SUPPORTING INFORMATION

Synthesis, Characterisation, and Oxygen Atom Transfer Reactions of the First Gold(I)-Alkylperoxo Complexes

*Alba Collado, Adrián Gómez-Suárez, Yoshihiro Oonishi, Alexandra M. Z. Slawin, and Steven P. Nolan**

†EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, U.K.

snolan@st-andrews.ac.uk

Table of contents

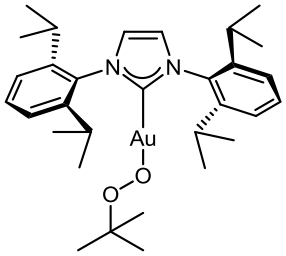
General information

- All reactions were carried under air and technical grade solvent were used.
- ^{t}BuOOH (5.5 M solution in decane) was used as received without any further purification.
- ^{1}H, and ^{13}C{^{1}H } Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometer at ambient temperature in CD_2Cl_2 and C_6D_6. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks.
- Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.
- **1** and **2** were prepared according to reported procedures.[1]
- Infrared spectra were recorded on a PE 2000 FT-IR spectrometer
- Crystals of **3** and **4** were grown by slow diffusion of pentane into a saturated toluene solution. CCDC 950318 (**3**), 950319 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Preparation of [Au(IPr)(OO^{t}Bu)] (3): Protected from the light, a vial was charged, under air, with [Au(IPr)OH] (100 mg, 0.166 mmol). The complex was suspended in 1.0

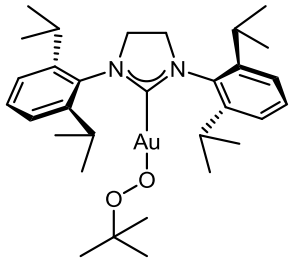
[1] A. Gomez-Suarez, R. S. Ramon, A. M. Z. Slawin, S. P. Nolan, *Dalton Trans.* **2012**, *41*, 5461-5463.

mL of toluene and ^{t}BuOOH (30 µL, 5.5 M solution in decane, 0.166 mmol) was added. The resulting mixture was stirred at r.t. for 30 min. After this time the solvent was concentrated and pentane (2.0 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1.0 mL) and dried under vacuum. Yield: 102 mg (91%).

