

# Synthesis, characterisation, and oxygen atom transfer reactions involving the first gold(i)-alkylperoxo complexes†

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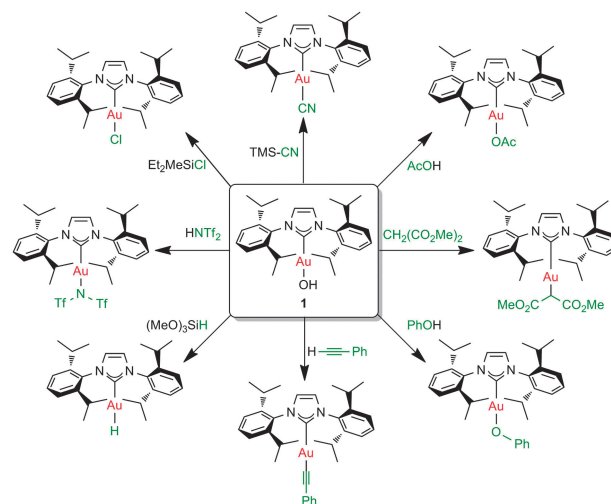
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The synthesis of a new class of organogold species containing a peroxo moiety is reported. Complexes  $[\text{Au}(\text{IPr})(\text{OO}^t\text{Bu})]$  and  $[\text{Au}(\text{SIPr})(\text{OO}^t\text{Bu})]$  have been synthesised via a straightforward methodology using the parent gold(i) hydroxide complexes as synthons. These complexes have been successfully used in oxygen-transfer reactions to triphenylphosphine.

Since the renaissance of gold chemistry more than a decade ago,<sup>1</sup> organometallic chemists have attempted to isolate key organogold species in order to gain a better understanding of their reactivity.<sup>2</sup> Amongst the plethora of gold complexes currently available, catalysts bearing N-heterocyclic carbenes (NHCs) as ancillary ligands have distinguished themselves due to their unique electronic and steric properties.<sup>3</sup> In addition, gold-complexes bearing NHC ligands are usually more stable than their phosphine analogues, thus providing a better scaffold for the synthesis of possible reaction intermediates.<sup>4</sup> For example, the use of NHC ligands has permitted the synthesis of the first example of a mononuclear Au(i)-hydroxide  $[\text{Au}(\text{IPr})\text{OH}]^{\ddagger}$  (**1**)<sup>5</sup> and its saturated derivative  $[\text{Au}(\text{SIPr})\text{OH}]^{\ddagger}$  (**2**).<sup>6</sup> The former has been shown to be a very useful synthon allowing the preparation of a wide variety of organogold species under very mild conditions (Scheme 1).<sup>5,7</sup>

Recently, there has been increased interest in the isolation of oxo-, hydroxo-, and alkoxo-gold(i) complexes, as oxygen nucleophiles are common reagents in gold-catalysed processes.<sup>8</sup> We have recently contributed to this field with the isolation of the aforementioned hydroxides **1** and **2**,<sup>5,6</sup> a series of  $[\{\text{Au}(\text{NHC})\}_2(\mu\text{-OH})][\text{BF}_4]$  species,<sup>9</sup> and finally various gold-phenolate complexes.<sup>7</sup>

As part of our research programme involving the preparation of novel organogold species, we have most recently focused our attention on the synthesis of gold complexes containing a



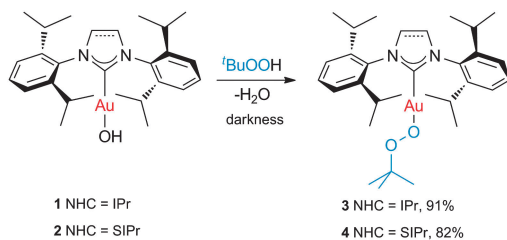
Scheme 1  $[\text{Au}(\text{IPr})\text{OH}]$  (**1**) as a powerful synthon.

