A Highly Asymmetric Gold(III) η³-Allyl Complex

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Abstract: A highly asymmetric Au(III) η³-allyl complex has been generated by treating Au(η³-allyl)Br(tpy) (tpy = 2-(p-tolyl)-pyridine) with AgNTf₂. The resulting η³-allyl complex has been characterized by NMR spectroscopy and X-ray crystallography. DFT calculations and variable temperature ¹H NMR suggest that the allyl ligand is highly fluxional.

Transition-metal allyl complexes have been thoroughly studied and are key intermediates in a variety of metal-catalysed organic reactions, such as the widely used Pd-catalysed Tsuji–Trost reaction which in one step gives access to highly functional compounds via nucleophilic addition to the η¹ allyl in a regio- and stereospecific manner.[1–2] Despite that the allyl ligand is one of the classical unsaturated, delocalized ligands in organometallic chemistry, Au(III) η¹-allyl complexes have been rarely described in the literature. There are a couple of reports on DFT calculations of such complexes and one experimental study in the gas phase using mass spectrometry techniques.[3,4] A few Au(III) η¹ allyl complexes[5] have been reported together with a handful of Au(I) η¹-allyl complexes.[6] Herein, we report for the first time the generation and full characterization of an isolable Au(III) η³-allyl complex.

Treatment of Au(OAc)₃(tpy) (1; OAc⁻ = OCOCH₃) with allylmagnesium bromide according to our previously developed methodology[7] led to the formation of Au(η³-allyl)Br-

(tpy) (2), with the allyl group trans to tpy-N (Scheme 1, left). Complex 2 was obtained in 52–69% yield and characterized by NMR, MS, elemental analysis and X-ray diffraction analysis.[13] The characteristic resonances of the protons on the allyl ligand are observed in the ¹H NMR spectrum of 2; the three vinylic signals are found at δ = 6.28 (H₂, see labelling in Scheme 1), 5.48 (H¹), and 5.02 (H³). The two allylic hydrogens H² are chemically equivalent and give rise to one resonance at δ 3.39. A ¹H–¹H NOESY experiment established that the η³ allyl ligand is located trans to tpy-N; a NOE is observed between H¹ and H³, H¹, and H³ (Figure 1).

Addition of AgNTf₂ to a CdCl₂ solution of 2 led to the formation of Au(η³-allyl)(tpy) (3) as the major product (Scheme 1, right), together with traces of what appeared to be a decomposition product. Complex 3 was characterized by NMR and X-ray diffraction analysis.[13] A comparison of the ¹H NMR spectra of 3 and 2 (Table 1 and Supporting Information) shows that H⁴ and H⁵ are found at higher chemical shift in 3 compared to in 2 (Δδ = 0.22 (H⁴) and 0.66 (H⁵)), whereas H⁶ is observed at a lower δ (Δδ = −0.18). The two H⁶ are found at a higher chemical shift (Δδ = 0.41).

Complex 3 can be described by the two Lewis (resonance) structures 3a and 3b (Scheme 1). The ¹H NMR data, however, suggest the prevalence of one structure over the other; three protons are observed in the vinylic region (H⁴, H⁵, and H⁶; see Table 1) and the two H⁶ are found at a significantly lower ppm value. This is rather unusual for η³ allyl complexes; normally the anti protons (defined relative to the central proton which is usually found at around δ = 6.5; H⁴ in complex 3) are found at δ = 1–3, whereas the syn protons are found at larger ppm values, around δ = 2–5.[12]