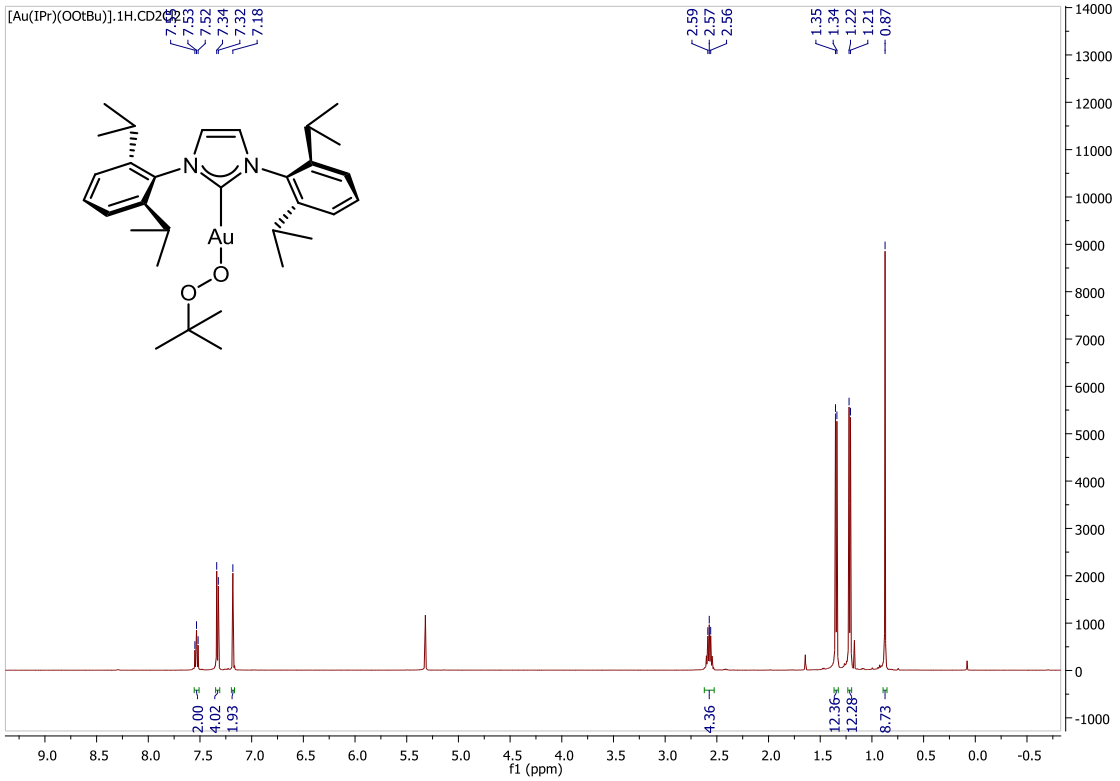


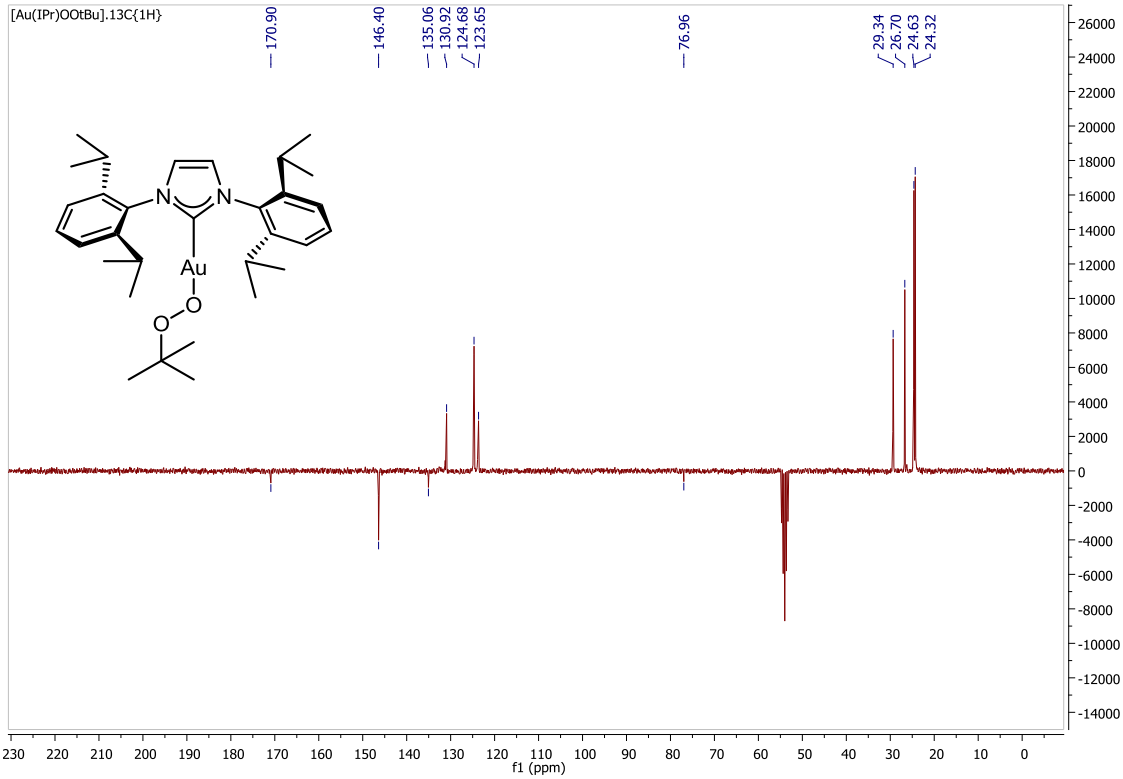
Anal. Calcd. for $C_{31}H_{45}AuN_2O_2$: C 55.19; H 6.72; N 4.15. Found: C 55.04; H 6.91; N 4.29. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.53 (t, $J_{H\text{-}H}$ = 7.8, 2H, CH_{Ar}), 7.33 (d, $J_{H\text{-}H}$ = 7.8, 4H, CH_{Ar}), 7.18 (s, 2H, CH_{imid}), 2.57 (sept, $J_{H\text{-}H}$ = 6.9, 4H, C*H*$(CH_3)_2$), 1.35 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.22 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 0.87 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 170.9 (s, C-Au), 146.4 (s, C_{Ar}), 135.1 (s, C_{Ar}),130.9 (s, CH_{Ar}), 124.7 (s, CH_{Ar}), 123.6 (s, CH_{imid}), 77.0 (O*C*$(CH_3)_3$), 29.4 (s, *C*H$(CH_3)_2$), 26.7 (s, OC(*C*H$_3)_3$) 24.6 (s, CH(*C*H$_3)_2$), 24.3 (s, CH(*C*H$_3)_2$). IR (toluene): $\nu_{O\text{-}O}$ 803 cm^{-1}.

