Gold(III)-CO and gold(III)-CO₂ complexes and their role in the water-gas shift reaction

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INTRODUCTION

The water-gas shift (WGS) reaction is an important process for the generation of hydrogen. Heterogeneous gold catalysts exhibit good WGS activity, but the nature of the active site, the oxidation state, and competing reaction mechanisms are very much matters of debate. Homogeneous gold WGS systems that could shed light on the mechanism are conspicuous by their absence; gold(I)-CO is inactive and gold(III)-CO complexes were unknown. We report the synthesis of the first example of an isolable CO complex of Au(III). Its reactivity demonstrates fundamental differences between the CO adducts of the neighboring d₈ ions Pt(II) and Au(III): whereas Pt(II)-CO is stable to moisture, Au(III)-CO compounds are extremely susceptible to nucleophilic attack and show WGS reactivity at low temperature. The key to understanding these dramatic differences is the donation/back-donation ratio of the M–CO bond: gold-CO shows substantially less back-bonding than Pt-CO, irrespective of closely similar ν(CO) frequencies. Key WGS intermediates include the gold-CO₂ complex [([C²N²C]Au)₂(μ-CO₂)], which reductively eliminates CO₂. The species identified here are in accord with Au(III) as active species and a carboxylate WGS mechanism.

RESULTS

Treatment of (C²N²C)AuOAc²⁻ (OAc²⁻ = trifluoroacetate) with B(C₆F₅)₃ in dichloromethane at −30°C gave a single product in quantitative yield [by ¹H NMR (nuclear magnetic resonance) spectroscopy], formulated as [(C²N²C)Au]⁺[B(C₆F₅)₃]₂OAc²⁻ (1). This intermediate is sufficiently stable at −20°C to permit subsequent reactions with weak donor ligands. Thus, treatment with CO gas cleanly generated [(C²N²C)Au–CO]⁺ [B(C₆F₅)₃]BOAc²⁻ (2a), which can be precipitated with light petroleum and was isolated as a yellow microcrystalline solid (Fig. 2). The ¹³C-labeled analog [(C²N²C)Au–¹³CO]⁺ (2a-¹³C) was similarly obtained. The same product was obtained when the ethylene complex [(C²N²C)Au(C₂H₄)]⁺[B(C₆F₅)₃]BOAc²⁻ (2b) was exposed to CO at −20°C. The ligand exchange process is monitored by ¹H NMR spectroscopy (fig. S6). Over
a period of 30 min, the signal for bound ethylene at δ 6.25 disappeared, accompanied by spectral changes confirming the quantitative formation of the CO complex. The hexafluorophosphate salt 2b was prepared by reacting (C\(^{\equiv}N\equivC\))AuOAc\(^{\theta}\) with [Ph\(_3\)C][PF\(_6\)] and CO in CH\(_2\)Cl\(_2\) at −30°C. The CO complexes 2a, b are temperature-sensitive and must be handled at temperatures lower than −10°C.

These reactions can be conveniently monitored by \(^{1}H\) NMR spectroscopy (Fig. 2). The signals in the aromatic region of the spectrum are highly diagnostic, in particular the triplet resonance of the H atom in the para position of the pyridine ring, and they confirm that, within detection limits, the reactions are clean and quantitative. The \(^{13}C\) NMR signal of coordinated CO in 2a, b is observed at δ 167.6 (cf. δ 184 for free CO).

The most sensitive tools for probing the nature of the Au(III)–CO bond in these compounds are vibrational spectroscopy and chemical reactivity. The ν\(_{\text{CO}}\) stretching frequency of 2a is observed at 2167 cm\(^{-1}\), compared to 2143 cm\(^{-1}\) of free \(^{12}\text{CO}\). The ν\(_{\text{CO}}\) stretch of the \(^{13}\text{C}\)-labeled version 2a-\(^{13}\text{C}\) is found at 2143 cm\(^{-1}\). The value found for 2a is close to that of CO bound to Au\(^{3+}\) centers in titania-supported heterogeneous gold–CO oxidation catalysts (2158 cm\(^{-1}\)) (28), which suggests that the CO bonding in our complexes closely mirrors that found in heterogeneous catalysts (29).

