Correspondence to:
Professor W. Henderson,
Department of Chemistry,
University of Waikato,
Private Bag 3105,
Hamilton,
New Zealand
e-mail w.henderson@waikato.ac.nz
FAX 0064-7-838-4219

Five-coordinate gold(III) complexes of the Kläui ligands $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ (R = Me, Et)

Kelly J. Kilpin, William Henderson* and Brian K. Nicholson*

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

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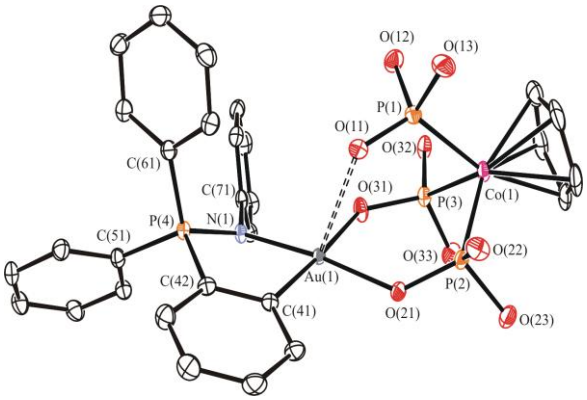
Synopsis

Reactions of the cycloaurated complexes $[LAuCl_2]$ (L = 2-$C_6H_4CH_2NMe_2$ or 2-$C_6H_4PPh_2$=NPh) with the tripodal Kläui ligands $Na[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]$ (R = Me or Et) and $Tl[BF_4]$ gives cationic gold(III) salts $[LAu\{OP(OR)_2\}_3Co(\eta^5\text{-}C_5H_5)]^+$. In the solid state the Kläui ligand of $[(2\text{-}C_6H_4PPh_2{=}NPh)Au\{OP(OR)_2\}_3Co(\eta^5\text{-}C_5H_5)]^+$ is strongly coordinated through two oxygens, and weakly coordinated by the third, giving the gold a distorted square pyramidal geometry, but in solution there is rapid equilibration of the phosphorylic oxygen atoms.

Graphic for synopsis



Abstract

The reactions of cycloaurated gold(III) dichloride complexes [$LAuCl_2$] (L = 2-$C_6H_4CH_2NMe_2$ or 2-$C_6H_4PPh_2$=NPh) with monoanionic tripodal oxygen donor Kläui ligands [(η^5-C_5H_5)Co{P(O)$(OR)_2$}$_3$]$^-$ (R = Me or Et) results in the formation of cationic gold(III) salts [LAu{P(O)$(OR)_2$}$_3$Co(η^5-C_5H_5)]$^+$. An X-ray structure determination on [(2-$C_6H_4PPh_2$=NPh)Au{P(O)$(OR)_2$}$_3$Co(η^5-C_5H_5)]BF_4 shows that the Kläui ligand coordinates strongly to the gold through two oxygen atoms, and weakly through the third, giving the gold(III) a distorted square pyramidal geometry. This is the first structurally characterised example of this geometry for gold(III) with ligands other than those containing rigid bipyridine or phenanthroline backbones. In solution at room temperature there is rapid interchange (on the NMR timescale) between the oxygen atoms of the Kläui ligands, which is frozen out on cooling.

Keywords: Gold complexes; Cyclometallated ligands; Kläui ligands; Fluxionality; X-ray crystal structure; Five-coordination

Introduction

Ligands of general formula $[(\eta^5\text{-}C_5R_5)Co\{P(O)R'R''\}_3]^-$, first synthesised in 1977 by Wolfgang Kläui, are monoanionic tridentate oxygen donor ligands, the chemistry of which has been summarised in two comprehensive reviews.[1,2] Complexes can be formed between these Kläui ligands and almost every metal ion, and also with a selection of non-metals (e.g. boron). As the Kläui ligands tend to favour octahedral coordination it is not surprising that gold(III) complexes have not been reported. However, complexes with the isoelectronic square-planar palladium(II) centre are known[3,4] where the Kläui ligand is strongly coordinated *via* only two of the oxygen atoms. Here we report a study of gold(III) complexes containing Kläui ligands, which follows on from our earlier work on the coordination chemistry of these ligands to tin and germanium.[5,6] Our current studies utilise gold(III) complexes containing cycloaurated C,N donor ligands,[7] which provide kinetic stabilisation of the gold(III) centre, which is otherwise prone to reduction.

