Formation of Gold(III) Alkyls from Gold Alkoxide Complexes

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Ⓢ Supporting Information

ABSTRACT: The gold(III) methoxide complex (C^N^C)AuOMe (**1**) reacts with tris(*p*-tolyl)phosphine in benzene at room temperature under O abstraction to give the methylgold product (C^N^C)AuMe (**2**) together with O=P(*p*-tol)$_3$ ((C^N^C) = [2,6-(C$_6$H$_3$^{t}Bu-4)$_2$pyridine]$^{2-}$). Calculations show that this reaction is energetically favorable (ΔG = −32.3 kcal mol^{-1}). The side products in this reaction, the Au(II) complex [Au(C^N^C)]$_2$ (**3**) and the phosphorane (*p*-tol)$_3$P(OMe)$_2$, suggest that at least two reaction pathways may operate, including one involving (C^N^C)Au• radicals. Attempts to model the reaction by DFT methods showed that PPh$_3$ can approach **1** to give a near-linear Au−O−P arrangement, without phosphine coordination to gold. The analogous reaction of (C^N^C)AuOEt, on the other hand, gives exclusively a mixture of **3** and (*p*-tol)$_3$P(OEt)$_2$. Whereas the reaction of (C^N^C)AuOR (R = Bu^t, *p*-C$_6$H$_4$F) with P(*p*-tol)$_3$ proceeds over a period of hours, compounds with R = CH$_2$CF$_3$, CH(CF$_3$)$_2$ react almost instantaneously, to give **3** and O=P(*p*-tol)$_3$. In chlorinated solvents, treatment of the alkoxides (C^N^C)AuOR with phosphines generates [(C^N^C)Au(PR$_3$)]Cl, via Cl abstraction from the solvent. Attempts to extend the synthesis of gold(III) alkoxides to allyl alcohols were unsuccessful; the reaction of (C^N^C)AuOH with an excess of CH$_2$=CHCH$_2$OH in toluene led instead to allyl alcohol isomerization to give a mixture of gold alkyls, (C^N^C)AuR′ (R′ = −CH$_2$CH$_2$CHO (**10**), −CH$_2$CH(CH$_2$OH)OCH$_2$CH=CH$_2$ (**11**)), while 2-methallyl alcohol affords R′ = CH$_2$CH(Me)CHO (**12**). The crystal structure of **11** was determined. The formation of Au−C instead of the expected Au−O products is in line with the trend in metal−ligand bond dissociation energies for Au(III): M−H > M−C > M−O.
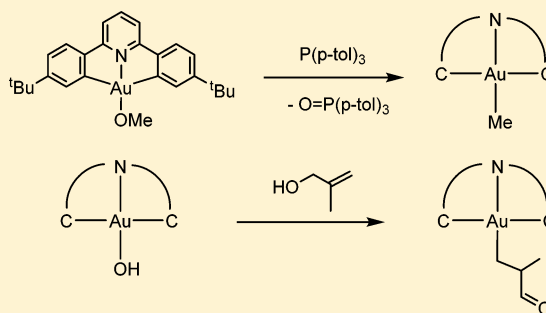
INTRODUCTION

The application of gold complexes as mediators or catalysts in organic transformations has seen a rapid rise in the last 15 years.[1] An important factor in this development is the high electronegativity of gold, which is almost identical with that of carbon and gives rise to highly covalent Au−C bonds, such that cations LAu$^+$ have been characterized as "carbophilic electrophiles".[2] Apart from the widespread application of gold(I) catalysts, gold(III) complexes are used in many catalytic transformations.[3] However, although Au(III) is isoelectronic and often isostructural with its Pt(II) analogues, it is becoming increasingly apparent that simple Pt(II)/Au(III) analogies concerning reaction mechanisms can be quite misleading; the reaction pathways of gold(III) are only just beginning to be explored.[4,5] Different energetic driving forces operate for gold and platinum; for example, whereas for Pt(II) the bond dissociation energies decrease in the order M−O > M−H > M−C, gold(III) follows the order M−H > M−C > M−O.[6] These energetic differences will determine product formation.

As we have recently shown, in line with this ordering of bond strengths (C^N^C)gold(III) pincer complexes allow the transformation of gold hydroxides into gold hydrides simply by O abstraction with phosphines ((C^N^C) = [2,6-(C$_6$H$_3$^{t}Bu-4)$_2$pyridine]$^{2-}$).[7] Following the same bond strength trend, gold hydrides can even be formed from suitable reactive gold−carbon compounds, such as Au−COOH species, where facile transformation to the hydride by CO$_2$ elimination was observed.[8] Calculations also show that the O abstraction from the gold methoxide **1** to give the gold methyl complex **2** is energetically favorable (Scheme 1).

We decided to explore whether this computationally predicted transformation could indeed be realized in practice and whether it might provide a possible alternative pathway to gold alkyl complexes without the need for conventional alkylating agents based on metal alkyls.

RESULTS AND DISCUSSION

Monitoring the reaction of (C^N^C)AuOMe (**1**) with tris(*p*-tolyl)phosphine as reducing agent in C$_6$D$_6$ at 25 °C by ^{1}H NMR spectroscopy shows the disappearance of **1** and formation of **2**, in line with the predicted reactivity trend. It is convenient to follow these reactions by monitoring the signal

Scheme 1. Conversion of Au^{III}−O into Au^{III}−H and Au^{III}−C Compounds and Calculated Energy Balances for These Transformations^a
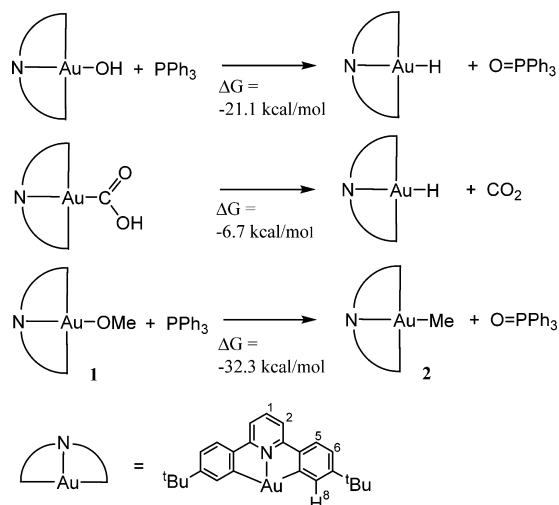
^{a}The pincer ligand structure shows the atomic numbering scheme used for the assignment of ^{1}H NMR spectra.

for the H8 proton (d, J = 2 Hz). For complex **1** this signal is found at δ 8.44. After 72 h this signal is diminished, and a new signal has appeared at δ 8.18, with the same small through-ring coupling (Figure 1). At the same time, the methoxy signal at δ 4.78 is replaced by the methyl signal at δ 1.94. These assignments were confirmed by comparison with the spectrum of an independently prepared sample of the known[9] methyl complex **2**. The ^{31}P NMR spectra also showed the conversion of (p-tolyl)$_3$P (δ −7.6) into (p-tolyl)$_3$P=O (δ 25.3); however, another phosphorus signal was also apparent, at δ −52.5, which was assigned to dimethoxytris(p-tolyl)phosphorane, (p-tolyl)$_3$P(OMe)$_2$.[10]