On the other hand, the differences in infrared (IR) parameters between structurally related Pt(II) and Au(III) are more pronounced; for example, the Pt(II) pincer complex [(N\(^{\equiv}N\equivC\)Pt-CO)]\(^{+}\) shows a ν\(_{\text{CO}}\) vibration at 2094 cm\(^{-1}\) (24), that is, substantially lower than that...
of 2 \([\text{N}^\text{N}^\text{N}^\text{C}] = 2-(\text{C}_2\text{H}_3\text{N})-6-(\text{C}_6\text{H}_4)\text{pyridine}\). Evidently, the back-bonding contribution in Au(III)–CO is significantly weaker than that in its Pt(II) congeners. This is reflected in dramatic differences in chemical reactivity: whereas the \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Pt}–\text{CO}]^{+}\) compound could be re-crystallized from boiling methanol, the Au complexes \(2a, b\) are highly sensitive to temperature and nucleophilic attack on CO (vide infra).

To explain the reactivity differences between the carbonyls of Pt(II) and Au(III), we probed the nature of the Au–CO interaction by density functional theory (DFT) calculations. Simulation of the \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Au}(\text{CO})]^+\) cation revealed that the highest occupied molecular orbital (HOMO) shows no electron density in the Au–C region (Fig. 3), and there is also no evidence for an Au–C \(\pi\)-bonding contribution in other high-energy occupied orbitals, that is, HOMO-1, HOMO-2, and HOMO-3 (Fig. S20). The lowest unoccupied molecular orbital (LUMO) does show \(\pi\)-symmetry around the Au–C vector but is some 0.138 Ha higher in energy than the HOMO (for comparison, the HOMO-1 is only 0.021 Ha below the HOMO).

Natural bond orbital analysis classifies the Au–C interaction as a single bond, with major contributions from gold derived from the 6\(s\), 6\(p\), and 6\(d_x\)/\(d_y\) molecular orbitals. Support for formulating the Au–CO interaction as a single \(\sigma\)-bond was provided by further analysis of the DFT structure. The donation/back-donation (\(d/b\)) ratio, as estimated by charge decomposition analysis (CDA), proved to be particularly informative: \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Au}(\text{CO})]^+\) shows a \(d/b\) ratio of 2.26, compared to a value of only 1.54 \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Pt}(\text{CO})]^+\), in line with a relatively stronger back-bonding in Pt(II)–CO complexes.

This view is further reinforced by the bond analysis of \(\text{cis-PtCl}_2(\text{CO})_2\), a complex that shows \(v_{\text{CO}}\) stretching frequencies of 2178 and 2137 cm\(^{-1}\) (\(v_s\) and \(v_u\), respectively, in benzene solution) (22), closely comparable to the value of 2167 cm\(^{-1}\) found for 2. However, the \(d/b\) ratio of PtCl\(_2\)(CO)\(_2\) is only 0.65; that is, despite the high stretching frequency, the back-donation from Pt(II) to CO is relatively much stronger than that in Au(III). Although high CO frequencies above those found for free CO (2143 cm\(^{-1}\)) are generally taken as diagnostic for high electrophilicity, it is the \(d/b\) ratio, rather than the \(v_{\text{CO}}\) value, that best explains the chemical reactivity.

This difference in \(d/b\) ratios between the two \(d^8\) systems Pt(II) and Au(III) has consequences. The low-temperature solution IR spectra of 2a and 2a–\(^{13}\)C in CD\(_2\)Cl\(_2\) were always accompanied by bands at 2338 cm\(^{-1}\) for \(^{12}\)CO and 2273 cm\(^{-1}\) for \(^{13}\)CO (Fig. 2). Because the CO\(_2\) must have originated from the CO complex, this observation pointed to a gold-mediated WGS reaction due to the presence of traces of moisture condensation under the recording conditions (\(-20^\circ\text{C}\)), an indication of the facile nucleophilic attack by water on the cationic gold–CO complex, in contrast to Pt(II) carbonyls. To demonstrate the reaction pathways of the Au(III)–CO system, we decided to use \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuOH}\) (30) as a surrogate for water, because this would allow precise stoichiometry control and facilitate the reaction monitoring by NMR spectroscopy. If WGS reactions were observed, the process would of course lead to the formation of \((\text{N}^\text{N}^\text{N}^\text{C})\text{Au}–\text{H}\) instead of \(\text{H}_2\), and again, this gold hydride gives a unique NMR signature (25). The expected reactions are summarized in Fig. 4. Reactions A, B, and C are part of a WGS cycle according to the carboxylate mechanism.

