Synthesis and Characterisation of Au(I)-(ITent) Complexes

Scott R. Patrick, Alba Collado, Sebastien Meiries, Alexandra M. Z. Slawin and Steven P. Nolan *

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, KY16 9ST, UK.

Email: snolan@st-andrews.ac.uk

Abstract

The synthesis of novel [AuCl(ITent)] and [Au(OH)(ITent)] complexes is reported. They have been fully characterised and their steric parameters were assessed by calculating percent buried volumes and producing steric maps from their crystal structures in the solid state.

Introduction

N-heterocyclic carbenes (NHCs) have proven to be a convenient alternative to phosphine ligands. They offer highly tuneable steric and electronic properties, which can lead to metal complexes with greater stability to air and moisture.[1] The property of "flexible steric bulk" describes the ability of a ligand to adapt to approaching substrates while offering protection to reactive metal centres.[2]

Pursuing such a ligand, Organ *et al*. adapted the structure of the ubiquitous and privileged IPr to produce IPent, increasing the steric bulk by modifying the length of the alkyl chains.[2f,2g,3] Our group was inspired by the approach first proposed by Glorius[2c-e] and developed a simple and scalable procedure to obtain new ligands with "flexible steric bulk." This has given rise to the ITent family of ligands (Tent = tentacular), comprised of IPr, IPent, IHept and INon (Figure 1).[4]

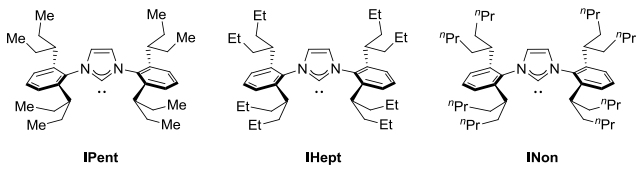


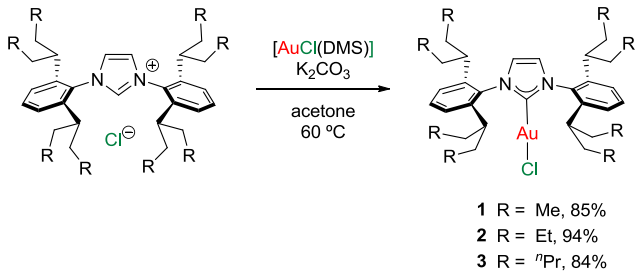
Figure 1. Structures of the ITent family of ligands.

The electronic properties of these ligands were then assessed by forming the [Ni(ITent)$(CO)_3$] complexes and measuring their Tolman Electronic Parameters (TEP) using infrared spectroscopy. In comparison with the analogous IPr complex, the TEP values decreased as the length of the alkyl chains grew. Therefore, the σ-donation strength of the ligands followed the order: IPr << IPent < IHept ~ INon.[4a]

Organ attributed the high catalytic activity of [Pd(PEPPSI)(IPent)] to its flexibility and bulkiness.[2f,2g,3,5] Our group recently examined this principle by preparing the [PdCl(cin)(ITent)] and [PdCl(acac)(ITent)] series.[4a] These new complexes gave increased catalytic activity in challenging Suzuki-Miyaura and Buchwald-Hartwig cross-coupling reactions. The results were more favourable than for the IPr complexes, with optimal alkyl chain lengths being found for either IPent or IHept, depending on the reaction. This was taken as further evidence of the positive effect of *flexible bulk* in catalysis.

Results and Discussion

Gold(I) complexes have been proposed as a model system for assessing ligand sterics, since their linear geometries minimise the influence of spectator ligands.[6] Recently, our group investigated the steric effect of IPent by preparing [AuCl(IPent)] (**1**).[4b] We also disclosed a new methodology for preparing gold(I)-NHC complexes that avoids the isolation of the free carbene or the use of copper or silver congeners as transmetallating reagents.[7] Using this procedure, the ITent•HCl salts could be reacted with [AuCl(DMS)] (DMS = dimethylsulfide) to furnish complexes **1**-**3** with excellent yields and purity (Scheme 1).