This indicated a more complex reaction than was postulated for the O abstraction of (C^N^C)AuOH to the corresponding gold hydride, where kinetic and isotope labeling studies had suggested a second-order, concerted O-extrusion pathway.[7] The existence of competing alternative reaction channels in the transformation of **1** to **2** was also indicated by the appearance of signals due to the known[11] Au(II) complex (C^N^C)Au−Au(C^N^C) (**3**). The final **2**:**3** molar ratio was 3:1. The formation of this Au(II) product, as well as the formation of (p-tolyl)$_3$P(OMe)$_2$, hint at the participation of single-electron pathways in this reaction, with transfer of MeO radicals. The possible contribution of hydrolysis of (p-tolyl)$_3$P(OMe)$_2$ as a source for (p-tolyl)$_3$P=O proved difficult to exclude.

A plausible mechanistic scenario is shown in Scheme 2. From the product distribution it seems clear that at least two

Scheme 2. Possible Reaction Pathways in the O Abstraction from Gold(III) Methoxide
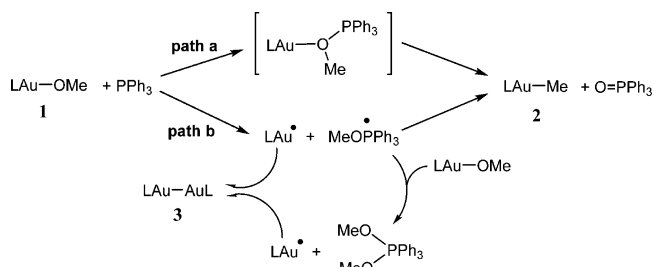
competing pathways may be operational. On the basis of the analogy with the deoxygenation of (C^N^C)AuOH by phosphines, which involved a concerted reaction step without prior phosphine coordination,[7] a direct attack of the phosphine on the OMe ligand of **1** cannot be excluded (Scheme 2, path a). However, given the formation of (MeO)$_2$P(p-tol)$_3$ as one of the products, methoxide transfer to the phosphine clearly also
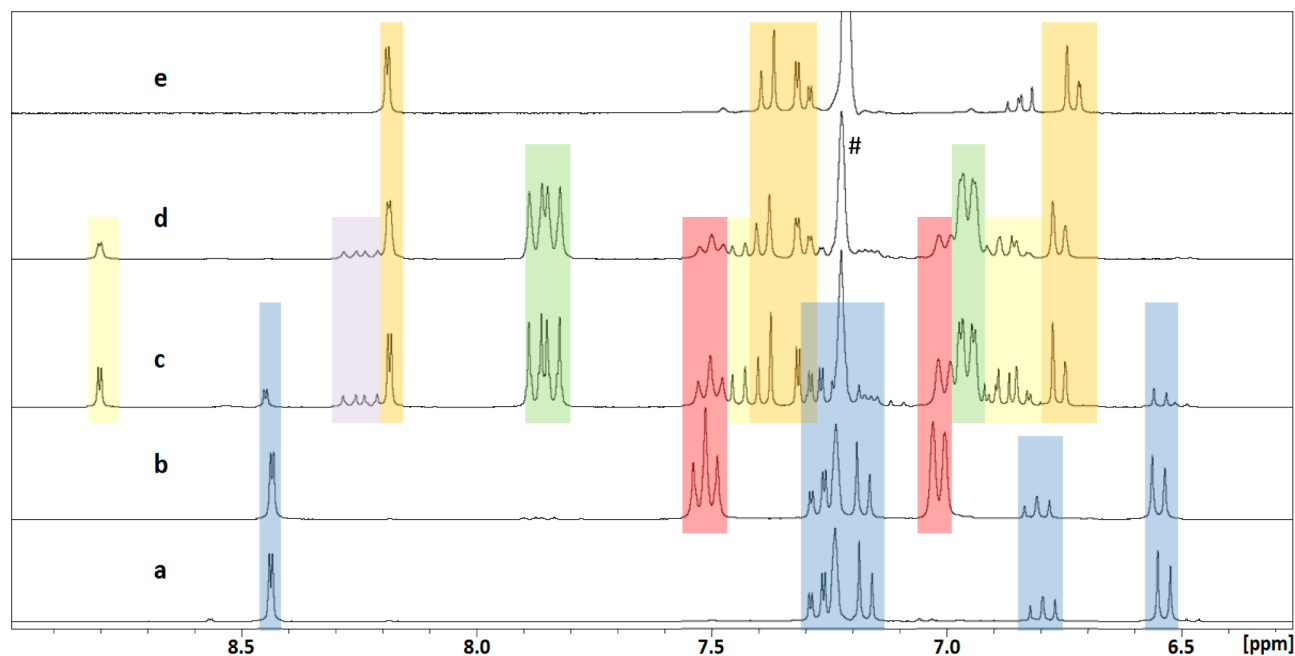
Figure 1. ^{1}H NMR spectra (6.5−9 ppm region, C$_6$D$_6$, 300 MHz) monitoring the reaction of (C^N^C)AuOMe with (p-tolyl)$_3$P: (a) spectrum of **1**; (b) spectrum immediately after addition of (p-tolyl)$_3$P; (c) spectrum after 72 h; (d) spectrum after 7 days; (e) spectrum of (C^N^C)AuMe (**2**). Color scheme: blue, **1**; orange, **2**; red, P(tol)$_3$; green, O=P(tol)$_3$; purple, P(tol)$_3$(OMe)$_2$; yellow, **3**. # indicates the solvent peak (benzene).

plays a role, which implies either homolytic or heterolytic Au−O bond cleavage. Since the reaction proceeds smoothly in nonpolar solvents such as benzene, and given the relative weakness of the Au−O bond (50 kcal mol^{-1} in **1**, in comparison to the Au−C value of 63 kcal mol^{-1} in **2**),[6] bond homolysis seems at least possible, generating the gold(II) radical species (C^N^C)Au$^{\bullet}$ (Scheme 2, path b). The possible involvement of (C^N^C)Au$^{\bullet}$ gains support by previous observation of the involvement of this Au(II) species in the electrochemical reduction of Au(III),[12] as well as in the radical-initiated trans addition of Au−H bonds to alkynes.[13]

