Cycloaddition of 1,1,3,3-Tetramethyl-disiloxane to Alkynes with [Au]/TiO$_2$

\[
R^1\equiv\equiv R^2 + \text{TMDS} \overset{[\text{Au}]/\text{TiO}_2 (0.3 \text{ mol\% Au}), \text{CH}_2\text{Cl}_2, 25 \degree \text{C}}{\text{[eq. 1]}} \overset{\text{time}}{\rightarrow} R^1\equiv\equiv R^2
\]

Selected examples:

- \(2a\) (30 min, 84\% isolated yield)
- \(2b\) (40 min, 99\% isolated yield)
- \(2c\) (40 min, 96\% isolated yield)
- \(2d\) (40 min, 81\% isolated yield)
- \(2e\) (20 min, 85\% isolated yield)
- \(2f\) (20 min, 91\% isolated yield)
- \(2g\) (30 min, 98\% isolated yield)
- \(2h\) (30 min, 72\% isolated yield)
- \(2i\) (1 h, 87\% isolated yield)
- \(2j\) (40 min, 78\% isolated yield)
- \(2k\) (1 h, 42\% isolated yield)
- \(2l\) (24 h, 88\% isolated yield)

Proposed reaction pathway:

\[
\text{[eq. 2]}
\]

**Significance:** TiO$_2$-supported gold nanoparticles ([Au]/TiO$_2$) catalyzed the oxidative cycloaddition of 1,1,3,3-tetramethyl-disiloxane (TMDS) to alkynes \(1\) to give the corresponding cycloadducts \(2\) in up to 99\% isolated yield (22 examples, eq. 1).

**Comment:** The authors proposed a reaction pathway for the present oxidative cycloaddition as follows (eq. 2): (1) oxidative addition of TMDS to [Au] giving \(\text{H}[-\text{Au}]-\text{Me}_2\text{SiOSiMe}_2\text{Me} (\text{A})\); (2) insertion of alkynes \(1\) into the Si–Au bond forming gold adducts \(B\); (3) intramolecular elimination of \(\text{H}_2\) and [Au] to give cycloadducts \(2\).