Bubbling CO through a solution of \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuOH}\) for 30 s at room temperature, followed by the replacement of excess CO by \(\text{N}_2\), does indeed generate the hydride \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuH}\), in agreement with reaction steps A and B. This sequence implies the formation of an unstable carboxylate intermediate \((\text{N}^\text{N}^\text{N}^\text{C})\text{Au–COOH}\), which readily decomposes by \(\beta\)-H elimination, to give CO\(_2\) and \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuH}\) (Fig. 4).

Hydrolysis of the gold(III) hydride, with liberation of \(\text{H}_2\) and regeneration of \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuOH}\) (reaction C), would close the cycle. However, this step cannot proceed under the neutral reaction conditions used for the NMR experiments because the Au–H bond in \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuH}\) is highly covalent; the complex is stable to water and mild acids. DFT calculations confirm the observed reactivity, with enthalpy values of \(-141\) and \(-28\) kJ mol\(^{-1}\) for reaction steps A and B, respectively, whereas C is endothermic (\(+95\) kJ mol\(^{-1}\)).

A different outcome was observed when a benzene solution of \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuOH}\) was exposed to CO and left to crystallize in the dark for 20 hours. The yellow crystalline product was identified as the CO\(_2\) complex \((\text{N}^\text{N}^\text{N}^\text{C})\text{Au}(\mu-\text{C}x\text{C}O–\text{CO})\text{Au}(\text{N}^\text{N}^\text{N}^\text{C})–\text{C}_6\text{H}_6\) (3–C\(_6\text{H}_6\)). The formation can be explained by the reaction of \((\text{N}^\text{N}^\text{N}^\text{C})\text{Au–COOH}\) with \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuOH}\) with elimination of water, reaction D (Fig. 4), with a calculated reaction enthalpy of \(-31\) kJ mol\(^{-1}\). The same product was obtained by treating the gold(III) oxide \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Au}]_2(\mu-O)\) with CO; this reaction proceeds even with the crystalline oxide in the solid state. Such reactivity is central to CO oxidation with heterogeneous gold catalysts (28). Complex 3 is the first CO\(_2\) complex of gold in any oxidation state.

The crystal structure of 3–C\(_6\text{H}_6\) confirmed the presence of a bridging CO\(_2\) ligand that adopts a \(\mu-\text{C}x\text{C}O–\text{O}\) position between two Au(III) centers (Fig. 4). There is disorder because CO\(_2\) gives two linkage isomers, each with 50% occupancy, similar to that described before for complex \([2.6-\text{C}_6\text{H}_4(\text{CH}_3\text{P})_2\text{Pd}]_2(\mu-\text{CO}_2)\) (31). The Au–C bond to CO\(_2\), 2.111(1) \(\text{Å}\), is long compared to conventional Au–C(sp\(^3\)) and Au–C(sp\(^2\)) bonds (for comparison, the bonds to ethyl and aryl ligands in \((\text{N}^\text{N}^\text{N}^\text{C})\text{AuEt}\) and \((\text{N}^\text{N}^\text{N}^\text{C})\text{Au(C}_6\text{H}_4\text{F})\text{(OAc)}\) are 2.042(8) and 2.029(7) \(\text{Å}\), respectively (32)). The short C=O (1.18 \(\text{Å}\)) and long C–O (1.29 \(\text{Å}\)) distances, together with the interatomic angles, point to a low degree of charge delocalization in the CO\(_2\) ligand.

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Fig. 3. Molecular orbitals involved in Au–CO bonding, showing, from left to right, HOMO-1, HOMO, and LUMO in \([(\text{N}^\text{N}^\text{N}^\text{C})\text{Au}(\text{CO})]^+\) as simulated by DFT. None of the lower-lying occupied orbitals shows any \(\pi\)-bonding interactions along the Au–CO vector.
Complex 3 is stable under ambient conditions in the solid state. However, heating the solid to 80° to 120°C under vacuum leads to the reductive elimination of CO₂ and formation of the known (C^N^C)Au-COOMe (4) as a white crystalline solid. Compound 4 is thermally stable and there is no reaction of 4 with excess (C^N^C)AuOH to produce 3 and MeOH.