Furthermore, there is only a small increase (by 14 Hz) in ¹J(H⁴–C⁵) going from 2 to 3 (Table 1) indicating that the sp³ hybridization of C⁵ remains essentially unchanged. This result also agrees with the thermodynamic preference of having the high trans influence C(sp³) end of the allyl ligand trans to the lower trans influence ligand tpy-N, instead of the higher trans influence tpy-C, and leads us to infer the structural preference of 3a over 3b. In symmetric η³-allyl complexes the syn and anti H⁶ protons usually give rise to two distinct signals. However, if double bond decodination[9] followed by rotation around the MCH₂–CHCH₃ bond and re-coordination occurs relatively fast on the NMR time scale, the resonances for these two protons will coalesce into one averaged resonance. The fact that a coalesced signal is seen for the two H⁶, but not for H⁴ and H⁵, suggests that double bond decodination/recoordination of the η³-allyl ligand occurs selectively trans to the tpy-C atom in 3a. No evidence is seen in the NMR spectra for an analogous process starting from Lewis structure 3b which would lead to a coalescence of the resonances of H⁴ and H⁵. This supports the notion that
Scheme 1. Top: Generation of AuI and η1-allyl complexes 2 and 3. Bottom: Crystallographic structure determination of 2 (left).[13] Owing to twinning and disorder limiting the high-resolution diffraction in the measured crystal, only Au and Br are refined as thermal ellipsoids (set at 50% probability). ORTEP plot of the cationic part of complex 3 with thermal ellipsoids set at 50% probability (right). Selected bond lengths [Å] and bond angles [°] for 2: Au1–N1 = 2.11(3), Au1–C1 = 2.02(4), Au1–C2 = 2.10(4), Au1–Br1 = 2.493(5), C2–C3 = 1.41(5), C3–C4 = 1.31(5); Br1–Au1–N1 = 95.0(9), N1–Au1–C1 = 81.7(15), C1–Au1–C2 = 94.9(16), C2–Au1–Br1 = 88.7(12). Selected bond lengths [Å] and bond angles [°] for 3: Au1–N1 = 2.119(16), C1–Au1–C2 = 84.9(16), C2–Au1–Br1 = 88.7(12). Selected DFT optimized bond lengths [Å] and bond angles [°] for 3: Au1–N1 = 2.119(16), Au1–C1 = 2.021(4), Au1–C2 = 2.129(5), C2–C3 = 1.42(5), C3–C4 = 1.32(5); Br1–Au1–N1 = 95.0(9), N1–Au1–C1 = 81.7(15), C1–Au1–C2 = 94.9(16), C2–Au1–C4 = 65.2(8). Selected bond lengths [Å] for 3a and bond angles [°] for 3b: Au1–N1 = 2.119(16), Au1–C1 = 2.021(4), Au1–C2 = 2.129(5), C2–C3 = 1.42(5), C3–C4 = 1.32(5); Br1–Au1–N1 = 95.0(9), N1–Au1–C1 = 81.7(15), C1–Au1–C2 = 94.9(16), C2–Au1–C4 = 65.2(8).

Figure 1. Depiction of selected 1H–1H NOE correlations of complexes 2 and 3.

Table 1: δ(H) and J(H,13C) data for the allylic groups of complexes 2[a] and 3[b] in CDCl3.

| Atom | δ(H) | J(H,13C) |
|------|------|----------|
| H[a] | 3.39 | 142 Hz   |
| H[b] | 6.28 | 154 Hz   |
| H[c] | 5.48 | 154 Hz   |
| H[d] | 5.02 | 158 Hz   |

[a] Measured at 600 MHz (ca. 27°C). [b] Measured at 800 MHz (ca. 28°C). Δδ = δ(3) – δ(2). Coupling constants were measured from a nondecoupled 1H–13C HMBC experiment.

resonance structure 3b is a minor contributor due to the unfavourable trans relationship between the C(sp3) end of the allyl group and the coordinating tpy-C atom.

The structure and dynamic behaviour of 3 were explored by DFT calculations at the PBE0 level, including solvation by dichloromethane (see Supporting Information for computational details). The optimized structure shows inequivalent C–C bonds in the allyl ligand of 1.438 Å and 1.382 Å for C2–C3 and C3–C4, respectively, in agreement with 3a as the predominant Lewis structure (Scheme 1). Double bond decoordination to furnish an η1-allyl species occurred favourably only trans to the coordinating tpy-C atom and led to two structures with the empty coordination site trans to the tpy-C atom and the η1-allyl trans to the tpy-N atom (4, 12.3 kcal mol−1, and 5, 11.9 kcal mol−1, Scheme 2). Interestingly, two different TSs of similar energies (TS3–4 and TS5–3) were located connecting these two η1 allylic intermediates with enantiomers 3 and 3’, indicating the existence of two TSs for the double bond decoordination. Starting from a given enantiomer, these TSs correspond to clockwise and counterclockwise rotations of the Au–C bond (see ESI). The two η1-allyl intermediates 4 and 5 are also connected by a TS involving rotation of the α(C2–C3) bond (TS4–5). The energy associated with this TS (17.7 kcal mol−1) is the highest in the computed energy landscape that facilitates the exchange of H’ and H”, with barriers that are consistent with a process that occurs at room temperature.