We made numerous attempts to model the observed O transfer to phosphines by DFT methods, using both PPh$_3$ and the more reducing PMe$_3$ as models. For the direct O transfer, pathway **a**, a transition state was found, but at a comparatively high energy ($\Delta G^{\ddagger} = 39.7$ kcal mol^{-1}), close to that required for Au−O bond homolysis ($\Delta G = 52.1$ kcal mol^{-1} calculated at the same level). The approach of PPh$_3$ to **1** gives a near-linear Au−O−P arrangement (Figure 2). The movement associated
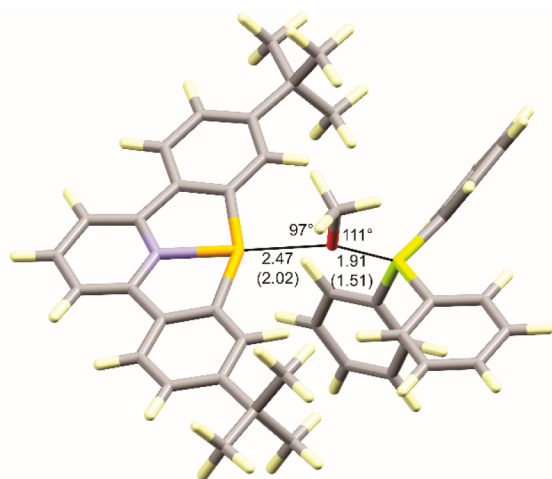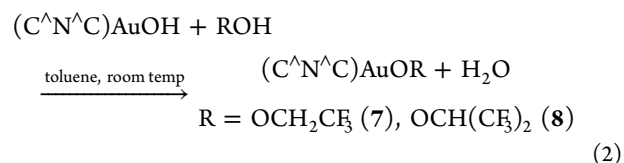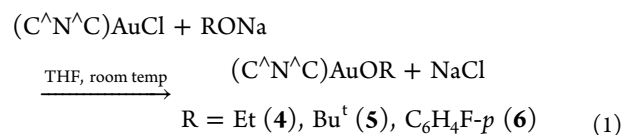

Figure 2. Optimized transition state geometry for the postulated O abstraction via Scheme 2, path a, showing bond lengths (Å) and angles (deg) around O. Distances to O in the reactant and product are given in parentheses.

with the transition state is nearly pure O translation between Au and P, with the Me group hardly moving. Following this motion toward Au leads back to the LAuOMe reactant, as expected. Following it toward P leads to "LAu + MeOPR$_3$", as suggested in pathway b. Undoubtedly a subsequent Me transfer from MeOPR$_3$$^{\bullet}$ to Au would be facile. Other possible intermediates were also investigated, including the five-coordinate phosphorus species Ph$_3$P(OMe)(AuL), which might be postulated to explain the methoxide transfer from Au to P without the need for Au−O bond homolysis. This would involve formally a phosphine insertion into the Au−O bond; however, no realistic path to such an intermediate could be identified. Calculating alternative pathways involving odd-electron Au(II) and MeO$^{\bullet}$ radical species proved problematic and did not result in a clearly identifiable low-energy trajectory.

The gold(III) alkoxide starting materials are generally most conveniently prepared either from the gold chloride (eq 1) or from the hydroxide (C^N^C)AuOH[14] with ROH in toluene (eq 2), to give the alkoxides **4−8**.

$$\text{(C^N^C)AuCl + RONa}$$
$$\xrightarrow{\text{THF, room temp}} \text{(C^N^C)AuOR + NaCl}$$
$$R = \text{Et (4), Bu}^t \text{ (5), C}_6\text{H}_4\text{F-}p \text{ (6)} \qquad (1)$$

$$\text{(C^N^C)AuOH + ROH}$$
$$\xrightarrow{\text{toluene, room temp}} \text{(C^N^C)AuOR + H}_2\text{O}$$
$$R = \text{OCH}_2\text{CF}_3 \text{ (7), OCH(CF}_3)_2 \text{ (8)} \qquad (2)$$

This preparation from the hydroxide worked well when R = fluoroalkyl but failed to give a clean product for R = ethyl, benzyl; the reaction of (C^N^C)AuCl with the sodium salt of allyl alcohol also failed. The reaction of (C^N^C)AuX (X = Cl, OAc^F) with p-ClC$_6$H$_4$CH$_2$ONa led exclusively to reduction to the Au(II) product **3**, even at low temperature (THF, −20 °C), while no reaction was observed with p-ClC$_6$H$_4$CH$_2$OH in the presence of triethylamine.

The scope of the O abstraction was explored for the alkoxide starting materials (C^N^C)AuOR (R = Et (**4**), ^{t}Bu (**5**), p-FC$_6$H$_4$ (**6**), CH$_2$CF$_3$ (**7**), CH(CF$_3$)$_2$ (**8**)). The contributions of pathways a and b to the outcome of the overall reaction appear to depend on the nature of the alkoxide ligand. The ethoxide (C^N^C)AuOEt (**4**) reacted with P(p-tol)$_3$ under conditions identical with those employed for **1** in benzene over a period of 72 h to give exclusively the Au(II) dimer **3** and (EtO)$_2$P(p-tol)$_3$, without formation of (C^N^C)-AuEt[9] in detectable quantities. The analogous reaction with (C^N^C)AuO^{t}Bu (**5**) gave mainly **3** together with (p-tol)$_3$P=O but the reaction only went to about 60% completion, even after several days. In order to ascertain the presence or absence of (C^N^C)Au^{t}Bu (**9**) among the possible products, complex **9** was prepared independently from the trifluoroacetate (C^N^C)-AuOAc^F and ^{t}BuMgCl at −20 °C as a colorless crystalline solid.[15] Its NMR spectrum confirmed, however, that **9** was not formed in the reaction of **5** with phosphines. Similarly, the reaction of (C^N^C)AuOC$_6$H$_4$F (**6**) with P(p-tol)$_3$ gave exclusively the Au(II) product **3** and (p-tol)$_3$PO.

In contrast to the slow reactions of **4** and **5**, the trifluoroethoxide (C^N^C)AuOCH$_2$CF$_3$ (**7**) reacted almost instantaneously with the phosphine, again forming exclusively the Au(II) complex **3**, although in this case the oxidation product was (p-tol)$_3$P=O, whereas the expected phosphorane (p-tol)$_3$P(OCH$_2$CF$_3$)$_2$ was not detected.

