Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supporting Information

Mechanistic examination of Au^{III}-mediated 1,5-enyne cycloisomerization by $AuBr_2$(*N*-imidate)(NHC) / AgX precatalysts – is the active catalyst Au^{III} or Au^{I}?

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Additional NMR spectroscopic investigations

The spectral data for the additional NMR spectroscopic investigations mentioned in the paper are detailed below.

Reaction of $AuBr_2$(*N*-TFS)(I^tPe) with AgOTf in acetone-d_6

The ^{19}F NMR spectroscopic data mentioned in the paper is given below (the ^{1}H NMR spectroscopic data is given in the paper, Figure 7).

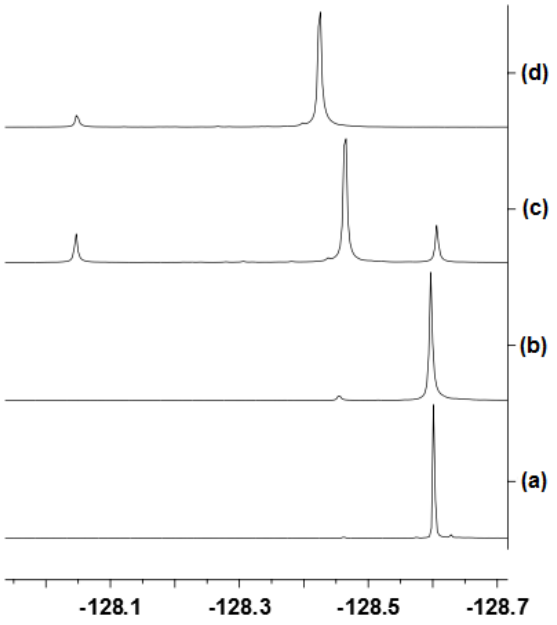

Figure S1. ^{19}F NMR spectroscopic analysis of the reaction of $AuBr_2$(*N*-TFS)(I^tPe) with AgOTf in acetone-d_6 over time. Key: (a) $AuBr_2$(*N*-TFS)(I^tPe) in acetone-d_6 (reference spectrum); (b) $AuBr_2$(*N*-TFS)(I^tPe) + AgOTf (1:1) after 10 mins; (c) as for (b) after 4.5 h; (d) as for (b) after 22.5 h

Comment: the ^{19}F signal seen evolving at δ -128.46 corresponds to Au(*N*-TFS)(I^tPe) {spectrum (d)}. A second minor signal at δ -128.1 ppm, which may relate to free tetrafluorosuccinimidate (or *N*-bromotetrafluorosuccinimide), was observed. This signal has a maximum intensity after 4.5 h {spectrum (c)}, and then is reduced after 22.5 h. A possible explanation is that the free ligand recombined with $[Au(I^tPe)]^+$ to form Au(*N*-TFS)(I^tPe) {or exchanged with $[Au(I^tPe)Br]$}. This

would suggest that reduction of $AuBr_2$(*N*-TFS)(I^tPe) to Au(*N*-TFS)(I^tPe) occurs *via* loss of tetrafluorosuccinimidate anion or *N*-bromotetrafluorosuccinimidate. A small amount of hydrolysed tetrafluorosuccinimidate was also observed in these ^{19}F NMR spectra.

Reaction of $AuBr_2$(*N*-TFS)(I^tPe) with Ag[Al(OC(CF_3)$_3$)$_4$] in acetone-d_6