The process described in Scheme 2 (red pathway) involves the interconversion of one enantiomer of 3 to its enantiomeric counterpart (3’) via a chiral pathway. It has been argued[10] that such a process is not in violation of the principle of microscopic reversibility provided that there exists a degenerate alternative pathway, of opposite chirality but energetically degenerate to the first one (see Supporting Information). Burke and co-workers[11] recently reported metallacycle ring inversions that were suggested to occur by chiral, degenerate
pathways. Interestingly, the interconversion of the enantiomers 3 and 3′ by this pathway does not involve a C₅ symmetric intermediate or transition state which might be considered to arise from double bond decoordination and Au-C and C-C bond rotations. Optimization of the η¹-allyl geometry within C₅ symmetry constraints leads to a C₅ symmetric TS at 17.9 kcal mol⁻¹ (blue pathway, Scheme 2). This transition state was found to directly connect 3 and 3′. The similar energies obtained for the symmetric pathway and the chiral one (Scheme 2) suggest the co-existence of the two pathways at the experimental conditions.

Complex 3 slowly decomposes at ambient temperature and complete NMR characterization was therefore performed at 7°C. The resonances of H¹, H², and H³, as well as several of the ¹³C NMR resonances are broadened at this temperature (see Supporting Information). The temperature-dependent broadening phenomena in the ¹H and ¹³C NMR spectra further support the dynamic behaviour of the allyl ligand on the NMR time scale. Selected key ¹H-¹H NOE correlations in complex 3 are depicted in Figure 1. A NOE between H⁴ and H⁵ is observed, which is not observed in complex 2, indicating a coordination of the double bond to Au, trans to the tpy-C atom. In contrast, H⁴ (bonded to the same C as H⁵) shows a NOE with H⁵, but upon increasing the intensity of the peaks in the NOESY spectrum, what appears to be a weak NOE between H⁴ and H⁵ becomes visible. These observations might indicate that 3, with the allyl ligand bound in an η¹ fashion, interconverts to the corresponding η¹-allyl complex during the time scale of the NMR experiment, as depicted in Scheme 2.

Assuming the behaviour depicted in Scheme 2, a further slowing of the process by lowering the temperature will cause the resonance of the two H⁴ to split into two signals. Thus, the temperature further, the resonance of H⁴ undergoes de-coalescence and eventually emerges as three resonances. At −55.5°C these are significantly broadened and are barely discernible as three featureless, broadened distortions of the baseline. At −79.2°C these resonances, at δ = 4.26, 3.82, and 3.09, are sharper and integrate for approximately 1H, 1H, and 2H, respectively (see the spectrum at the bottom of Figure 2 and Supporting Information). At this temperature, two resonances are also observed for H⁶ (each integrating for ca. 1H), whereas the signals of H⁷ and H⁸ each appear as one broadened resonance (ca. 2H each). Furthermore, two sets of peaks for most of the resonances of the tpy ligand are observed (see Supporting Information). The broadening/coalescence behaviour is reversible, as evidenced by the restoration of signals upon sample heating. Based on these observations it is suggested that there is an interconversion between the η¹-allyl complexes 3 and 3′, and the η¹-allyl complexes 4 and 5 (perhaps with NTf₂ or solvent coordinated trans to the tpy-C atom) in solution (Scheme 2). At −79.2°C, this process is slow enough to enable the detection of coexisting η¹(3/3′) and η¹(4/5, with an eventuated coordinated...
counteranion or solvent molecule) forms by 1H NMR spectroscopy. In an η1-allyl complex, the two H atoms are chemically equivalent, and therefore it is suggested that the resonance at δ = 3.09 arises from such a complex; this chemical shift is slightly lower than that observed for the two chemically equivalent H atoms in the η1-allyl complex 2 (δ = 3.39) and nearly the same as that in [Au(η1-allyl)(CD3CN)(tpy)]+–[NTf2]– (δ = 3.12, see Supporting Information). The resonances at δ = 4.26 and 3.82 are thus assigned to η1-allyl complex 3.

Based on the findings from low-temperature NMR spectroscopy, what is observed by 1H NMR spectroscopy at room temperature is not strictly an η1-allyl complex, but rather the averaged signals arising from the η1-η1-η1 interconversions whereby complex 3 interconverts to and equilibrates with an η1-allyl complex.