Results and discussion

Synthesis and structural characterisation

When cycloaurated 2-benzylpyridine gold(III) dichloride (2-bp)$AuCl_2$ **1** was reacted with the Kläui ligands **2** (**a** R = Me; **b** R = Et) in dichloromethane in the presence of $Tl[BF_4]$ for 24 hours, the complexes **3a** and **3b** were isolated as yellow BF_4 salts in adequate yields (Scheme 1). Varying the reaction times (to either 6 or 48 hours) did not improve the yields and there was evidence for the decomposition of the gold(III) starting material to elemental gold. A similar reaction with the cycloaurated iminophosphorane **4** gave the analogous

complexes **5a** and **5b**, again in adequate yields (Scheme 1). The resulting complexes were analysed by ESI mass spectrometry, which gave very clean parent ions for the cationic complexes, and variable temperature NMR analysis. Satisfactory microelemental data could be obtained for three of the complexes, but despite several attempts, satisfactory data could not be obtained for **5a**. Even after successive recrystallisations the ^{1}H NMR spectrum showed traces of an impurity that could not be removed.

An X-ray crystal structure of **5b** was carried out in order to determine the bonding of the Kläui ligand to the gold(III) centre. Figure 1 shows the molecular structure and Table 1 gives important bond lengths and angles. The structure shows that the ligand is strongly bound to the gold centre through two oxygen atoms, with the third positioned above the gold coordination plane. The gold atom thus shows distorted square pyramidal coordination. The nitrogen [N(1)] and carbon [C(41)] atoms of the iminophosphorane ligand, along with two oxygen [O(21) and O(31)] atoms of the Kläui ligand constitute the base of the pyramid, while the apex is provided by the weakly coordinated third oxygen, O(11), of the Kläui ligand. The gold coordination plane (i.e. the base of the pyramid) is slightly distorted which is expected for square pyramidal coordination [Au(1) sits 0.0562(13) Å above the mean plane]. The Au(1)-O(11) vector is at an angle of approximately 80° to the base of the pyramid.

Five-coordinate square pyramidal complexes of gold(III) are rare but are not entirely unknown. To date, most of the structurally characterised complexes contain rigid ligands such as bipyridyl[8,9,10,11] or phenanthroline[12,13] which coordinate to the gold through two nitrogen atoms. In all cases, one nitrogen atom forms a corner of the base of the square pyramid, and because of the rigidity of the ligand the other nitrogen is placed at the apex of the pyramid, in an ideal position to interact with the gold. The remaining ligands are halides or pseudohalides, with the exception of one complex which contains PPh_3 and the bidentate orthometallated *N*,*N*-dimethylbenzylamine $C_6H_4CH_2NMe_2$ (damp) ligand.[14] Square-

pyramidal structures with four nitrogens defining the base and an apical Cl are found in gold(III) complexes with dipyridyloximate[15] or tetraphenylporphyrin[16] ligands.

In **5b** the interaction between Au(1) and apical oxygen O(11) appears to be strong enough to hold the complex in a square pyramidal arrangement. The Au(1)–O(11) bond length [2.722(2) Å] is significantly (*ca.* 0.7 Å) longer than the Au(1)–O(21) and Au(1)–O(31) bond lengths provided by the formally coordinated oxygen atoms [2.023(2) Å and 2.083(2) Å respectively]. This is similar to the palladium(II) π-allyl Kläui complex **6**,[4] where in addition to the two coordinated P=O groups [Pd-O distances 2.151(2) and 2.138(3) Å] the third oxygen also has a weak interaction with the palladium centre [Pd-O 2.622(2) Å]. By contrast, in the palladium(II) Kläui complex **7**, the two non-coordinating P=O oxygen atoms are twisted away from the palladium centre.[3] In the five-coordinate palladium(II) and platinum(II) β-diketonate complexes **8a** and **8b** the metal–oxygen distances of the weakly coordinated oxygen (i.e. the apex of the pyramid) are also approximately 0.7 Å longer than the metal oxygen distances in the base of the pyramid but the angle between the vertical axis of the pyramid (i.e. the metal–axial oxygen vector) and the base is much more acute [65.3(2)° in **8a** and 66.9(3)° in **8b**].[17]

The O(21)-Au(1)-O(31) bite angle of the Kläui ligand in **5b** is 91.82(9)°, close to ideal for square planar geometry. Because of *trans* influence differences, the gold–oxygen bond *trans* to the carbon [Au(1)–O(31) 2.083(2) Å] is longer than the gold–oxygen bond *trans* to the nitrogen [Au(1)–O(21) 2.023(2) Å]. Not surprisingly, the P=O bond lengths of the coordinated oxygens [P(2)–O(21) and P(3)–O(31)] are longer than the P=O bond length of the weakly coordinated oxygen P(1)-O(11).