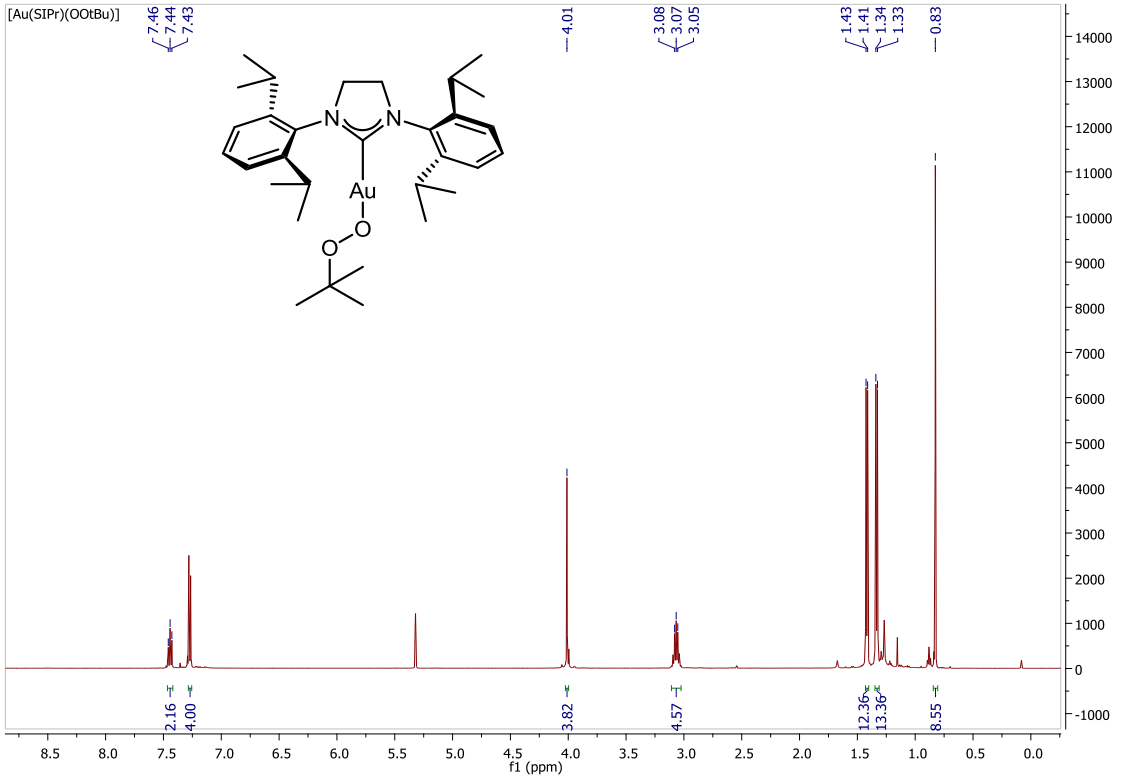
Preparation of [Au(SIPr)(OO^{t}Bu)] (4): Protected from the light, a vial was charged, under air, with [Au(SIPr)OH] (50 mg, 0.083 mmol). The complex was suspended in 0.5 mL of toluene and ^{t}BuOOH (15 µL, 5.5 M solution in decane, 0.083 mmol) was added. The resulting mixture was stirred at r.t. for 30 min. After this time the solvent was concentrated and pentane (2.0 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1.0 mL) and dried under vacuum. Yield: 45.7 mg (82%).