In all of these reactions the correct choice of solvent is important. Although solutions of gold alkoxides (C^N^C)AuOR in CH$_2$Cl$_2$ are stable for several hours, in the presence of phosphines the use of chlorinated solvents invariably led to chlorine abstraction from the solvent and the formation of [(C^N^C)-Au{P(tol-p)$_3$}]Cl, via (C^N^C)AuCl as intermediate (eq 3).

$$\text{(C^N^C)AuCl + P(p-tol)}_3$$
$$\xrightarrow{\text{CH}_2\text{Cl}_2} [\text{(C^N^C)Au\{P(p-tol)}_3\}]^+ \text{Cl}^- \qquad (3)$$

Unlike the reactions with benzylic alcohols, attempts to make gold complexes using allyl alcohols proved more successful. Whereas the reaction between (C^N^C)AuCl and NaOCH$_2$CH=CH$_2$ led to electron transfer to afford exclusively the Au(II) dimer **3**, treating (C^N^C)AuOH and excess allyl alcohol in toluene in the presence of molecular sieves gave a mixture of two products, **10** and **11**. However, none of these products was the expected gold allyloxide complex. The compounds were

Scheme 3. Reactions of Gold Hydroxides with Allyl Alcohols

Figure 3. Structure of complex **11**, showing the two independent molecules. Selected bond distances (Å) and angles (deg) for molecule 1: Au(1)−N(11) 2.034(8), Au(1)−C(17) 2.057(10), Au(1)−C(122) 2.083(8), Au(1)−C(162) 2.084(9), C(17)−C(173) 1.503(15), O(171)−C(172) 1.36(3), C(172)−C(173) 1.505(18), O(178)−C(172) 1.35(3), C(173)−O(174) 1.460(14), O(174)−C(175) 1.394(14), C(175)−C(176) 1.48(2), C(176)−C(177) 1.22(2); N(11)−Au(1)−C(17) 177.3(3), N(11)−Au(1)−C(122) 81.1(3), C(17)−Au(1)−C(122) 97.6(4), N(11)−Au(1)−C(162) 80.8(4), C(17)−Au(1)−C(162) 100.5(4), C(122)−Au(1)−C(162) 161.8(4).

separated and isolated by chromatography. Compound **10** was obtained only in trace amounts and identified as the gold(III) 3-propanalyl complex, formed by the isomerization of the allyl alcoholate to the aldehyde. The main product **11** proved to be the result of allyl alcohol dimerization (Scheme 3). Compound **10** appears to be light sensitive in solution; it gradually turns purple under ambient light and could not be crystallized, whereas crystals of compound **11** were obtained by slow evaporation of a toluene solution. The analogous reaction of (C^N^C)AuOH with methallyl alcohol also led to isomerization and formation of the gold alkyl **12**; however, in this case the presence of the methyl side chain prevents the addition of a second alcohol molecule.

The crystal structure of **11** (Figure 3) confirms the ^{1}H NMR spectroscopic assignments. The unit cell contains two independent, albeit similar, molecules which show disorder in one of the ^{t}Bu substituents. Also, in molecule 1, the −CH$_2$OH moiety is disordered over two positions, by rotation about the C(172)−C(173) bond; in molecule 2 the terminal −CH=CH$_2$ vinyl group is disordered, principally by rotation about the C(275)−C(276) bond. The two molecules lie adjacent and are overlapping (ca. 3.4 Å apart, with the gold atoms 3.619 Å apart).

The two molecules shown are of opposite chirality; there are other pairs of molecules, related through centers of symmetry, with the opposite pairs of chiral centers. None of the hydroxyl hydrogen atoms has been located; that on O271 has no apparent hydrogen-bonding acceptor available, but those on O171 and O178 are likely to be linked with a symmetry-related group.

The metal-mediated isomerization of allyl alcohol to propionaldehyde, and the coupling and isomerization of allyl alcohol with acetylenes are of course well-known.[16−18] However, whereas in the case of the iron carbonyl mediated isomerization η^3-allyl intermediates have been postulated, the rigid, coordinatively saturated structure of (C^N^C)AuOR pincer complexes does not permit such a bonding mode. Instead, a Claisen-type rearrangement can be envisaged (eq 4). In view of the coordinatively saturated nature of (C^N^C)AuX compounds, the involvement of Au−O bond homolysis and Au(II) radicals cannot be ruled out.

$$(4)$$
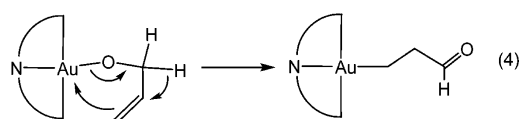
■ CONCLUSION

Gold(III) alkoxides show reaction patterns that are driven by the relative weakness of the Au−O bond. The pincer-stabilized gold methoxide (C^N^C)AuOMe undergoes an O abstraction reaction with phosphines, leading to the corresponding gold methyl (C^N^C)AuMe and phosphine oxide, although there are indications that odd-electron intermediates such as (C^N^C)Au^{II}• may also play a role. Most other alkoxides tested under the same conditions give almost exclusively reduction to [Au(C^N^C)]$_2$. On the other hand, the attempted synthesis of allyl alcohol derivatives (C^N^C)AuOCH$_2$CH=CH$_2$ led to isomerization and formation of functionalized gold(III) alkyls. These reactions provide therefore a facile one-step method for the generation of gold alkyls carrying functional groups with −CHO or −CH$_2$OH termini, which are not accessible by conventional alkylation routes. Whereas catalytic allyl alcohol isomerization is well-known, the application of this process to the generation of functionalized metal alkyl complexes has, to our knowledge, not been observed before. The thermodynamic driving force for these O-abstraction and isomerization reactions is undoubtedly the difference between the Au−C and Au−O bond dissociation energies.

■ EXPERIMENTAL SECTION

General Considerations. Unless stated otherwise, all reactions were carried out in air. Solvents were distilled and dried as required. (C^N^C)AuOH, (C^N^C)AuOMe, and (C^N^C)AuOAc^F were obtained according to literature procedures.[14] ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded using a Bruker Avance DPX-300 MHz NMR spectrometer. ^{1}H NMR spectra (300.13 MHz) and ^{13}C{^{1}H} (75.47 MHz) were referenced to CD$_2$Cl$_2$ at δ 5.32 (^{13}C, δ 54.0) and C$_6$D$_6$ at δ 7.16 (^{13}C, δ 128.4). ^{19}F NMR spectra (282.4 MHz) were referenced externally to CFCl$_3$ and internally to C$_6$F$_6$ (δ_F −164.9). ^{31}P NMR spectra (121.5 MHz) were referenced internally to trimethylphosphate (δ_P 0.0). IR spectra were recorded using a PerkinElmer Spectrum One FT-IR spectrometer equipped with a diamond ATR attachment. MALDI-TOF mass spectra were measured using a Shimadzu Biotech MALDI mass spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Elemental analyses were performed by the London Metropolitan University.