Substitution of the two chloride ligands of **4** by the Kläui ligand also results in some subtle changes to the iminophosphorane moiety. The N-Au-C bite angle of the iminophosphorane increases from 84.86(17)° to 85.55(11)° in **5b** and this is accompanied by

a shortening of the gold–carbon [2.035(5) to 1.995(3) Å] and gold–nitrogen [2.034(4) to 2.008(2) Å] bonds, and lengthening of the P=N bond [1.618(4) to 1.636(3) Å]. In complex **4** the N-bonded phenyl ring is twisted 54° from the metallacyclic plane[18] but in complex **5b** the ring is almost perpendicular (81°) to the metallacyclic plane, presumably as a result of steric constraints imposed by the bulky Kläui ligand.

NMR spectroscopic analysis

The ^{1}H and $^{31}P\{^{1}H\}$ NMR chemical shifts of the Kläui ligands in the complexes **3** and **5** are very similar to those in the sodium salts **2**. However, the C_5H_5 protons of the Kläui ligand move downfield upon coordination. The phosphorus atoms in the iminophosphorane moieties of **5a** (δ 68.6 ppm) and **5b** (δ 68.2 ppm) are at similar chemical shifts to the dichloride **4** (δ 65.5 ppm) confirming the phosphorus remains in a five-membered ring.[19] Table 2 gives a comparison of these chemical shifts.

Kläui complexes of square planar palladium(II) show fluxionality in solution[3,4] and it appeared from a first inspection of the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra that the gold(III) complexes were showing similar behaviour. The tridentate (nitrogen donor) poly(pyrazolyl)borate ligand also shows fluxional behaviour when coordinated to gold(III);[20] at room temperature all three pyrazolyl moieties appeared equivalent, however when cooled it was possible to distinguish two coordinated and one non-coordinated pyrazolyl groups. For comparison, a variable temperature NMR study was carried out on the gold complexes of the Kläui ligand.

At room temperature there is a broad peak present between 110 and 120 ppm in the $^{31}P\{^{1}H\}$ NMR spectra of all complexes. This is only slightly different from the sodium salts of the ligands (**2a** δ 112.5 ppm, **2b** δ 110.1 ppm). For complexes **5a** and **5b**, this peak integrates 3:1 relative to the phosphorus of the iminophosphorane ligand. When the sample

was cooled the behaviour of the complex was dependent on the cycloaurated ligand present (i.e. the 2-benzylpyridine **3** or iminophosphorane **5** chelating group).

Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra for complex **3b** are shown in Figure 2. For the 2-benzylpyridine derived complexes **3a** and **3b** two broad peaks start to appear at 283 K at 135 ppm and 110 ppm in a 1:2 ratio. Presumably the peak at 135 ppm is from the non-coordinated (or weakly coordinated[1]) arm of the Kläui ligand. On cooling to 263 K the second peak starts to split into two distinct triplets (at 115 ppm and 105 ppm which integrate in a 1:1 ratio), corresponding to the phosphorus atoms of the coordinated arms of the ligand; because of the nonsymmetrical nature of the benzylpyridine ligand two signals are observed. The signal from the non-coordinating group is also a triplet. Cooling further to 223 K results in the two peaks from the coordinated phosphorus atoms becoming broader and resolution is lost. The uncoordinated P=O signal now separates into a well-resolved doublet of doublets ($^{2}J_{PP} \approx 159$ Hz) because of coupling to two distinct (coordinated) phosphorus atoms. Heating the sample from room temperature to 323 K resulted in sharpening of the signal – presumably further heating would have resulted in a sharp signal but limitations of the solvent precluded this.

The iminophosphorane complexes **5a** and **5b** showed related behaviour. At 283 K **5a** and **5b** are still fluxional and it is not until 243 K that the broad peak starts to split into two signals (at 135 ppm and 110 ppm), which again integrate 1:2. At 223 K, the limit imposed by the solvent, the peak at 135 ppm (corresponding to the dangling arm of the ligand) is a definite triplet ($^{2}J_{PP} \approx 153$ Hz) however the peak at 110 ppm is still broad and unresolved. Presumably, if the sample could be cooled further this peak would split into two triplets, analogous to those seen for the benzylpyridine complexes. Again, heating the sample from room temperature to 323 K results in the peak becoming sharper.

[1] It is not possible to distinguish between a non-coordinating or weakly coordinating third P=O group of the Klaui ligand; for the purposes of this discussion it will be referred to as non-coordinating

These results suggest a similar behaviour to that which was observed with the poly(pyrazolylborate) ligands.[20] At 303 K there is rapid interchange between the coordinated and the non-coordinated arms of the Kläui ligand making the three arms equivalent. When cooled, fluxionality is lost and three signals are observed which correspond to the three different environments that the arms occupy. The low temperature NMR data thus support the crystallographic observations.

