^3$                    | 5531.4(4)                          |
| Z                               | 4                                  |
| $\rho_{\text{calc}}$/cm$^3$     | 1.377                              |
| μ/mm$^{-1}$                     | 2.762                              |
| F(000)                          | 2352.0                             |
| Crystal size/mm$^3$             | 0.14 × 0.13 × 0.11                 |
| Radiation                       | MoKα (λ = 0.71073)                 |
| 2Θ range for data collection/* | 5.006 to 50.054                    |
| Index ranges                    | -17 ≤ h ≤ 16, -19 ≤ k ≤ 17, -28 ≤ l ≤ 28 |
| Reflections collected           | 54133                              |
| Independent reflections         | 9628 [R$_{\text{int}}$ = 0.0809, R$_{\text{sigma}}$ = 0.0539] |
| Data/restraints/parameters      | 9628/0/643                         |
| Goodness-of-fit on F$^2$        | 1.066                              |
| Final R indexes [I>2σ (I)]      | R$_1$ = 0.0488, wR$_2$ = 0.1136     |
| Final R indexes [all data]      | R$_1$ = 0.0685, wR$_2$ = 0.1255     |
| Largest diff. peak/hole / e Å$^3$| 3.75/-2.25                        |
**Computational Details**

All electronic structure calculations in this article are performed using Gaussian16 package.\cite{59} All molecular geometries are optimized using B3LYP\cite{510,512} exchange-correlation functional. To account for the non-covalent interactions, Grimme’s D3 dispersion model is employed.\cite{513} We have used 6-31G(d) basis set for the lighter atoms (C, H, N, O, P, Cl) and LANL2DZ basis set along with the corresponding effective core potential for Au and Ni. This basis set combination is hereafter denoted as BS1. A harmonic vibrational frequency analysis is performed on each optimized structure to characterize the nature of the stationary points as local minima. To further refine the electronic energies, single point calculations are carried out using M062X-D3 exchange-correlation functional along with 6-31+G(d,p) basis set for lighter atoms (H, C, N, O, P) and SDD basis set paired with the corresponding pseudopotential for Au.\cite{513,515} This basis set combination is hereafter denoted as BS2. Solvent (toluene) effects are taken into account using SMD solvation model by Truhlar and Cramer.\cite{516} All thermochemical data are estimated within ideal gas-rigid rotor-simple harmonic oscillator approximations at 298.15 K and 1 atm pressure. All free energy values include electronic energies at the M062X-D3/BS2//B3LYP-D3/BS1 level of theory.

**Computational Results**

Our computational results are summarized in the following points,

The donor strength of $1\cdot$NHC$_{Me}^{4}$ has been estimated by calculating its Tolman electronic parameter (TEP), which is determined from the carbonyl stretching (A1) mode of corresponding Ni(CO)$_3$ complex. The calculated TEP values for $1\cdot$NHC$_{Me}^{4}$ is computed to be lower than Ph$_3$P (2127.4 vs. 2150.6 cm$^{-1}$), suggesting that the former is a stronger donor compared to the latter one.

In order to compare the stabilities of $1\cdot$NHC$_{Me}^{4}$ and $2$, we have calculated the dissociation free energy (Table S5) of NHC$_{Me}^{4}$ from both the complexes $1\cdot$NHC$_{Me}^{4}$ and $2$ in THF at 298.15 K. Our results suggest that dissociation of the NHC$_{Me}^{4}$ from $2$ is thermodynamically less favored compared to that from $1$, which is agreement with the experimental observation.
Table S5. Calculation of dissociation free energy.

| Reactions                              | $\Delta G_{298}$ (in kcal/mol) |
|----------------------------------------|---------------------------------|
| $1 \cdot $NHC$_{Me}^4 \rightarrow 1 + $NHC$_{Me}^4$ | 6.7                            |
| $2 \rightarrow 1 \cdot $AuCl + $NHC_{Me}^4$        | 21.8                           |

We have computed the binding energies (BEs) of various phosphine, diphosphene and NHC-coordinated diphosphenes with $\text{AuCl}$ for comparison purposes. The binding energies are calculated at the M062X-D3/BS2//B3LYP-D3/BS1 level.

Table S6. Calculation of binding energies.

| Structures                              | Binding energies with $\text{AuCl}$ (in kcal/mol) |
|-----------------------------------------|---------------------------------------------------|
| I (R = Ph)                              | -50.1                                             |
| II (R=Ar; Ar = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$) | -38.5                                             |
| III (R=Ar; Ar = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$ and NHC = NHC$_{Me}^4$) | -55.8                                             |
| IV (R = Ar; Ar = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$ and NHC = NHC$_{Me}^4$) | -61.1                                             |
**Figure S34.** Frontier molecular orbitals of the compound 2.

**Figure S35.** Calculated P-Au σ-NBO in 2 (28.3 % of Au and 71.7% of P).
**Figure S36.** Frontier molecular orbitals of the compound 3.

![HOMO and LUMO of compound 3](image)

**Figure S37.** Frontier molecular orbitals of the compound 4.

![HOMO and LUMO of compound 4](image)

**Figure S38.** Frontier molecular orbitals of the compound 5.

![HOMO and LUMO of compound 5](image)
Figure S39. Frontier molecular orbitals of the compound 7.

Table S7. Absolute energies of the computed structures.

| Structures | \( E_0 \) | \( E_{sp} \) |
|------------|---------|---------|
| 1\( \cdot \)NHC\(^{\text{Me}}_4 \) | -2925.6309778 | -2924.56298012 |
| NHC\(^{\text{Me}}_4 \) | -383.447574535 | -383.282680268 |
| 1 | -2542.13975809 | -2541.235268 |
| III | -1654.55052933 | -1653.93161021 |
| 3 | -3061.70890129 | -3060.7989476 |
| 5 | -3250.32773185 | -3249.35973837 |
| CO\(_2\) | -188.581128851 | -188.515859976 |
| 4 | -3061.74793815 | -3060.83316075 |
| NHC\(^{\text{Pr}}_2\text{Me}_2\) | -540.724875861 | -540.476632326 |
| NHC\(^{\text{Pr}}_2\text{Me}_2\)\(\cdot\)CO\(_2\) | -729.330352279 | -729.013534792 |
| HCO\(_2\)H | -189.756476718 | -189.693463031 |
| H\(_2\) | -1.1754824296 | -1.16735772928 |
| 1\( \cdot \)AuCl | -3137.85902934 | -3137.08448356 |
| III\( \cdot \)AuCl | -2250.30134796 | -2249.80836895 |
| AuCl | -595.661038001 | -595.787825833 |
| 2 | -3521.38239565 | -3520.44812879 |
| PPh\(_3\) | -1036.32939613 | -1036.00157363 |
| PPh\(_3\)\(\cdot\)AuCl | -1632.07679328 | -1631.86917626 |
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