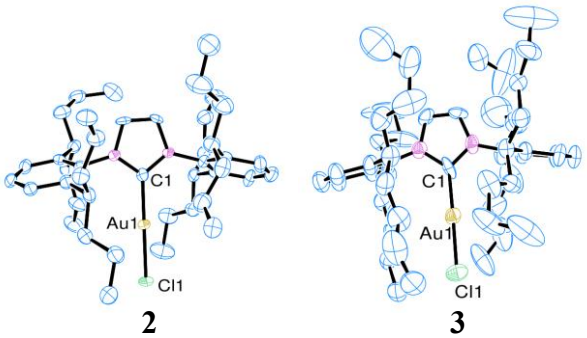


Scheme 1. Synthesis of [AuCl(ITent)] complexes.

These complexes have been fully characterised by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, elemental analysis, and X-ray diffraction analysis (Figure 2). The percent buried volume (%V_{Bur}) – i.e. the volume of a sphere around the metal centre that is occupied by the ligand – was calculated for each new structure using the Samb*V*ca[8] software. Pertinent details can be found in Table 1.

As observed for the Pd complexes,[4a] all members of the ITent family provided greater coverage than IPr,[9] with some even exceeding the steric bulk of IPr*.[10] The crystal obtained for [AuCl(IPent)] also showed two possible conformations with different buried volumes,[4b] highlighting its ability to adapt to incoming and outgoing substrates.

The steric maps of the [AuCl(ITent)] complexes were calculated in order to visualise the localisation of steric hindrance (Figure 3). The models show a far wider distribution of steric bulk than was observed for the square-planar [Ir] and [Pd] steric maps.[4] This can be explained by fewer ligands existing around the metal centre to hinder the



2 **3**

Figure 2. ORTEP diagrams of molecular structures of **2** and **3** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

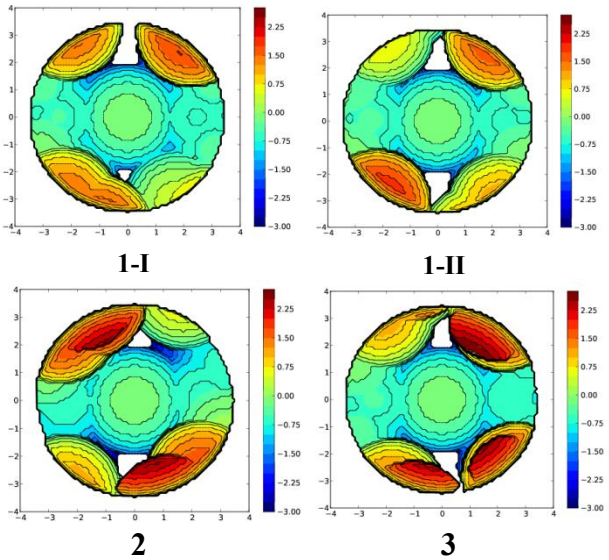
Table 1. Comparison of [AuCl(NHC)] Complexes

NHC	Au–C1 (Å)	C–Au–Cl (°)	%V_{Bur} [a]
IPr[b]	1.942(3)	177.0(4)	44.5
IPr*[c]	1.987(7)	178.3(2)	50.4
IPent-I[d]	1.979(10)	175.9(4)	49.0
IPent-II[d]	1.968(11)	177.2(3)	48.6
IHept	1.973(9)	179.1(3)	51.5
INon	1.96(2)	178.7(5)	51.3

[a] Parameters used for Samb*V*ca calculations: sphere radius, 3.50 A; Au–C1, 2.00 A; mesh spacing, 0.10; Bondi radius, 1.17. H atoms are excluded. [b] Taken from ref. 8. [c] Taken from ref. 9. [d] Taken from ref. 4b.

spreading of the alkyl chains. This improved coverage of the metal centre is in agreement with the calculated %V_{Bur} values being higher than for the corresponding Pd complexes.[4a]