peroxo (O–O) unit. Peroxo-metal complexes have been postulated as intermediates in important biochemical and industrial processes.<sup>10</sup> They are involved in enzymatic cycles, and are key intermediates in dioxygen activation and selective oxidation reactions.<sup>11</sup> In this context, much effort has been devoted to the isolation and characterisation of different metal complexes containing a peroxo moiety in order to better understand the mechanism of such processes.<sup>11a–c,12</sup> A handful of these have been isolated, typically prepared by insertion of  $\text{O}_2$  into a metal-hydride bond.<sup>13</sup> Amongst others, Rh-,<sup>14</sup> Fe-,<sup>11c,12a</sup> Cu-,<sup>12h,15</sup> Mn-,<sup>16</sup> Pt-,<sup>13a,17</sup> or Pd-peroxo<sup>13b</sup> complexes have been successfully isolated. The formation of gold-peroxo species has been proposed to occur on the surface of gold nanoparticles during  $\text{O}_2$  activation<sup>18</sup> and on gold electrodes as intermediates in water splitting processes.<sup>19</sup> Homogeneous mononuclear gold(III) complexes have been used for oxidative esterification reactions using *tert*-butylhydroperoxide as oxidants<sup>20</sup> and homogeneous gold(i) catalysts have been reported to tolerate organic hydroperoxides.<sup>21</sup> During the preparation of this manuscript, Bochmann reported the first example of Au(III)-peroxo complexes.<sup>22</sup> To the best of

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**Scheme 2** Synthesis of [Au(IPr)(OO<sup>t</sup>Bu)] and [Au(SIPr)(OO<sup>t</sup>Bu)].

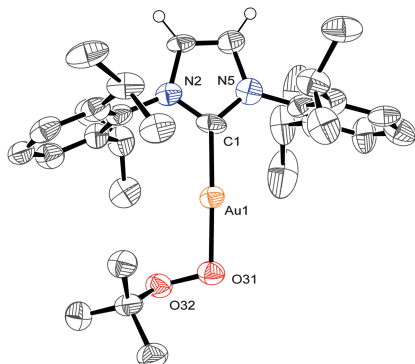
our knowledge, gold(i)-peroxy compounds remain unknown. Therefore, the formation of these species was explored, using complexes **1** and **2** as starting materials.

Treatment of [Au(IPr)OH] (**1**) or [Au(SIPr)OH] (**2**) with 1 equivalent of <sup>t</sup>BuOOH in toluene at room temperature leads to the formation of the new alkylperoxy species **3** and **4** as white microcrystalline solids (Scheme 2). It should be noted that these reactions were conducted under air in technical grade solvents. However, they were protected from light to avoid decomposition of the final product. Complexes **3** and **4** have been fully characterised by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, infrared spectroscopy, elemental analysis and single crystal X-ray diffraction analysis.

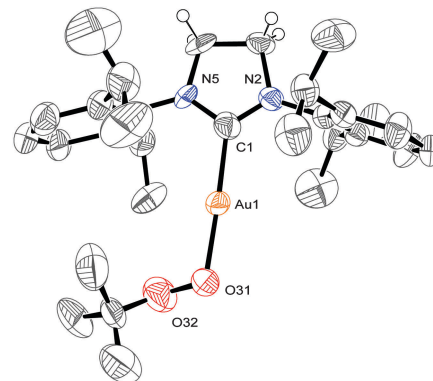
The <sup>1</sup>H NMR spectra of **3** and **4** display singlets at 0.87 and 0.83 ppm, respectively, which correspond to the *tert*-butyl moieties. The most noticeable feature of the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these complexes is the presence of a low field signal corresponding to the carbenic carbon atom. This signal appears at 170.9 ppm for **3** and 192.4 ppm for **4**, and compares well with the related data for **1** and **2**.<sup>5,6</sup> As observed for the precursors **1** and **2**, the signal corresponding to the carbenic atom appears at lower field for the complex containing the saturated ligand, SIPr.

The IR spectra of **3** and **4** in toluene solution showed bands at 803 and 804 cm<sup>-1</sup>, respectively, consistent with the presence of the O–O unit.

In order to unambiguously confirm the atom connectivity in **3** and **4**, single crystals were obtained by slow diffusion of pentane into their saturated toluene solutions.<sup>23</sup> Two conformers of complex **3** (**3a** and **3b**) were found in the crystal lattice (Fig. 1) while only one variant of **4** was obtained (Fig. 2). The three structures show the expected linear geometry around the metal centre, typical for Au(i) complexes with C<sub>carbene</sub>–Au–O angles



**Fig. 1** ORTEP representation of **3a** [Au(IPr)(OO<sup>t</sup>Bu)] showing 50% thermal ellipsoid probability. Most H atoms were omitted for clarity.