Evidence of fluxionality can also be seen in the ^{1}H NMR spectra. At 303 K the methyl protons of the Kläui ligand in **3a** appear as a virtual quartet. At this temperature the molecule is fluxional and there is rapid interchange between the two bonded arms and the one non-bonded arm of the Kläui ligand. Therefore, the virtual quartet arises from 18 equivalent protons coupled to three equivalent phosphorus atoms (i.e. an $A_{18}X_3$ spin system). A similar pattern was observed for **5a**. When the complex was cooled it loses fluxionality and as a result the methyl protons (and phosphorus atoms) are no longer equivalent. The virtual quartet that is present at 303 K splits into two signals which integrate in a 1:2 ratio; again these signals show virtual coupling.

Complexes **3b** and **5b**, which contain ethyl groups on the Kläui ligand, show similar behaviour however there is additional complexity arising from the ethyl versus methyl groups. At 303 K the methyl groups show coupling only to the neighbouring protons thus appearing as a simple triplet. The signal for the methylene protons was a broad multiplet, from coupling to both the neighbouring protons and the phosphorus. Again, when the complex is cooled the signal splits into two, which integrate with a 1:2 ratio.

The benzylpyridine ring in **3a** and **3b** also shows fluxionality (because of the inversion of the six-membered auracycle), and this has been discussed in detail for other examples.[21] As a result, at 303 K the CH_2 protons appear as a broad singlet; cooling to 223 K results in the signal splitting into two doublets.

In conclusion, we have synthesised the first examples of gold(III) complexes containing the tridentate oxygen donor Kläui ligands, which have a pseudo five coordinate coordination geometry. The presence of fluxional processes is demonstrated by NMR spectroscopy.

Experimental

The gold dichloride complexes **1**[22] and **4**[18] were synthesised by literature procedures, and the Kläui ligands **2a** and **2b** were purchased from Strem Chemicals.

General experimental procedures were as described previously.[23] High resolution ESI mass spectra were acquired on a Bruker Daltonics MicrOTOF spectrometer, with samples (0.1 mg mL^{-1}, in CH_2Cl_2-methanol) introduced *via* a syringe pump. The spectrometer was calibrated with a sodium formate standard prior to each use. The NMR chemical shifts that are reported hereafter are those observed at 303 K.

Synthesis of 3a

The complex (2-bp)$AuCl_2$ **1** (1.00 g, 0.230 mmol) and the Kläui ligand **2a** (0.109 g, 0.230 mmol) were dissolved in dichloromethane (20 mL) with Tl[BF_4] (0.201 g, excess) and stirred in a foil-covered flask for 24 hours. After filtration and reduction in volume, slow addition of diethyl ether to the solution precipitated **3a** as a yellow solid (0.066 g, 32%). Found: C 30.5, H 3.4, N 2.3; $C_{23}H_{33}BNO_9F_4P_3CoAu$ requires C 30.6, H 3.7, N 1.6%. NMR: ^{1}H: δ 3.67 (vq, 18H, CH_3), 4.58 (br s, 2H, CH_2), 5.20 (s, 5H, Cp), 7.00 (m, 1H, Ar-H), 7.17 (m, 3H, Ar-H), 7.69 (t, 1H, Ar-H), 7.88 (d, 1H, Ar-H), 8.14 (t, 1H, Ar-H), 8.96 (d, 1H, Ar-H); ^{13}C{^{1}H}: δ 46.6 (CH_2), 52.7 (CH_3), 90.5 (Cp), 125.5, 126.9, 127.0, 128.2 128.5 (all aryl C-H), 129.0, 130.0, 131.1 (all aryl C), 143.7, 150.6, 156.9 (all aryl C-H); ^{31}P{^{1}H}: δ 113.1 (br s). ESI-MS: *m/z*: 816.040 (100%, $[M]^+$, calculated 816.036).