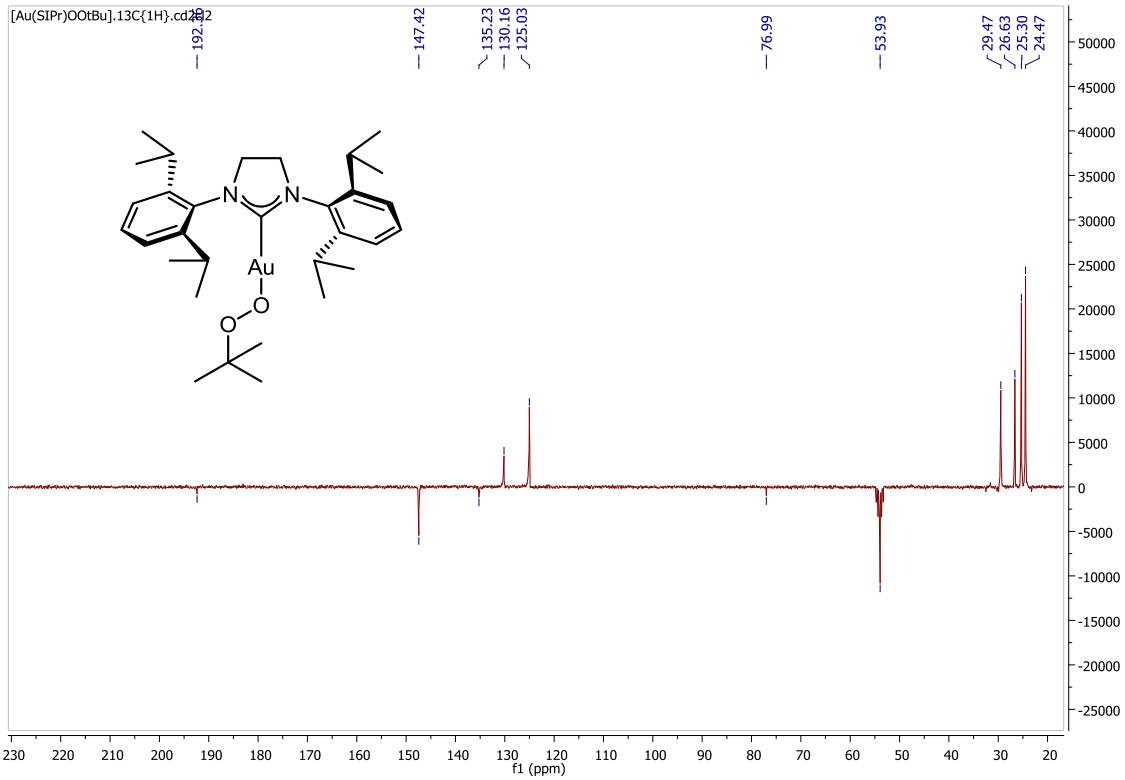


Anal. Calcd. for $C_{31}H_{47}AuN_2O_2$: C 55.02; H 7.00; N 4.14. Found: C 54.86; H 6.92; N 4.16. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 (t, $J_{H\text{-}H}$ = 7.8, 2H, CH_{Ar}), 7.27 (d, $J_{H\text{-}H}$ = 7.8, 4H, CH_{Ar}), 4.01 (s, 4H, $CH_{2\text{-}imid}$), 3.07 (sept, $J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.42 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.34 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 0.83 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 192.4 (s, C-Au), 147.4 (s, C_{Ar}), 135.2 (s, C_{Ar}), 130.2 (s, CH_{Ar}), 125.0 (s, CH_{Ar}), 77.0 (O*C*$(CH_3)_3$), 53.9 (s, $CH_{2\text{-}imid}$), 29.6 (s, *C*H$(CH_3)_2$), 25.3 (s, CH(*C*H$_3)_2$), 24.5 (s, CH(*C*H$_3)_2$). IR (toluene): $\nu_{O\text{-}O}$ 804 cm^{-1}.