The DFT free energies obtained for intermediates 4 and 5 do not account for the existence of η1 allyl intermediates in solution. However, upon coordination of NTf2 at Au (4-NTf2 and 5-NTf2, see Supporting Information), the species became almost isoenergetic to the η1-allyl complex 3 (ΔG = −3.6 kcal mol⁻¹).[13] Therefore, the equilibrium observed in solution may involve coordination and decoordination of NTf2 (see Figure S33).

Crystallographic structure determination of complexes 2 and 3 were performed and selected parameters are given in Scheme 1. As can be seen from Scheme 1, complex 2 is an η1-allyl complex with the allyl trans to the tpy-N atom and Br trans to the coordinating tpy-C atom, in full agreement with the NMR data. In complex 3, the double bond of the allyl has coordinated trans to tpy-C to form an η1-allyl complex as depicted in Scheme 1.

In 3, the C(sp3) end of the allyl ligand (C2) is more tightly bound to Au than the C(sp2) C–C carbon atoms (C3 and C4) with Au–C bonds of 2.062(19), 2.21(2) and 2.23(2) Å, respectively, indicative of a highly asymmetric allyl complex which is best described by Lewis structure 3a and not 3b.

The allyl ligand in 3 is more asymmetrically bonded than what is seen in related PdII(NC) cyclometalated complexes reported previously[12] (where the chelate N is a pyridine-N atom, and the chelate C is either an aryl-C or a NH-C atom), with Pd–allyl bonds of 2.105(5)/2.095(4) Å (Pd–C2), 2.135(5)/2.152(4) Å (Pd–C3) and 2.257(5)/2.225(5) Å (Pd–C4). In addition, in complex 3, the DFT determined C2–C3 distance is significantly longer than C3–C4 (1.438 vs. 1.382 Å), again indicating an asymmetric allyl complex. The distances are taken from DFT calculations because the experimental C–C bond lengths of the allyl ligand have a high uncertainty due to the absence of high resolution diffraction signals, probably originating from disorder and twinning in the crystals. However, the differences in crystallographically determined bond lengths are still significant. DFT calculations were also used to determine the geometry expected for the isoelectronic, neutral complex Pt(η1-allyl)(tpy) (Figure S34). In this case, key bond lengths were found to be 1.433 Å for C2–C3, 1.402 Å for C3–C4, 2.091 Å for Pt–C2 and 2.221 Å for Pt–C4. While this system is also highly asymmetric, the differences between the C–C and M–C bond lengths are larger for AuIII (0.056 and 0.239 Å, respectively, for M = Au; 0.031 and 0.130 Å, respectively, for M = Pt).

In conclusion, we have generated and fully characterized the first AuIII η1-allyl complex.[14] NMR spectroscopy and XRD analysis together with DFT calculations show that the allyl ligand bound to Au is highly asymmetric. This asymmetric bonding appears to be dictated by the different trans influence of the coordinating atoms of the ancillary ligands (tpy-N vs. tpy-C). We are currently investigating how this asymmetry will affect the reactivity of this class of complexes.

Acknowledgements

This work was supported by the Research Council of Norway through grants 185513/I30, 221801/F20 (stipend to M.S.M.H.), FRINATEK Grant No. 250044 (stipend to A.N.), and Center of Excellence Grant No. 262695. The Research Council of Norway also supported us through the Norwegian NMR Platform, NNP (226244/F50). The Norwegian Metacenter for Computational Science (NOTUR, nn4654k) is gratefully acknowledged. Senior Engineer Dirk Petersen (University of Oslo NMR center) is thanked for variable temperature NMR assistance. Dmitry Chernyshov, ESRF, SNBL BM01, is acknowledged for performing synchrotron SC-XRD measurements of complex 2 and 3. Osamu Sekiguchi (University of Oslo) is acknowledged for the MS analyses.

Conflict of interest

The authors declare no conflict of interest.

Keywords: allyl ligands · gold(III) complexes · π complexes · structural elucidation

How to cite: Angew. Chem. Int. Ed. 2020, 59, 1516–1520
Angew. Chem. 2020, 132, 1523–1536

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Manuscript received: September 26, 2019
Accepted manuscript online: November 11, 2019
Version of record online: December 12, 2019