Synthesis of 3b

The complex (2-bp)$AuCl_2$ **1** (0.100 g, 0.230 mmol) and Kläui ligand **2b** (0.129 g, 0.230 mmol) were dissolved in dichloromethane (20 mL) and stirred in a foil-covered flask with $Tl[BF_4]$ (0.202 g, excess) for 24 hours. The insoluble thallium salts were filtered off and the solution was reduced in volume. Addition of diethyl ether to the solution until it went cloudy and storage overnight at -20 ^oC gave yellow crystals (0.139 g, 61%) of **3b**. Found: C 35.3, H 4.6, N 1.5; $C_{29}H_{45}BNO_9F_4P_3CoAu$ requires C 35.3, H 4.6, N 1.4%. NMR: ^1H: δ 1.25 (t, 18H, CH_3), 4.06 (br s, 12H, CH_2 - Kläui), 4.56 (br s, 2H, CH_2 - benzylpyridine), 5.14 (s, 5H, Cp), 6.96 (m, 1H, Ar-H), 7.14 (m, 3H, Ar-H), 7.60 (t, 1H, Ar-H), 7.93 (d, 1H, Ar-H), 8.16 (t, 1H, Ar-H), 8.86 (d, 1H, Ar-H); $^{31}C\{^1H\}$: δ 16.5 (CH_3), 46.4 (CH_2 – benzylpyridine), 61.4 (CH_2 – Kläui), 90.7 (Cp), 124.9 – 157.0 (all aryl C). $^{31}P\{^1H\}$: δ 110.4 (br s). ESI-MS: *m/z*: 900.133 (100%, $[M]^+$, calculated 900.130).

Synthesis of 5a

Complex **4** (0.100 g, 0.162 mmol), Kläui ligand **2a** (0.077 g, 0.162 mmol) and $Tl[BF_4]$ (0.142 g, excess) were dissolved in dichloromethane (20 mL). The resulting solution was stirred in a foil-covered flask for 24 hours. The insoluble salts were removed by filtration and addition of diethyl ether to the filtrate caused immediate precipitation of **5a** as a yellow solid (0.047 g, 27%). Found: C 40.3, H 3.9, N 2.0; $C_{35}H_{42}BNO_9F_4P_4CoAu$ requires C 38.7, H 3.9, N 1.3%. NMR: ^1H: δ 3.54 (vq, 18H, CH_3), 5.13 (s, 5H, Cp) 7.01-7.07 (m, 5H, Ar-H), 7.08 (m, 5H, Ar-H), 7.40-7.90 (m, 14H, Ar-H); $^{13}C\{^1H\}$: δ 52.3 (CH_3), 90.2 (Cp), 123-150 (aryl C); $^{31}P\{^1H\}$: δ 68.6 (s, P=N), 120.4 (br, P Kläui), integral 1:3. ESI-MS: *m/z*: 1000.083 (100%, $[M]^+$, calculated 1000.080).

Synthesis of 5b

Complex **4** (0.101 g, 0.163 mmol) and ligand **2b** (0.091 g, 0.163 mmol) were dissolved in dichloromethane (20 mL) with Tl[BF_4] (0.142 g, excess) and stirred for 24 hours in a foil-covered flask. After filtration to remove the insoluble thallium salts, slow evaporation of the dichloromethane solvent gave yellow crystals of **5b** (0.102 g, 54%). Found: C 42.1, H 4.7, N 1.3; $C_{41}H_{54}BNO_9F_4P_4CoAu$ requires C 42.0, H 4.7, N 1.2%. NMR: ^{1}H: δ 1.22 (t, 18H, CH_3), 3.90 (m, 12H, CH_2), 5.07 (s, 5H, Cp), 7.01-7.07 (m, 5H, Ar-H), 7.10-7.17 (m, 1H, Ar-H), 7.41-7.50 (m, 2H, Ar-H), 7.53-7.60 (m, 5H, Ar-H), 7.70-7.76 (m, 2H, Ar-H), 7.82-7.89 (m, 4H, Ar-H); ^{13}C{^{1}H}: δ 16.7 (CH_3), 61.1 (CH_2), 90.6 (Cp), 126-150 (aryl C); ^{31}P{^{1}H}: δ 68.2 (s, P=N), 117.2 (br, P Kläui), integral 3:1. ESI-MS: *m/z*: 1084.180 (100%, $[M]^+$, calculated 1084.174).

X-ray crystal structure determination of 5b

Yellow crystals of X-ray quality were grown by slow evaporation of a dichloromethane solution of the crude product at room temperature. Unit cell dimensions and reflection data were collected at the University of Canterbury on a Bruker Nonius Apex II CCD diffractometer at 93 K. Absorption corrections to the data were made by SADABS.[24] Crystal and refinement data for the complex are presented in Table 3.

The structure was solved using the Patterson methods option of SHELXS-97.[25] The gold atom was initially located, with all other non-hydrogen atoms subsequently found by a series of difference maps (SHELXL-97[26]), and the hydrogen atoms were included in calculated positions. All non-hydrogen atoms were refined as anisotropic. Two ethyl arms of the Kläui ligand displayed slight disorder and as a result the CH_3 groups (and corresponding methylene hydrogen atoms) were refined in two positions. The BF_4^- anion was also disordered, twirling around a BF bond, however the disorder was not resolved.