[Au(IPr)(OOtBu)].1H.CD2Cl2
7.53
7.52
7.34
7.32
7.18
2.59
2.57
2.56
1.35
1.34
1.22
1.21
0.87
Au
O
O
2.00
4.02
1.93
4.36
12.36
12.28
8.73
f1 (ppm)

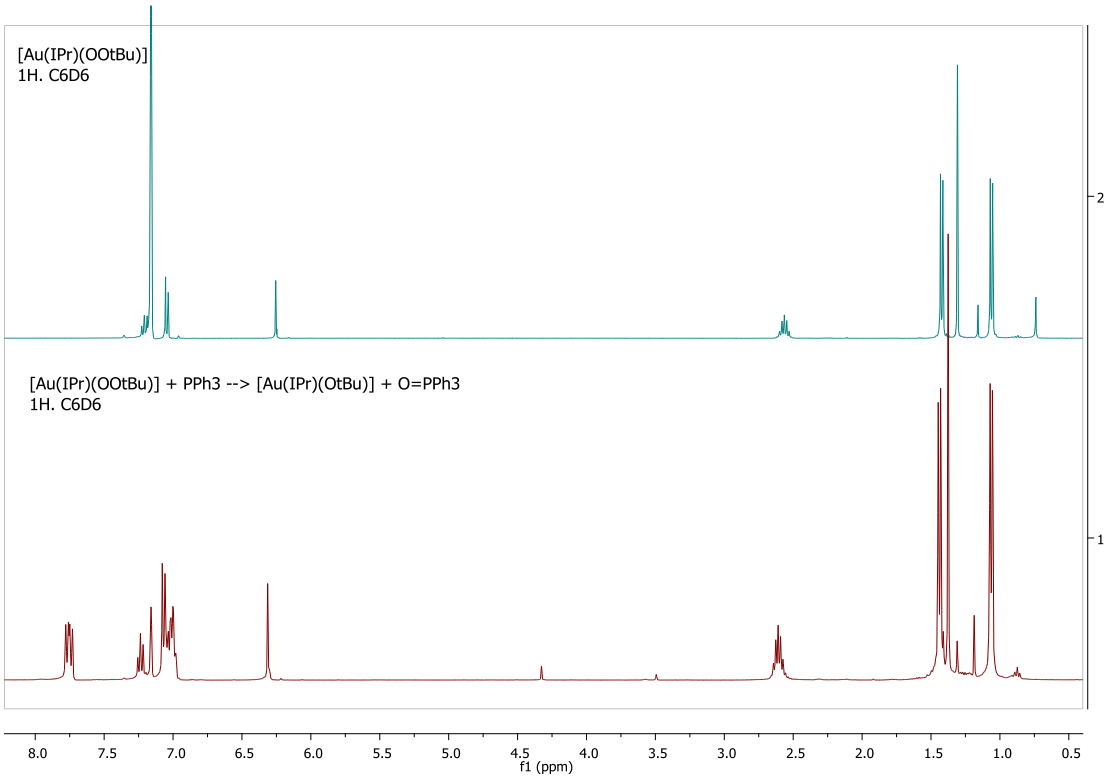

[Au(IPr)OOtBu].13C{1H}
170.90
146.40
135.06
130.92
124.68
123.65
76.96
29.34
26.70
24.63
24.32
Au
O
O
f1 (ppm)


[Au(SIPr)(OOtBu)]
7.46
7.44
7.43
4.01
3.08
3.07
3.05
1.43
1.41
1.34
1.33
0.83
2.16
4.00
3.82
4.57
12.36
13.36
8.55
f1 (ppm)