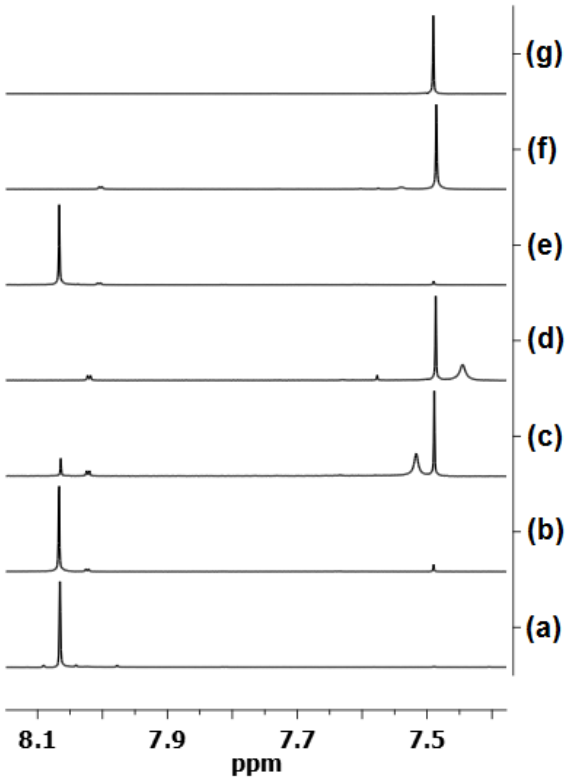

Figure S2. Stacked ^1H NMR spectra (expanded section) showing the reaction of $AuBr_2$(*N*-TFS)(I^tPe) with Ag[Al(OC(CF_3)$_3$)$_4$] in acetone-d_6 over time (monitoring the I^tPe imidazole proton signal by ^1H NMR spectroscopy, referenced to the residual acetone solvent signal at δ 2.05). Key: (a) $AuBr_2$(*N*-TFS)(I^tPe) in acetone-d_6 (reference spectrum); (b) $AuBr_2$(*N*-TFS)(I^tPe) + Ag[Al(OC(CF_3)$_3$)$_4$] (1:1) after 10 mins; (c) as for (b) after 7 h; (d) as for (b) after 24 h; (e) comparison of reaction of $AuBr_2$(*N*-TFS)(I^tPe) with AgOTf after 10 mins; (f) as for (e) after 22.5 h; (g) Au(*N*-TFS)(I^tPe) in acetone-d_6 (reference spectrum).

Comment: The reaction afforded Au(*N*-TFS)(I^tPe) and a new broad signal at slightly higher chemical shift {δ 7.52; spectrum (c)}, which is suggested to be [Au(κ^1-O=CMe_2)(I^tPe)]$^+$[Al(OC(CF_3)$_3$)$_4$]$^-$. This broad signal does move up-field after 24 h {spectrum (d)}.

Reaction of $AuBr_2$(*N*-TFS)(I^tPe) with AgOTf and varying equivalents of 1-hexene

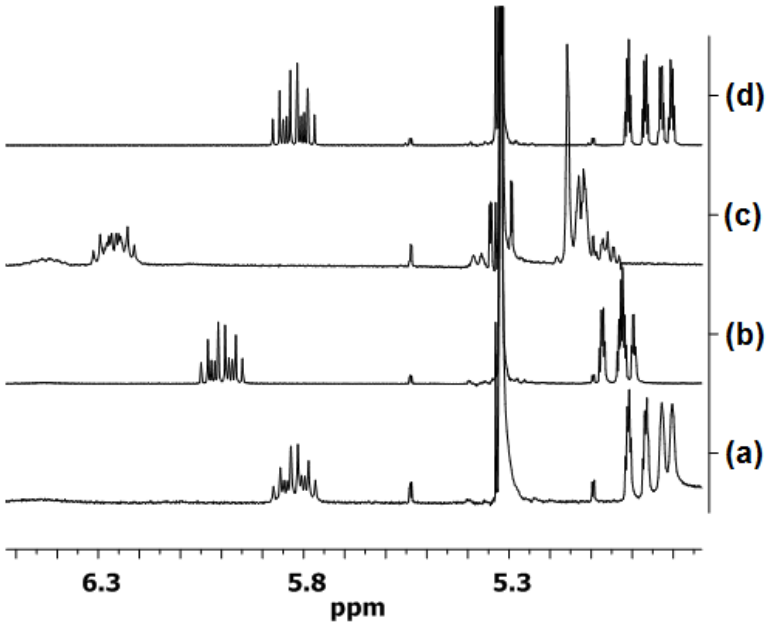

Figure S3. Stacked ^{1}H NMR spectra (expanded section) showing the reaction of $AuBr_2$(*N*-TFS)(I^tPe) with AgOTf (1 equiv.) and varying equivalents of 1-hexene over time in CD_2Cl_2 (referenced to the residual $CDHCl_2$ solvent signal at 5.31 ppm). Key: (a) $AuBr_2$(*N*-TFS)(I^tPe) / AgOTf with 2 equivalents of 1-hexene after 24 h; (b) $AuBr_2$(*N*-TFS)(I^tPe) / AgOTf with 2 equivalents of 1-hexene after 10 mins; (c) $AuBr_2$(*N*-TFS)(I^tPe) / AgOTf with 1 equivalent of 1-hexene after 10 mins; (d) 1-hexene alone in CD_2Cl_2.

Comment: No binding of 1-hexene to the neutral Au^{III} imidate complexes occur in the absence of AgOTf. $AuBr_2$(*N*-TFS)(I^tPe) / AgOTf (1:1) in the presence of 1 equivalent of 1-hexene shows no change in the imidazole signal but the alkene signals are shifted downfield (*ca.* 0.44 ppm, *spectrum c*). Also, another species is detected in this spectrum (visible against the baseline at *ca.* 6.4-6.5 ppm); other minor proton signals accompany this signal at *ca.* 4.9-5.4 ppm). The reaction of 2 equivalents of 1-hexene shows a smaller shift in the alkene signals shift (*ca.* 0.18 ppm), with little change in spin-spin coupling constants relative to free 1-hexene (after 10 mins, *spectrum b*). After 24 h the proton signals are closer to free 1-hexene, but broad (compare *spectrum a* with *spectrum d*). In control tests it was found that 1-hexene can bind AgOTf independently.