Supplementary material

Crystallographic data (excluding structure factors) for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 742112. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 1 Selected bond lengths (Å) and angles (°) for the complex **5b**

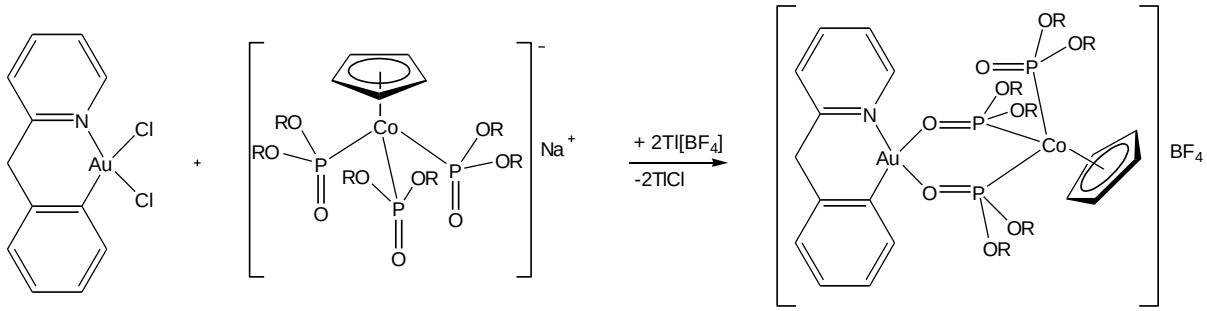
Atoms	Lengths (Å)	Atoms	Angles (°)
Au(1) – O(11)	2.722(2)	O(31) – Au(1) – O(21)	91.82(9)
Au(1) – O(21)	2.023(2)	O(31) – Au(1) – N(1)	90.54(9)
Au(1) – O(31)	2.083(2)	N(1) – Au(1) – C(41)	85.55(11)
O(11) – P(1)	1.487(2)	C(41) – Au(1) – O(21)	92.08(11)
O(21) – P(2)	1.537(2)		
O(31) – P(3)	1.522(2)		
Au(1) – C(41)	1.995(3)		
Au(1) – N(1)	2.008(2)		
P(4) – N(1)	1.636(3)		

Table 2 ^{1}H and $^{31}P\{^{1}H\}$ NMR chemical shifts (ppm) for the Kläui ligands **2a** and **2b** (as the sodium salts) and in the gold(III) complexes **3a,b** and **5a,b** in $CDCl_3$

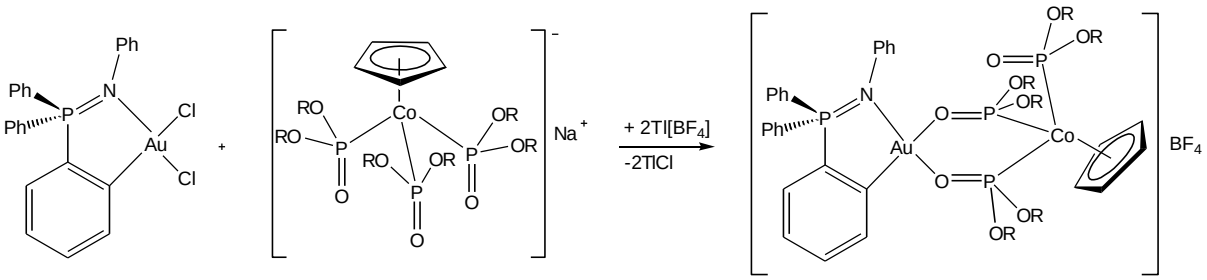
	CH_3	CH_2	Cp	P
2a	3.59 (vq)	-	5.03 (s)	112.5 (br)
3a	3.67 (vq)	-	5.20 (s)	113.1
5a	3.54 (vq)	-	5.13 (s)	120.4
2b	1.20 (t)	3.95 (m)	4.97 (s)	110.1 (br)
3b	1.25 (t)	4.06 (m)	5.14 (s)	110.4
5b	1.22 (t)	3.90 (m)	5.07 (s)	117.2

Table 3 Crystal and refinement data for the complex **5b**.