Synthesis of (C^N^C)AuOEt (4). To a suspension of NaH (60% in mineral oil, 30 mg, 0.75 mmol) under N$_2$ in THF (4 mL) was added dropwise excess EtOH (0.1 mL, 1.7 mmol). This was stirred for 30 min at room temperature. A 1 mL aliquot of this solution was added to a solution of (C^N^C)AuCl (50 mg, 0.087 mmol) under N$_2$ in THF (4 mL) and was stirred for 1 h at room temperature. Water was then added and the precipitate was filtered, washed with water and acetonitrile, and left to dry in air to afford a yellow powder (38 mg, 75%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.81 (d, 2H (H_8), J = 2 Hz), 7.78 (t, 1H (H_1), J = 8 Hz), 7.48 (d, 2H (H_5), J = 8.5 Hz), 7.37 (d, 2H (H_2), J = 8 Hz), 7.28 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8 Hz), 4.24 (q, 2H (OCH$_2$CH$_3$), J = 6.7 Hz), 1.39 (t, 3H (OCH$_2$CH$_3$), J = 6.8 Hz), 1.37 (s, 18H (C(CH$_3$)$_3$) ppm. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 8.35 (d, 2H, J = 2 Hz), 7.20 (dd, 2H, J_1 = 8.1 Hz, J_2 = 2 Hz), 7.1 (d, 2H, J = 8.2 Hz), 6.66−6.71 (m, 1H), 6.45 (d, 2H, J = 7.9 Hz), 4.81 (q, 2H, J = 6.6 Hz), 1.79 (t, 3H, J = 6.8 Hz), 1.34 (s, 18H) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz) 170.6 (C^N^C ipso), 164.4 (C^N^C ipso), 154.7 (C^N^C ipso), 145.2 (C^N^C ipso), 142.2 (C_1), 129.6 (C_8), 124.5 (C_5), 123.9 (C_6), 115.9 (C_2), 66.9 (OCH$_2$CH$_3$), 35.3 (C_{10}), 30.9 (C_{11}), 21.9 (OCH$_2$CH$_3$) ppm. Anal. Calcd for C$_{27}$H$_{32}$AuNO (found): C, 55.58 (56.06); H, 5.53 (6.23); N, 2.4 (2.28).

Synthesis of (C^N^C)AuO^{t}Bu (5). To a suspension of NaH (60% in mineral oil, 35 mg, 0.9 mmol) under N$_2$ in THF (3 mL) was added dropwise excess tert-butyl alcohol (0.2 mL, 2.1 mmol). The mixture was stirred for 3 h at room temperature. Some of this solution (1 mL) was added to a solution of (C^N^C)AuCl (50 mg, 0.087 mmol) under N$_2$ in THF (3 mL) and was stirred for 1 h at room temperature. Water was then added and the precipitate was filtered and washed with water followed by acetonitrile. The residue was left to dry in air, to afford the product as a yellow powder (49 mg, 92%). The compound slowly hydrolyzes in air to form the corresponding gold hydroxide (C^N^C)AuOH. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.96 (d, 2H (H_8), J = 2 Hz), 7.79 (t, 1H (H_1), J = 8 Hz), 7.49 (d, 2H (H_5), J = 8.1 Hz), 7.4 (d, 2H (H_2), J = 8 Hz), 7.27 (dd, 2H (H_6), J_1 = 2.1 Hz, J_2 = 8.1 Hz), 1.47 (s, 9H (OC(CH$_3$)$_3$)), 1.36 (s, 18H (C(CH$_3$)$_3$)) ppm. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 8.48 (d, 2H, J = 2 Hz), 7.19 (dd, 2H, J_1 = 8.1 Hz, J_2 = 2 Hz), 7.09 (d, 2H, J = 8.1 Hz), 6.59−6.65 (m, 1H), 6.43 (d, 2H, J = 8 Hz), 1.88 (s, 9H), 1.35 (s, 18H) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz) 171.7 (C^N^C ipso), 164.6 (C^N^C ipso), 154.4 (C^N^C ipso), 145.2 (C^N^C ipso), 142.3 (C_1), 131.9 (C_8), 124.3 (C_5), 123.7 (C_6), 115.9 (C_2), 74.3 (OC(CH$_3$)$_3$), 35.4 (C_{10}), 34.8 (OC(CH$_3$)$_3$), 30.9 (C_{11}) ppm. Anal. Calcd for C$_{29}$H$_{36}$AuNO (found): C, 56.95 (56.71); H, 5.93 (6.11); N, 2.29 (2.30).

Synthesis of (C^N^C)AuO(C$_6$H$_4$F-p) (6). To a suspension of NaH (60% in mineral oil, 30 mg, 0.75 mmol) under N$_2$ in THF (3 mL) was added dropwise p-fluorophenol (100 mg, 0.8 mmol) in THF (3 mL). This was stirred for 30 min at room temperature. This solution was added to a solution of (C^N^C)AuCl (150 mg, 0.24 mmol) under N$_2$ in THF (3 mL), and the resulting mixture was stirred for 3 h at room temperature. Water was subsequently added and the precipitate was filtered, washed with water followed by acetonitrile, and left to dry in air to afford a yellow solid (160 mg, 100%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.83 (t, 1H (H_1), J = 8.1 Hz), 7.49 (d, 2H (H_5), J = 8.2 Hz), 7.4 (d, 2H (H_2), J = 8.2 Hz), 7.34 (d, 2H (H_8), J = 2 Hz), 7.25 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8.3 Hz), 6.97−7.01 (m, 2H (p-FC$_6$H$_4$)), 6.81−6.87 (m, 2H (p-FC$_6$H$_4$)), 1.23 (s, 18H (C(CH$_3$)$_3$)) ppm. ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz): δ −129.35 (hept, J = 4.1 Hz) ppm. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.88 (d, 2H, J = 1.9 Hz), 7.32−7.36 (m, 2H), 7.22 (dd, 2H, J_1 = 2 Hz, J_2 = 8 Hz), 7.13 (d, 2H, J = 8 Hz), 6.97−7.02 (m, 2H), 6.77 (t, 1H, J = 8 Hz), 6.49 (d, 2H, J = 8 Hz), 1.27 (s, 18H) ppm. ^{19}F NMR (C$_6$D$_6$, 282.4 MHz): δ −128.04 (hept, J = 4.1 Hz) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz) 170.3 (C^N^C ipso), 164.9 (C^N^C ipso), 155.1 (C^N^C ipso), 144.7 (C^N^C ipso), 142.8 (C_1), 130.0 (C_8), 124.6 (C_5), 124.2 (C_6), 121.0 (O-pFC$_6$H$_4$), 120.9 (O-pFC$_6$H$_4$), 116.2 (C_2), 114.8 (O-pFC$_6$H$_4$), 114.6 (O-pFC$_6$H$_4$), 35.2 (C_{10}), 30.8 (C_{11}) ppm. Anal. Calcd for C$_{31}$H$_{31}$AuFNO (found): C, 57.32 (57.37); H, 4.81 (4.89); N, 2.16 (2.22) %.