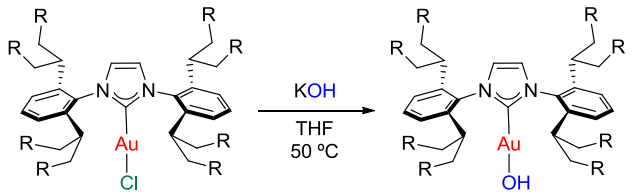
Gold(I) hydroxides are invaluable species for various catalytic processes, as well as identifying possible reactive intermediates.[11] Following on from our successful attempts to expand this library of compounds,[11a,12] we then applied the reaction to the ITent series (Scheme 2). The reaction temperature was increased from 30 to 50 °C



1-I **1-II**

2 **3**

Figure 3. Steric maps of complexes **1**-**3**.

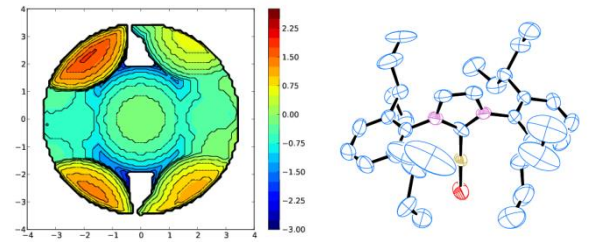


4 R = Me, 70%
5 R = Et, 71%
6 R = ^{n}Pr, 75%

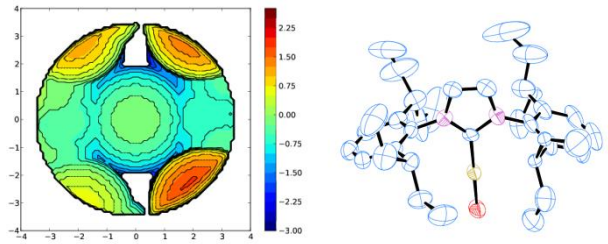
Scheme 2. Synthesis of [Au(OH)(ITent)] complexes.

in order to obtain full conversion after 24 h. No associated decomposition was observed and complexes **4-6** were obtained in very good yields.

Single crystals of [Au(OH)(IPent)] (**4**) were also characterized by X-ray diffraction (Figure 4). As before, two conformations, **4-I** and **4-II**, were observed. They may be differentiated by a slight rotation of one of the alkyl termini. Unlike their Au(I) chloride precursors, **4-I** and **4-II** had the same steric bulk (%V_{Bur} = 46.6). The steric maps of the two conformations showed very similar steric environments.



4-I



4-II

Figure 4. Steric maps and ORTEP diagrams of molecular structures of conformers **4-I** and **4-II**. 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected interatomic bond distances (Å) and angles (°) are as follows: C1–Au1 = 1.931(7); Au1–O1 = 2.012(6); C1–Au1–O1 = 179.3(3).

The ITent family of ligands has displayed remarkable steric bulk and flexibility in Au(I) complexes. The relatively high stability[12b] of the [Au(OH)(ITent)] series suggests that they will be reliable reagents in future transformations.

Conclusion

New synthetic strategies have been employed to obtain (ITent)Au(I) chlorides and hydroxides in very good to excellent yields. They have demonstrated similar steric trends to the previously reported Pd complexes while in a different coordination environment. Further synthetic work with these strongly flexible and bulky complexes is currently ongoing in our laboratories.

Supporting Information

Supplementary material featuring experimental details and NMR spectra can be found at website.

CCDC 977383 (**2**), CCDC 977384 (**3**) and CCDC 977385 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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Abbreviations

IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IPent = 1,3-bis(2,6-di(3-pentyl)phenyl)imidazol-2-ylidene; IHept = 1,3-bis(2,6-di(4-heptyl)phenyl)imidazol-2-ylidene; INon = 1,3-bis(2,6-di(5-nonyl)phenyl)imidazol-2-ylidene; IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)-imidazol-2-ylidene.

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