As an alternative to the carboxylate pathway in the WGS reaction, a formate pathway has been suggested, where CO formally inserts into the O–H bond of Au–OH to give Au–OC(O)H (7, 8). Alternatively, formic acid may be generated by hydrogenolysis of a metal–COOH species. The search for this reaction pathway was, however, unsuccessful for our system: Complex 4 is stable under 4 bar of H₂ up to 80°C without any sign for the presence of methyl formate. The attempted hydrogenolysis of 3 (4 bar of H₂) exclusively led to the reductive elimination of CO₂. In any case, in the present system, the hydrogenolysis of Au–COOH to Au–H + HCOOH is effectively thermoneutral (by DFT, ΔH = −96 kJ mol⁻¹).

This work has shown that, given suitable supporting ligands, CO complexes of Au(III) can indeed be isolated, nearly 150 years after the preparation of the isoelectronic Pt(II) analogs. This has allowed a detailed comparison of their reactivity. The susceptibility to nucleophilic attack and DFT modeling suggest a minimal contribution by backdonation to the Au–CO bond, which contrasts with structurally related Pt(II)–CO complexes. The d/b ratio, obtained by way of CDA, proved to be a more reliable indicator of chemical reactivity than the ν(CO) frequencies and explains subtle but important differences in metal–CO bonding between the neighboring elements platinum and gold. The result is WGS-type reactivity in the gold system at low temperature and the absence of such reactions for platinum(II) carboxyls. These studies have enabled the use of a homogeneous gold system to probe the viability of the carboxylic mechanism proposed for the WGS reaction catalyzed on gold surfaces and provide support for gold(III) ions in this process.

MATERIALS AND METHODS

General

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry nitrogen or using Saffron Scientific or MBRAUN glove boxes. Nitrogen was purified by passing through columns of supported P₂O₅, with moisture indicator and activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. (C^N^C)AuOH (30), (C^N^C)Au(OAc)₆ (30), [C(C=O)Au]₂(O) (27), (C^N^C)AuH (25), [C(C=O)Au]₂ (25), [C(C=O)Au(n^2-C₆H₄)][B(C₆F₅)₃(OAc)₅] (26), and B(C₆F₅)₃ (34) were prepared using literature methods. [Ph₃C][PF₆] (Sigma) was used.

Fig. 4. Gold(III)-mediated WGS reactions showing reaction steps A to C, the formation of the Au(III)-CO₂ complex 3 via pathway D, and the reductive elimination of CO₂ from 3 (step E). The colors indicate the H atoms that are diagnostic for monitoring these processes by ¹H NMR spectroscopy, with associated chemical shifts. In the molecular structure of [(C^N^C)Au(μ-κ:κ-O-CO₂)]₂(C₂H₆) (3-C₂H₆), thermal ellipsoids are set at 50% probability level and hydrogen atoms and the solvent were omitted for clarity. The CO₂ group is 50% disordered between two positions; the box shows the central core of the other position. Selected bond distances (in angstroms) and angles (in degrees) are as follows: Au(1)-C(26) 2.11(1); C(26)-O(1a) 1.18(1); C(26)-O(2) 1.29(1); O(1a)-C(26)-O(2) 126(1); Au(1)-N(1) 1.999(6); Au(1)-C(1) 2.064(8); Au(1)-C(17) 2.068(8); N(1)-Au(1)-C(26) 169.5(5); Au(1)-C(26)-O(1a) 129(1); Au(1)-C(26)-O(2) 114(1); N(1)-Au(1)-O(2) 160.5(3).
as purchased. Natural abundance CO (BOC) and 13CO (Euirus-Top) were used as purchased or dried before use passing through columns with activated 4 Å molecular sieves.

1H, 13C{1H}, and 19F spectra were recorded using a Bruker Avance DPX-300 or a Bruker Avance DPX-500 spectrometer. Deuterated solvents were dried over CaH2 degassed by three freeze-pump-thaw cycles, and stored on 4 Å molecular sieves before use. 1H NMR spectra (300.13 MHz) were referenced to the residual protons of the deuterated solvent used. 13C[1H] NMR spectra (75.47 MHz) were referenced internally to the D-coupled 13C resonances of the NMR solvent. IR spectra were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer with a diamond attenuated total reflectance attachment or using liquid cells with KBr plates.