**Fig. 2** ORTEP representation of **4** [Au(SIPr)(OO<sup>t</sup>Bu)] showing 50% thermal ellipsoid probability. Most H atoms were omitted for clarity.

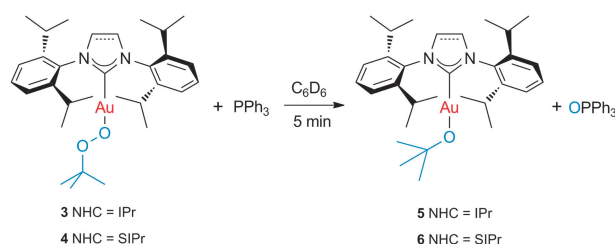
**Table 1** Selected distances (Å) for complexes **3–4**

Complex	C <sub>carbene</sub> –Au	Au–O	O–O
[Au(IPr)(OO <sup>t</sup> Bu)]( <b>3a</b> , <b>3b</b> )	1.964(16) 1.989(16)	2.014(11) 2.019(12)	1.512(17) 1.496(16)
[Au(SIPr)(OO <sup>t</sup> Bu)]( <b>4</b> )	2.000(12)	2.001(12)	1.51(2)

between 177.7° and 178.4°.<sup>24</sup> Table 1 presents the most relevant distances for these complexes. The Au–C<sub>carbene</sub> distances are 1.964(16) (**3a**), 1.989(16) (**3b**) and 2.000(18) Å (**4**). The Au–O distances are: 2.014(11) (**3a**), 2.019(12) (**3b**), and 2.001(12) Å (**4**). The O–O distances between 1.496(16) and 1.512(17) Å lie in the upper limit of the typical range observed for peroxy complexes.<sup>13,16b,17,25</sup> The Au–O–O and O–O–<sup>t</sup>Bu angles for the three structures are in the range 102.9–109.7°, in agreement with a sp<sup>3</sup> hybridisation of the oxygen atoms.

The ability of complexes **3** and **4** to transfer oxygen was tested by reacting them with PPh<sub>3</sub> (Scheme 3). Equimolar amounts of **3** or **4** and PPh<sub>3</sub> were mixed in C<sub>6</sub>D<sub>6</sub> under an argon atmosphere and the mixture was analysed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. After 10 min, the <sup>1</sup>H NMR spectra of the mixtures showed the formation of the corresponding *tert*-butoxy-gold complexes, **5** or **6**, and triphenylphosphine oxide as a result of the transfer of one oxygen atom from the peroxy species to triphenylphosphine. Complexes **5** and **6** have been previously described and the signals observed are in agreement with the reported data.<sup>8c,26</sup> The formation of triphenylphosphine oxide was further confirmed by the presence of a singlet at 25.0 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.

In conclusion, we have synthesised the alkylperoxy species [Au(IPr)(OO<sup>t</sup>Bu)] (**3**) and [Au(SIPr)(OO<sup>t</sup>Bu)] (**4**) via a straightforward



**Scheme 3** Oxygen atom transfer reaction from **3** and **4** to PPh<sub>3</sub>.

route from the corresponding gold(I) hydroxide species [Au(IPr)OH] (1) and [Au(SIPr)OH] (2). These complexes are the first examples of isolated Au(I)-peroxo complexes and have been fully characterised by NMR spectroscopy and X-ray diffraction analysis. Complexes 3 and 4 have been shown to be able to transfer oxygen to triphenylphosphine. Further studies focusing on the mechanism of this transformation and other reactivity of these new species are currently underway.

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## Notes and references

‡ IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene, SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene.

§ General experimental procedure: protected from light (in the dark and wrapped in aluminium foil), a vial was charged, under air, with 1 or 2 and toluene. An equimolar amount of 'BuOOH (5.5 M solution in decane) was added to the suspension and the mixture was stirred at room temperature for 30 min. After this time, the solvent was concentrated under vacuum and pentane was added to precipitate a white solid that was washed with further portions of pentane. See ESI† for details.

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