Formula	$C_{41}H_{54}BNO_9F_4P_4CoAu$
M_r	1171.44
T/K	93
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	30.7189(10)
b (Å)	10.1416(3)
c (Å)	30.0068(10)
β (°)	100.490(1)
V (Å^3)	9192.3(5)
Z	8
D_{calc} (g cm^{-3})	1.693
$T_{max,min}$	0.5511, 0.1530
Number of unique reflections	10525
Number of observed reflections [I>2σ(I)]	9567
R_1[I>2σ(I)]	0.0278
wR_2 (all data)	0.0691
Goodness of Fit	1.049

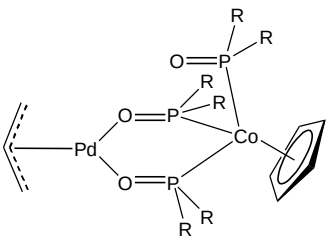


1 **2a, b** **3 a, b**

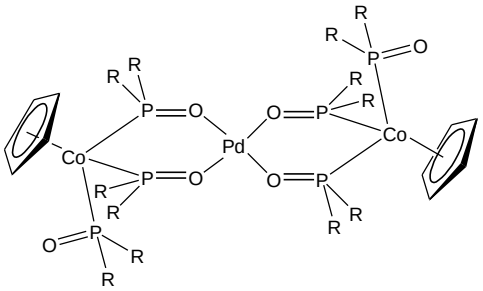


4 **5 a, b**

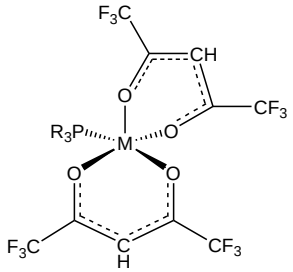
Scheme 1 Synthesis of Au(III) Kläui complexes **3** and **5** (**a** R = Me; **b** R = Et)



6 R = OMe



7 R = OMe



8a M = Pd, R = o-tolyl
8b M = Pt, R = cyclohexyl

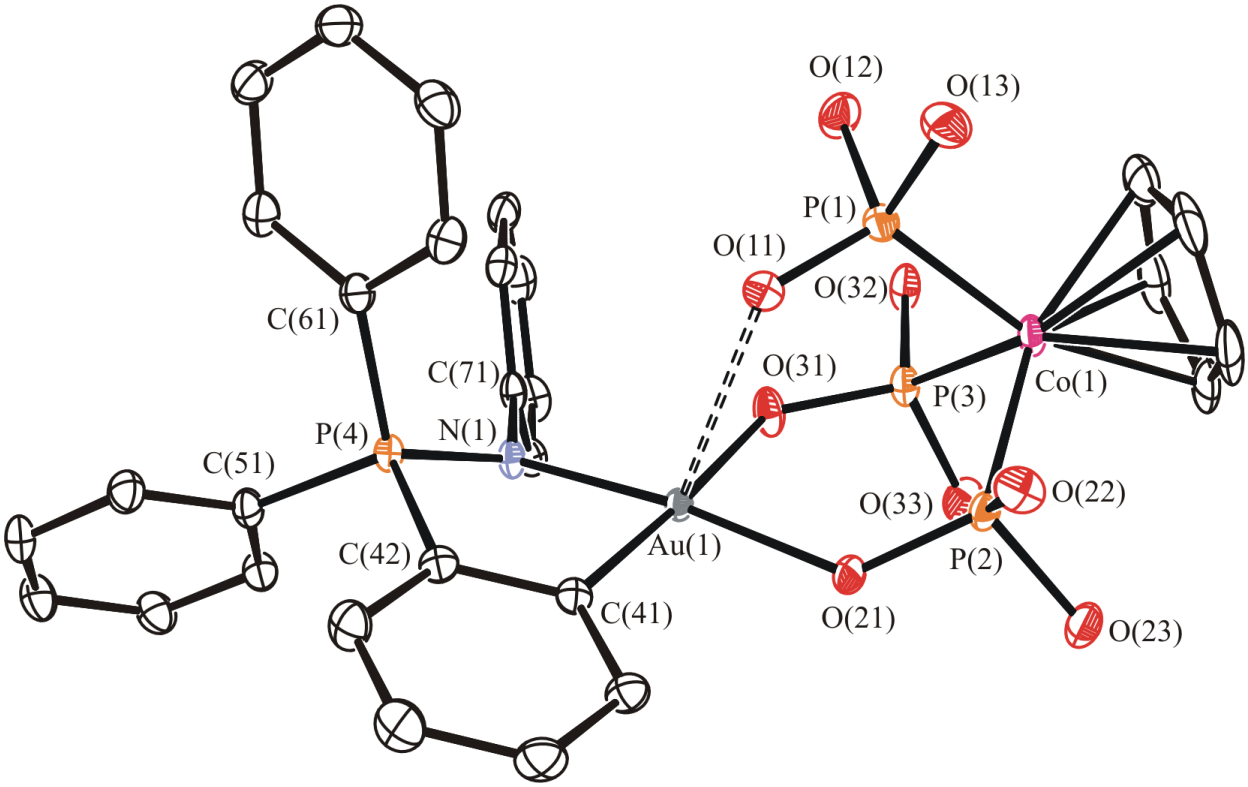


Figure 1 Diagram of the cationic moiety of **5b**. For clarity, the hydrogen atoms, $[BF_4]^-$ anion and the ethyl arms of the Kläui ligand have been excluded. Thermal ellipsoids are shown at the 50% probability level.