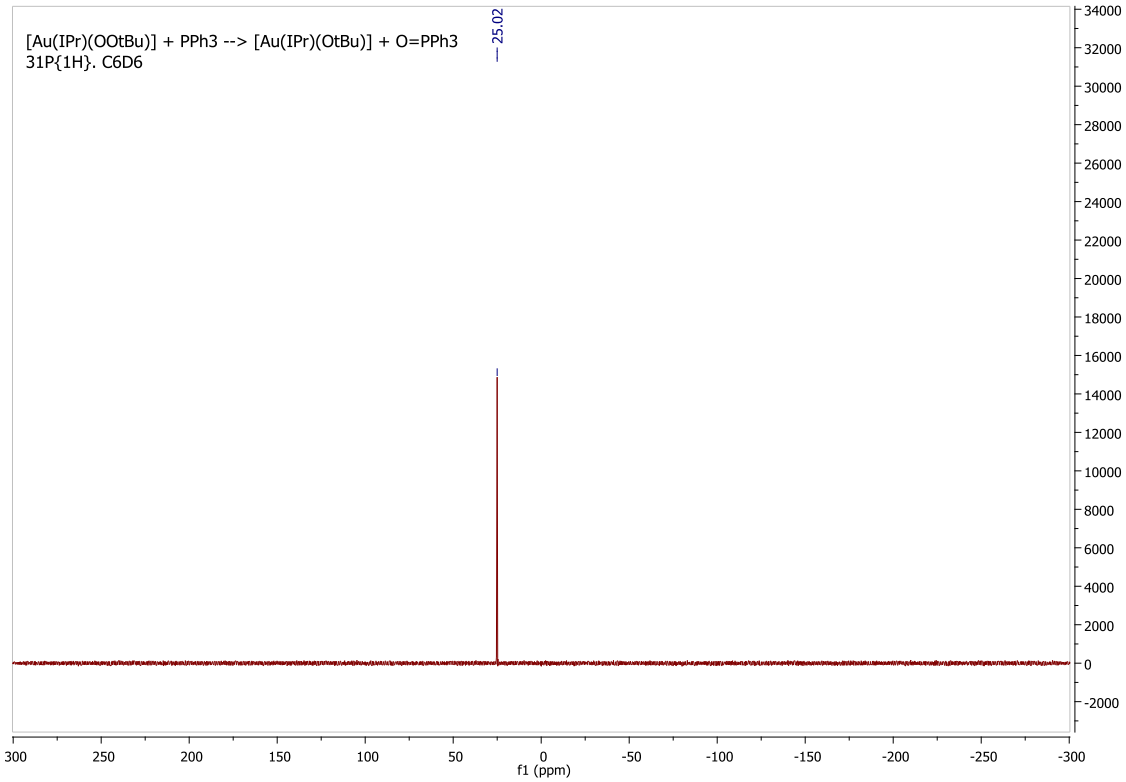

[Au(SIPr)OOtBu].13C{1H}.cd2
192.28
147.42
135.23
130.16
125.03
76.99
53.93
29.47
26.63
25.30
24.47
f1 (ppm)

Reaction of [Au(IPr)(OO^{t}Bu)] (3) with PPh_3:

A J-young tube was charged under argon with **3** (10.0 mg, 0.0148 mmol), PPh_3 (3.9 mg, 0.0148 mmol) and 0.5 mL of C_6D_6. The mixture was shaken and analised by NMR spectroscopy after 10 min. The ^1H NMR spectrum shows a new species and $O{=}PPh_3$. The new species has been identified as the reported complex [Au(IPr)(O^{t}Bu)].[2] A singlet at 25.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum confirms the formation of $O{=}PPh_3$.