**Synthesis of [[(C^N^C)Au][B(C6F5)3OAc]^+] (1)**

(C^N^C)Au(OAc)^+ (15 mg, 23.6 μmol) and B(C6F5)3 (12 mg, 23.6 μmol) were charged into a J. Young NMR tube and cooled to ~78°C. To this, we added precooled (~78°C) CD2Cl2 (0.6 ml), generating a yellow solution. The sample was inserted into an NMR spectrometer probe head precooled to ~40°C. Obvious signs of decomposition were observed above ~20°C by 1H NMR spectroscopy, which coincided with a darkening of the solution from yellow to brown. The numbering system used for assigning the 1H and 13C NMR signals of the C^N^C ligand is as follows:

\[
\begin{array}{cccccccccc}
\text{1} & \text{2} & \text{3} & \text{4} & \text{5} & \text{6} & \text{7} & \text{8} & \text{9} & \text{10} & \text{11}
\end{array}
\]

for a few seconds. The mixture was kept at 20°C by 1H NMR spectroscopy, which coincided with a darkening of the solution from yellow to brown.

**Synthesis of [[(C^N^C)Au](B(C6F5)3OAc)] (2a)**

**Method 1.** (C^N^C)Au(OAc)^+ (100 mg, 0.16 mmol) and B(C6F5)3 (80.5 mg, 0.16 mmol) were charged into a Schlenk flask and cooled to ~78°C. To this, we added CH2Cl2 (30 ml) precooled to ~78°C. The mixture was warmed to ~30°C and CO gas was bubbled through the mixture for a few seconds. The mixture was kept at ~30°C for 1 hour. While keeping the mixture below ~20°C, the CH2Cl2 solution was layered with light petroleum (1:1 v/v) and was stored at ~20°C. The spectroscopic parameters were identical to those of 2a, but the compound proved thermally too unstable to allow isolation.
Synthesis of $[(C^N^C)Au]_2(\mu-κ-CxO\cdot13CO_2)$ (3-13C)

The same conditions used for the synthesis of 3 were applied, but $^{13}$CO was used instead of $^{12}$CO. The $^{13}$C NMR spectrum of the mixture was recorded (fig. S8). The main difference is the higher intensity of the signal at 170.69 ppm, which corresponds to the bridging CO$_2$ ligand.

Thermolysis of $[(C^N^C)Au]_2(\mu-κ-CxO\cdotCO_2)$ (3 and 3-13C)

**Method 1.** A Schlenk flask was charged with $[(C^N^C)Au]_2$ (3 mg, 0.005 mmol) and $^{13}$CO (3 atm) in CD$_2$Cl$_2$ (5 ml) and stored under N$_2$ at 150°C. The quantitative conversion of 3 to $[(C^N^C)Au]_2$ was confirmed by $^1$H NMR spectroscopy.

**Method 2.** $^{13}$CO gas was bubbled for 30 s through a solution of $[(C^N^C)Au]_2$ (5 mg, 0.005 mmol) in CD$_2$Cl$_2$ (5 ml) and stored under $^{13}$CO for an additional 5 min. After this time, the reaction was subjected to three freeze-pump-thaw cycles and stored under N$_2$ at 60°C. Monitoring by $^1$H and $^{13}$C NMR spectroscopy at 25°C confirmed the conversion of $[(C^N^C)Au]_2(\mu-κ-CxO\cdotCO_2)$ to $[(C^N^C)Au]_2$ and CO$_2$ (fig. S9).

Reactivity of $[(C^N^C)Au]_2$ with CO

Fast reaction conditions: CO gas bubbled for 30 s through a solution of $[(C^N^C)Au]_2$ (5 mg, 0.005 mmol) in CD$_2$Cl$_2$ (2 ml). Then, the reaction was subjected to three freeze-pump-thaw cycles, stored under N$_2$, and monitored by $^1$H NMR spectroscopy at 25°C. The spectrum showed additional signals that corresponded to the formation of $[(C^N^C)Au]_2$ (figs. S10 and S11).