Synthesis of (C^N^C)AuOCH$_2$CF$_3$ (7). (C^N^C)AuOH (200 mg, 0.36 mmol) was stirred in toluene (10 mL) with excess trifluoroethanol (0.3 mL, 3.9 mmol) in the presence of 3 Å molecular sieves for 24 h at room temperature in the dark. The solvent and excess reagent were removed under vacuum. Dichloromethane was added to the residue, and the mixture was sonicated briefly and filtered. The solvent was removed, the residue was sonicated in hexane, and the solid was filtered to afford yellow (C^N^C)AuOCH$_2$CF$_3$ (130 mg, 57%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.83 (t, 1H (H_1), J = 8 Hz), 7.74 (d, 2H (H_8), J = 2.4 Hz), 7.51 (d, 2H (H_5), J = 8.1 Hz), 7.4 (d, 2H (H_2), J = 7.9 Hz), 7.31 (dd, 2H (H_6), J_1 = 8.3 Hz, J_2 = 1.7 Hz), 4.54 (q, 2H (OCH$_2$CF$_3$), J = 8.8 Hz), 1.37 (s, 18H (C(CH$_3$)$_3$)) ppm. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 8.16 (d, 2H, J = 1.75 Hz), 7.14−7.17 (m, 2H), 7.01 (d, 2H, J = 8.2 Hz), 6.65 (t, 1H, J = 8.1 Hz), 6.36 (d, 2H, J = 8 Hz), 4.88 (q, 2H, J = 9 Hz), 1.32 (s, 18H) ppm. ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz): δ −76.43 (t, J = 8.8 Hz) ppm. ^{19}F NMR (C$_6$D$_6$, 282.4 MHz): δ −75.54 (t, J = 9.2 Hz) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz) 170.7 (C^N^C ipso), 164.8 (C^N^C ipso), 155.2 (C^N^C ipso), 144.8 (C^N^C ipso), 142.7 (C_1), 129.3 (C_8), 124.7 (C_5), 124.2 (C_6), 116.2 (C_2), 35.3 (C_{10}), 30.9 (C_{11}), 30.8 (OCH$_2$CF$_3$), ppm. (CF$_3$ not observed). Anal. Calcd for C$_{27}$H$_{29}$F$_3$AuNO (found): C, 50.87 (50.15); H, 4.59 (4.52); N, 2.2 (2.64).

Synthesis of (C^N^C)AuOCH(CF$_3$)$_2$ (8). (C^N^C)AuOH (150 mg, 0.27 mmol) was stirred in toluene (10 mL) with excess hexafluoroisopropyl alcohol (0.4 mL, 3.8 mmol) in the presence of 3 Å molecular sieves for 24 h at room temperature in the dark. The solvent and excess alcohol were removed under vacuum. Dichloromethane was then added to the residue, and the mixture was sonicated briefly

and filtered. The solvent was removed, and the residue was taken up in hexane, sonicated, and then filtered to afford the title compound as a yellow powder (87 mg, 46%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.83 (t, 1H (H_1), J = 8 Hz), 7.66 (d, 2H (H_8), J = 1.9 Hz), 4.49 (d, 2H (H_5), J = 8.2 Hz), 4.38 (d, 2H (H_2), J = 7.9 Hz), 7.3 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8 Hz), 4.89 (hept, 1H (CH(CF$_3$)$_2$), J = 6 Hz), 1.35 (s, 18H (C(CH_3)$_3$)) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz) 170.6 (C^N^C ipso), 165.1 (C^N^C ipso), 155.5 (C^N^C ipso), 144.5 (C^N^C ipso), 143.0 (C_1), 128.7 (C_8), 124.8 (C_5), 124.5 (C_6), 116.3 (C_2), 35.4 (C_{10}), 30.9 (C_{11}), 30.8 (OCH(CF$_3$)$_2$) ppm. (CF$_3$ not observed). ^{19}F NMR (CD$_2$Cl$_2$, 282.4 MHz): δ −74.9 (d, J 5.1 Hz) ppm. Anal. Calcd for C$_{28}$H$_{28}$F$_6$AuNO (found): C, 47.67 (47.81); H, 4.0 (3.86); N, 1.99 (2.01).

Synthesis of (C^N^C)AuBu^t (9). To a solution of (C^N^C)-AuOAc^F (135 mg, 0.21 mmol) in THF (5 mL) under N$_2$ was added a solution of *tert*-butylmagnesium chloride (1 M in THF, 210 μL, 0.21 mmol) at −20 °C. The brown solution was stirred for 15 min, and then water was added and the dark solid was filtered. The solid was suspended in DCM, and the solution was sonicated. The solution was then filtered through a cotton plug. The clear solution was evaporated. Hexane was added, and the solution was sonicated and then transferred to a centrifuge tube and centrifuged. The solid that separated is [Au(C^N^C)]$_2$ **3** (74 mg, 59%). The solution was transferred to a flask, and the solvent was removed under vacuum to afford a cream-colored solid (44 mg, 35%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.21 (d, 2H (H_8), J = 2 Hz), 7.67 (t, 1H (H_1), J = 8 Hz), 7.61 (d, 2H (H_5), J = 8 Hz), 7.49 (d, 2H (H_2), J = 8 Hz), 7.27 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8 Hz), 1.74 (s, 9H (AuC(CH_3)$_3$), 1.37 (s, 18H (C(CH_3)$_3$)) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz): δ 169.1 (C^N^C ipso), 161.8 (C^N^C ipso), 153.3 (C^N^C ipso), 147.9 (C^N^C ipso), 140.8 (C_1), 133.2 (C_8), 124.7 (C_5), 122.9 (C_6), 115.7 (C_2), 35.2 (C_{10}), 35.0 (AuC(CH$_3$)$_3$), 34.7 (AuC(CH$_3$)$_3$), 31.0 (C_{11}) ppm. ATR-IR (neat) 2957.47, 2904.4, 2862.05, 2833.3, 1588.58, 1572.42, 1476.7, 1358.63, 1260.11, 1092.29, 1031.96, 788.91, 733.48, 684.01, 608.08 cm^{-1}. m/z (MALDI): 596.35 [M + H$^+$]. Anal. Calcd for C$_{29}$H$_{36}$AuN (found): C, 58.48 (58.40); H, 6.09 (6.09); N, 2.35 (2.44).

O Abstraction from (C^N^C)AuOMe (1). In an NMR tube under N$_2$, (C^N^C)AuOMe (10 mg, 1.8 μmol) was dissolved in benzene-d_6 (0.4 mL). The ^{1}H NMR spectrum was recorded. P(p-tol)$_3$ (5.3 mg, 1.8 mmol) was added, and the reaction was monitored by NMR spectroscopy at various time intervals. The ^{1}H NMR spectra show the slow conversion of (C^N^C)AuOMe to (C^N^C)AuMe as well as the formation of the Au(II) dimer complex in a 3:1 ratio, respectively. This is exemplified by monitoring the appearance of the H_8 aromatic signals at 8.18 and 8.81 ppm for (C^N^C)AuMe (**2**) and [Au(C^N^C)]$_2$ (**3**), respectively, concomitant with the disappearance of the 8.44 ppm H_8 signal for (C^N^C)AuOMe. In addition, the methoxy signal at 4.78 ppm in **1** is slowly replaced by the methyl signal at 1.94 ppm in (C^N^C)AuMe. The ^{31}P NMR spectra show the conversion of (p-tol)$_3$P (δ_P −7.64) to (p-tol)$_3$PO (δ_P +25.3) and (p-tol)$_3$P(OMe)$_2$ (δ_P −52.5).