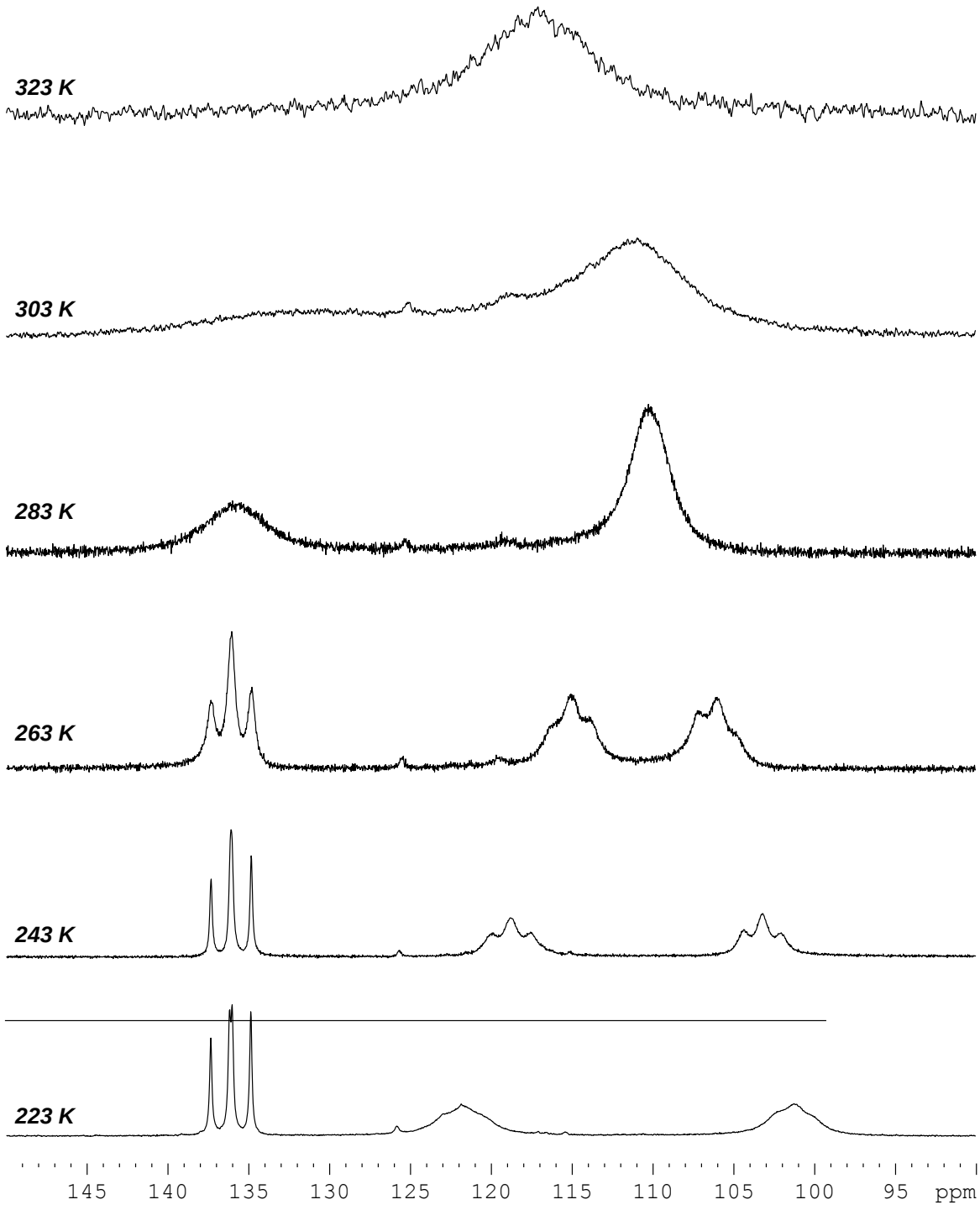


Figure 2 Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **3b** ($CDCl_3$)

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