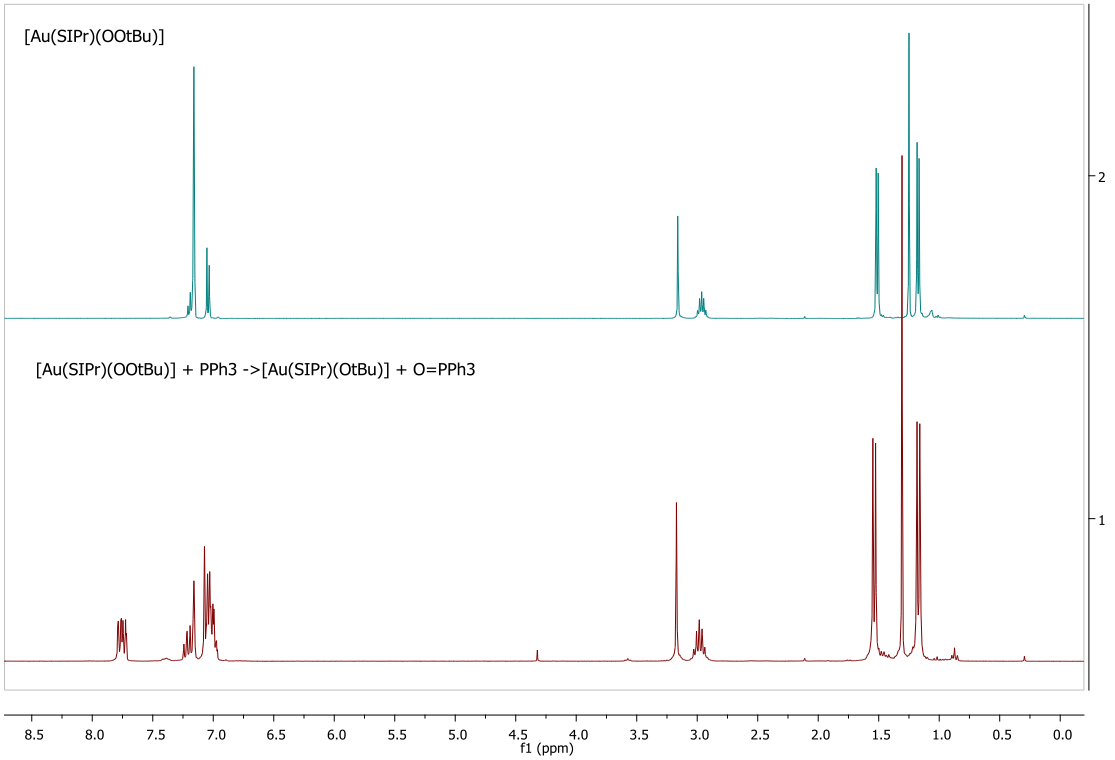
[2] E. Y. Tsui, P. Müller, J. P. Sadighi, *Angew. Chem., Int. Ed.* **2008**, *47*, 8937-8940.

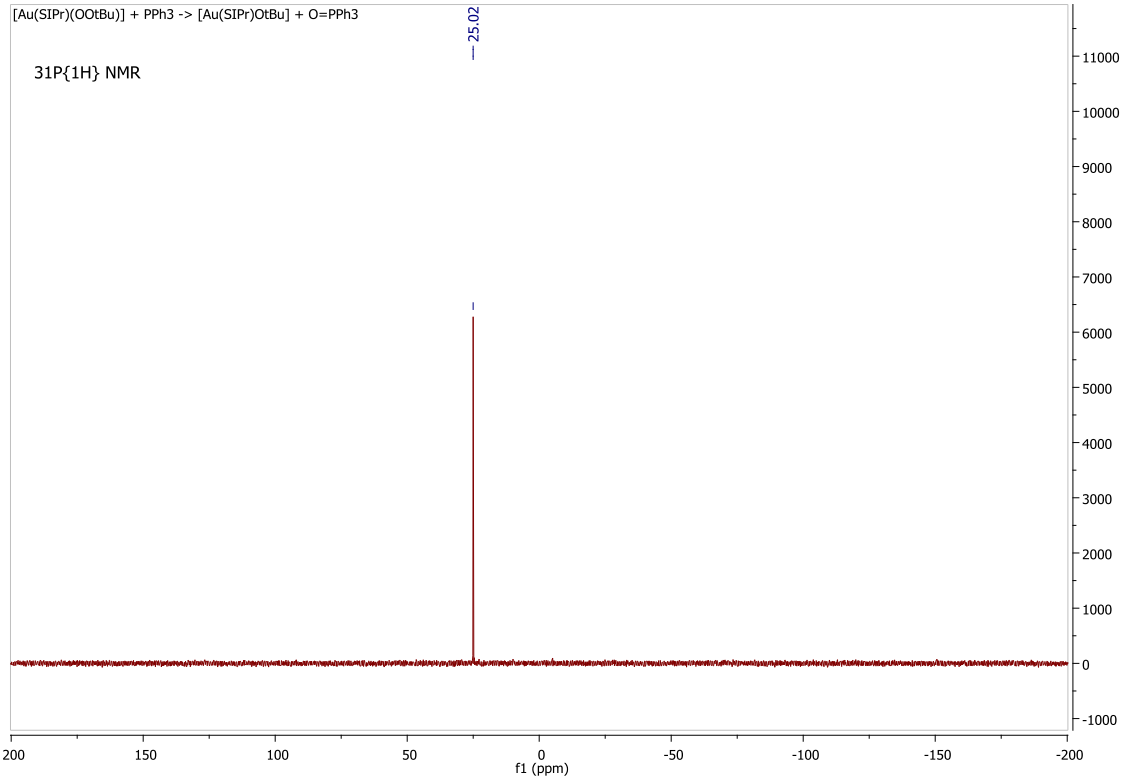


Reaction of [Au(SIPr)(OO^{t}Bu)] (4) with PPh_3:

A J-young tube was charged under argon with **4** (10.0 mg, 0.0147 mmol), PPh_3 (3.9 mg, 0.0147 mmol) and 0.5 mL of C_6D_6. The mixture was shaken and analised by NMR spectroscopy after 10 min. The ^1H NMR spectrum shows the presence of a new complex together with $O=PPh_3$. The new species has been identified as [Au(SIPr)(O^{t}Bu)] and the signals observed are in agreement with the reported data.[3] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 25.0 ppm corresponding to $O=PPh_3$.

[3] D. S. Laitar, P. Müller, T. G. Gray, J. P. Sadighi, *Organometallics* **2005**, *24*, 4503-4505.


[Au(SIPr)(OOtBu)]
[Au(SIPr)(OOtBu)] + PPh3 ->[Au(SIPr)(OtBu)] + O=PPh3
2
1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


[Au(SIPr)(OOtBu)] + PPh3 -> [Au(SIPr)OtBu] + O=PPh3
31P{1H} NMR
25.02
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

Crystallographic information:

- Experimental details for [Au(IPr)(OO^{t}Bu)] (3) CCDC 950318**:**

Crystal Data

Empirical Formula	$C_{31}H_{46}AuN_2O_{2.50}$
Formula Weight	683.68
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.100 X 0.100 X 0.100 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.984(4) Å b = 16.186(3) Å c = 16.922(3) Å α = 69.906(13) ^{o} β = 89.63(2) ^{o} γ = 79.21(2) ^{o} V = 3778.9(13) Å^3
Space Group	P-1 (#2)
Z value	4
D_{calc}	1.202 g/cm^3
F_{000}	1380.00
μ(MoKα)	39.307 cm^{-1}

Intensity Measurements

No. of Reflections Measured	Total: 23985 Unique: 13375 (R_{int} = 0.0639)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.491 - 0.675)

Structure Solution and Refinement

No. Observations (All reflections)	13375
No. Variables	667
Reflection/Parameter Ratio	20.05
Residuals: R1 (I>2.00σ(I))	0.0897
Residuals: R (All reflections)	0.1194
Residuals: wR2 (All reflections)	0.2537
Goodness of Fit Indicator	1.126
Max Shift/Error in Final Cycle	0.008
Maximum peak in Final Diff. Map	2.40 $e^-/Å^3$
Minimum peak in Final Diff. Map	-2.10 $e^-/Å^3$

- Experimental details for [Au(SIPr)(OO^{t}Bu)] (4) CCDC 950319

Crystal Data

Empirical Formula	$C_{31}H_{49}AuN_2O_3$
Formula Weight	694.71
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.100 X 0.030 X 0.030 mm
Crystal System	trigonal
Lattice Type	R-centered
Lattice Parameters	a = 31.468(6) Å c = 22.212(5) Å V = 19048(9) $Å^3$
Space Group	R-3 (#148)
Z value	18
D_{calc}	1.090 g/cm^3
F_{000}	6336.00
μ(MoKα)	35.108 cm^{-1}

Intensity Measurements

No. of Reflections Measured	Total: 29314
	Unique: 8293 (R_{int} = 0.1145)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.853 - 1.000)

Structure Solution and Refinement

No. Observations (All reflections)	8293
No. Variables	334
Reflection/Parameter Ratio	24.83
Residuals: R1 (I>2.00σ(I))	0.0916
Residuals: R (All reflections)	0.2024
Residuals: wR2 (All reflections)	0.2501
Goodness of Fit Indicator	1.156
Max Shift/Error in Final Cycle	0.042
Maximum peak in Final Diff. Map	5.60 $e^-/Å^3$
Minimum peak in Final Diff. Map	-2.08 $e^-/Å^3$