Reaction of (C^N^C)AuOH with Allyl Alcohol. (C^N^C)AuOH (130 mg, 0.23 mmol) and allyl alcohol (0.2 mL, 3 mmol) were stirred overnight at room temperature under an N$_2$ atmosphere in dry toluene in the presence of 3 Å molecular sieves. The solution was filtered, washed with water, dried (MgSO$_4$), and filtered, and the solvent was removed in vacuo to afford a yellow oil. This was chromatographed on silica gel using hexane/ethyl acetate 3/2 as eluent. Trace amounts of a first fraction were separated and identified as compound **10**. The compound darkened in solution and on the TLC plate with time. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 9.87 (t, 1H (CHO), J = 2.5 Hz), 7.80 (t, 1H (H_1), J = 8 Hz), 7.70 (d, 2H (H_8), J = 2 Hz), 7.59 (d, 2H (H_5), J = 8 Hz), 7.47 (d, 2H (H_2), J = 8 Hz), 7.29 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8 Hz), 2.94 (dt, 2H (CH_2CH$_2$CHO), J_1 = 2.5 Hz, J_2 = 7.7 Hz), 2.06 (t, 2H (CH$_2$CH_2CHO), J = 7.7 Hz), 1.38 (s, 18H (C(CH_3)$_3$)) ppm. ATR-IR (neat): 2955.23, 2865.93, 1718.6, 1588.10, 1564.98, 1477.70, 1259.40, 1179.62, 1099.64, 1035.63, 792.96, 738.05 cm^{-1}. A second fraction, the main product, was isolated and identified as compound **11** (65 mg, 43%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.74−7.79 (m, 3H

(H_1 + H_8)), 7.57 (d, 2H (H_5), J = 8 Hz), 7.44 (d, 2H (H_2), J = 8 Hz), 7.29 (dd, 2H (H_6), J_1 = 2 Hz, J_2 = 8 Hz), 6.00−6.13 (m, 1H), 5.33−5.4 (m, 1H), 5.17−5.22 (m, 1H), 4.44−4.51 (m, 1H), 4.13−4.20 (m, 1H), 3.92−4.00 (m, 1H), 3.76−3.84 (m, 1H), 3.59−3.67 (m, 1H), 2.42−2.46 (m, 1H), 2.14−2.18 (m, 1H), 1.66−1.73 (m, 1H), 1.39 (s, 18H) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz): δ 167.0 (C^N^C ipso), 163.2 (C^N^C ipso), 154.7 (C^N^C ipso), 148.7 (C^N^C ipso), 142.1 (C_1), 136.5 (OCH$_2$CH=CH$_2$), 131.2 (C_8), 125.8 (C_5), 124.1 (C_6), 116.8 (C_2), 83.1 (OCH$_2$CH=CH$_2$), 70.8 (CH$_2$OH), 68.8 (OCH$_2$CH=CH$_2$), 36.0 (C_{10}), 31.8 (C_{11}), 24.4 (AuCH$_2$CH), 1.6 (AuCH$_2$) ppm. ATR-IR (neat): 2953, 2920, 2867, 1589, 1566, 1478, 1259, 1178, 1065, 1035, 796, 740, 689, 612 cm^{-1}. Anal. Calcd for C$_{31}$H$_{38}$AuNO$_2$ (found): C, 56.97 (56.88); H, 5.86 (5.97); N, 2.14 (2.29) %. m/z (MALDI): 654.26 [M + H$^+$]. Single crystals of **11** suitable for X-ray diffraction were obtained from slow evaporation of a toluene solution at room temperature.

Reaction of (C^N^C)AuOH with β-Methallyl Alcohol. (C^N^C)AuOH (100 mg, 0.18 mmol) and β-methallyl alcohol (0.15 mL, 1.8 mmol) were stirred overnight at room temperature under an N$_2$ atmosphere in dry toluene, in the presence of 3 Å molecular sieves. The solution was filtered, washed with water, dried (MgSO$_4$), and filtered. Subsequently, the solvent was removed in vacuo and hexane was added to the residue, followed by sonication. The solid was filtered, dissolved in a small amount of ethyl acetate, and chromatographed on silica gel, with hexane/ethyl acetate 4/1 as eluent, to yield **12** as a yellow powder (16 mg). The hexane filtrate was evaporated to afford a second crop of **12** (40 mg, 51% overall yield). The compound darkened in solution and on the TLC plate with time. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 9.82 (d, 1H (CHO), J = 2.0 Hz), 7.78 (t, 1H (H_1), J = 8 Hz), 7.69 (d, 2H (H_8), J = 2 Hz), 7.58 (d, 2H (H_5), J = 8 Hz), 7.46 (d, 2H (H_2), J = 8 Hz), 7.29 (dd, 2H (H_6), J_1 = 8 Hz, J_2 = 2 Hz), 2.87−2.96 (m, 1H), 2.01−2.09 (m, 1H), 1.85−1.91 (m, 1H), 1.38 (s, 18H), 1.29 (d, 3H, J = 6.7 Hz) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz): δ 205.7 (CHO), 167.4 (C^N^C ipso), 163.1 (C^N^C ipso), 154.7 (C^N^C ipso), 148.8 (C^N^C ipso), 142.1 (C_1), 131.1 (C_8), 125.8 (C_5), 124.1 (C_6), 116.8 (C_2), 49.2 (CHCHO), 35.9 (C_{10}), 31.7 (C_{11}), 25.3 (CH$_3$), 17.9 (AuCH$_2$) ppm. ATR-IR (neat): 2955, 2904, 2866, 1716, 1589, 1566, 1478, 1280, 1260, 1179, 1098, 1037, 796, 739, 689, 612 cm^{-1}. m/z (MALDI): 610.40 [M + H$^+$].

Crystal Structure Analysis of Compound 11. Crystal data: C$_{31}$H$_{38}$AuNO$_2$, M_r = 653.59, monoclinic, space group $I2/c$ (No. 15), a = 28.8593(4) Å, b = 12.2845(2) Å, c = 33.8899(5) Å, β = 104.681(1)°, V = 11622.5(3) Å^3. Z = 16, D_c = 1.494 g cm^{-3}, $F(000)$ = 5216, T = 140(1) K, μ(Mo Kα) = 50.9 cm^{-1}, λ(Mo Kα) = 0.71073 Å.

Crystals are colorless blocks. One, ca. 0.31 × 0.17 × 0.06 mm, was mounted in oil on a glass fiber and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω and φ scans. The total number of reflections recorded, to θ_{max} = 27.5°, was 97464, 13313 of which were unique (R_{int} = 0.086); 9821 were "observed" with $I > 2\sigma_I$.

Data were processed using the CrysAlisPro-CCD and -RED[19] programs. The structure was determined by the intrinsic phasing routines in the SHELXT program[20] and refined by full-matrix least-squares methods, on F^2 values, in SHELXL.[20] There are two independent, but very similar, molecules in this crystal. There is disorder in both molecules. The non-hydrogen atoms in full-occupation sites were refined with anisotropic thermal parameters; some of the disordered atoms were refined isotropically. The hydroxyl hydrogen atoms were not located or included in any calculations. All other hydrogen atoms were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, wR2 = 0.144 and R1 = 0.087[20] for all 13313 reflections weighted by w = $[\sigma^2(F_o^2) + (0.0455P)^2 + 138.22]^{-1}$ with P = $(F_o^2 + 2F_c^2)/3$; for the "observed" data only, R1 = 0.060. In the final difference map, the highest peak (ca. 3.1 e Å^{-3}) was close to a gold atom. Scattering factors for neutral atoms were taken from ref 21. Computer programs used in this analysis have been noted above and were run through WinGX[22] on a Dell Optiplex 780 PC at the University of East Anglia.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00077. Complete details of the X-ray analyses reported herein have also been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 1528330). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, U.K. (fax +44 1223 336033).

> Additional experimental details and characterization data and computational details (PDF)
> Crystallographic data for **11** (CIF)

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Notes
The authors declare no competing financial interest.

REFERENCES

(1) For recent summaries see for example: (a) Lauterbach, T.; Asiri, A. M.; Hashmi, A. S. K. *Adv. Organomet. Chem.* **2014**, *62*, 261−297. (b) Yang, W.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2014**, *43*, 2941−2955. (c) Hashmi, A. S. K. *Top. Organomet. Chem.* **2012**, *44*, 143−164. (d) Liu, L.-P.; Hammond, G. B. *Chem. Soc. Rev.* **2012**, *41*, 3129−3139. (e) Debrouwer, W.; Heugebaert, T. S. A.; Roman, B. I.; Stevens, C. V. *Adv. Synth. Catal.* **2015**, *357*, 2975−3006. (f) Miró, J.; del Pozo, C. *Chem. Rev.* **2016**, *116*, 11924−11966. (g) Zi, W. W.; Toste, F. D. *Chem. Soc. Rev.* **2016**, *45*, 4567−4589.

(2) (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410−3449. (b) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208−3221. (c) Bandini, M. *Chem. Soc. Rev.* **2011**, *40*, 1358−1367.

(3) Schmidbaur, H.; Schier, A. *Arab. J. Sci. Engin.* **2012**, *37*, 1187−1225. (b) Leyva-Perez, A.; Corma, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 614−635. (c) Boorman, T. C.; Larrosa, I. *Chem. Soc. Rev.* **2011**, *40*, 1910−1925.

(4) Recent reviews: (a) Joost, M.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 15022−15045. (b) Kumar, R.; Nevado, C. *Angew. Chem., Int. Ed.* **2017**, *56*, 1994−2015. (c) de Haro, T.; Nevado, C. *Synthesis* **2011**, *2011*, 2530−2539.

(5) See for example: (a) Rekhroukh, F.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2016**, *138*, 11920−11929. (b) Rekhroukh, F.; Estevez, L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2016**, *35*, 995−1001. (c) Tlahuext-Aca, A.; Hopkinson, M. N.; Daniliuc, C. G.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 11587−11592. (d) Winston, M. S.; Wolf, W. J.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 7777−7782. (e) Winston, M. S.; Wolf, W. J.; Toste, F. D. *J. Am. Chem. Soc.* **2015**, *137*, 7921−7928. (f) Kawai, H.; Wolf, W. J.; DiPasquale, A. G.; Winston, M. S.; Toste, F. D. *J. Am. Chem. Soc.* **2016**, *138*, 587−593. (g) Wolf, W. J.; Winston, M. S.; Toste, F. D. *Nat. Chem.* **2013**, *6*, 159−164. (h) Kaphan, D. M.; Levin, M. D.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *Science* **2015**, *350*, 1235−1238. (i) Nijamudheen, A.; Karmakar, S.; Datta, A. *Chem. - Eur. J.* **2014**, *20*, 14650−14658. (j) Ghosh, M. K.; Tilset, M.; Venugopal, A.; Heyn, R. H.; Swang, O. *J. Phys. Chem. A* **2010**, *114*, 8135−8141. (k) Corrie, T. J. A.; Ball, L. T.; Russell, C. A.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **2017**, *139*, 245−254.

(6) Roşca, D.-A.; Wright, J. A.; Bochmann, M. *Dalton Trans.* **2015**, *44*, 20785−20807.

(7) Roşca, D.−A.; Wright, J. A.; Hughes, D. L.; Bochmann, M. *Nat. Commun.* **2013**, *4*, 2167.

(8) Roşca, D.-A.; Fernandez-Cestau, J.; Morris, J.; Wright, J. A.; Bochmann, M. *Science Adv.* **2015**, *1*, e1500761.

(9) Smith, D. A.; Roşca, D.-A.; Bochmann, M. *Organometallics* **2012**, *31*, 5998−6000.

(10) (a) Grochowski, E.; Hilton, B. D.; Kupper, R. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 6876−6877. (b) Mathieu-Pelta, I.; Evans, S. A., Jr. *J. Org. Chem.* **1994**, *59*, 2234−2237.

(11) (a) Roşca, D.-A.; Smith, D. A.; Hughes, D. L.; Bochmann, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 10643−10646. (b) Roşca, D.-A.; Bochmann, M. *Organometallics* **2016**, *35*, 27−31.

(12) Dann, T.; Roşca, D.−A.; Wildgoose, G. G.; Wright, J. A.; Bochmann, M. *Chem. Commun.* **2013**, *49*, 10169−10171.

(13) Pintus, A.; Rocchigiani, L.; Fernandez-Cestau, J.; Budzelaar, P. H. M.; Bochmann, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 12321−12324.

(14) Roşca, D.-A.; Smith, D. A.; Bochmann, M. *Chem. Commun.* **2012**, *48*, 7247−7249.

(15) The formation of **9** is very sensitive to the reaction conditions. Reacting (C^N^C)AuCl with *t*-BuMgCl at room temperature gives exclusively **3**, as did mixtures of (C^N^C)AuOAc^F and ^tBu₂Mg at −78 °C, whereas the reaction of (C^N^C)AuOAc^F and *t*-BuMgCl at −78 °C afforded (C^N^C)AuCl.

(16) (a) Hendrix, W. T.; Cowherd, F. G.; von Rosenberg, J. L. *Chem. Commun.* **1968**, *0*, 97−99. (b) Chase, H. M.; McDonough, T. J.; Overly, K. R.; Laperle, C. M. *J. Phys. Org. Chem.* **2013**, *26*, 322−326.

(17) Dérien, S.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2551−2552.

(18) Rüba, E.; Gemel, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 2275−2280.

(19) *Programs CrysAlisPro*; Oxford Diffraction Ltd., Abingdon, U.K., 2014.

(20) Sheldrick, G. M. SHELX-97 − Programs for crystal structure determination (SHELXT) and refinement (SHELXL). *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122; *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8; and *Acta Crystallogr.* **2015**, *C71*, 3−8.

(21) *International Tables for X-ray Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, pp 500, 219, and 193.

(22) Farrugia, L. J. *J. Appl. Crystallogr.* **2012**, *45*, 849−854.