Synthesis of $[(C^N^C)Au]_2(\mu-κ-CxO\cdotCO_2)\cdot4$ CO$_2$ Me 4

CO gas was bubbled through a solution of $[(C^N^C)Au]_2$ (10 mg, 0.11 mmol) in CH$_2$Cl$_2$ for 5 min, in the presence of 4 Å molecular sieves. After stirring under a CO atmosphere for an additional 5 min, filtration through celite, evaporation of the filtrate to dryness, and washing with light petroleum afforded 4 as a white solid that was dried in vacuo (figs. S14 to S16). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20°C): δ = 4.73 (t, J = 8.0 Hz, 1H, H'), 7.73 (d, J = 2.0 Hz, 2H, H'), 7.55 (d, J = 8.2 Hz, 2H, H'), 7.45 (d, J = 8.0 Hz, 2H, H'), 7.30 (dd, J = 8.2, 2.0 Hz, H'), 3.93 (s, 3H, Me, CO$_2$Me), 1.34 (s, 18H). $^{13}$C{1H} NMR (75 MHz, CD$_2$Cl$_2$, 20°C): δ = 175.55 (COOMe), 156.03 (C8), 154.99 (C9), 147.64 (C7), 143.16 (C4), 134.84 (C1), 125.95 (C12), 125.59 (C13), 124.73 (C7), 117.10 (C5), 52.69 (COOCH$_3$), 36.04 (C10), 31.85 (C11). Anal. calcd. (found) for CH$_5$(C$_2$H$_5$)$_2$O$_4$ 54.84 (54.70); 4.96 (4.75); 2.30 (2.60). IR: ν(C=O) = 1675 cm$^{-1}$.

Reaction of $[(C^N^C)Au]_2$ with $^{13}$CO

$^{13}$CO gas was bubbled through a solution of $[(C^N^C)Au]_2$ (5 mg, 0.01 mmol) in CD$_2$Cl$_2$ (2 ml) for 10 min at −30°C (fig. S17). Further, CD$_2$Cl$_2$ was added to restore the evaporation losses. The mixture was subjected to three freeze-pump-thaw cycles, stored under N$_2$, and monitored by $^1$H and $^{13}$C NMR spectroscopy. The $^1$H NMR spectrum shows a pattern identical to 4, but the signal at 3.93 ppm appeared as a $^{13}$C-coupled doublet. In addition, because of the difficulty of drying $^{13}$CO as thoroughly as $^{12}$CO, the complex appeared mixed with $^{13}$C$_3$C and $[(C^N^C)Au]_2$, because of the hydrolisis of ($C^N^C$)AuOMe, which generates CH$_3$OH and ($C^N^C$)AuOH and opens the path to 4 and reductive CO$_2$ elimination (figs. S17 and S18).

Attempted hydrogenolysis of $[(C^N^C)Au]_2$ with CO

A high-pressure NMR tube was charged with ($C^N^C$)AuCO$_2$Me 4 (5 mg, 0.01 mmol) in CD$_2$Cl$_2$ (5 ml), pressurized with 4 bar of H$_2$, and warmed to 60°C. No formation of methyl formate was detectable after 1 week.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/9/e1500761/DC1

Text

Fig. S1. $^1$H NMR (CD$_2$Cl$_2$, −25°C) spectrum of 1.

Fig. S2. Superposition of the IR spectra of $[\text{[(C}^N\text{C)}Au]}_2^{12}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2 and $[\text{[(C}^N\text{C)}Au]}_2^{13}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2-a.

Fig. S3. $^1$H NMR spectrum of 2 (CD$_2$Cl$_2$, −20°C).

Fig. S4. Stacked plot of the aromatic region of the $^1$H NMR spectra (CD$_2$Cl$_2$, −20°C) of ($C^N^C$)AuOMe, $[\text{[(C}^N\text{C)}Au]}_2^{13}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2, and $[\text{[(C}^N\text{C)}Au]}_2^{13}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2-a.

Fig. S5. $^{13}$C NMR (CD$_2$Cl$_2$, −20°C) spectrum of 2-a.

Fig. S6. Monitoring by $^1$H NMR (CD$_2$Cl$_2$, −20°C) of the conversion of $[\text{[(C}^N\text{C)}Au]}_2^{13}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2 to $[\text{[(C}^N\text{C)}Au]}_2^{13}\text{CO}]^{-}\left[[\text{C(C}_6\text{F}_5)_3\text{OAcF}\right]_2}$ 2-a.

Fig. S7. $^{13}$C NMR spectrum of 3 (CD$_2$Cl$_2$, 25°C). The inset shows the τ-butyly resonances.

Fig. S8. $^1$H NMR spectrum of complex 3-13C (CD$_2$Cl$_2$, 25°C).

Fig. S9. Monitoring by $^1$H and $^{13}$C NMR spectroscopy of the thermolysis of complex 3-13C in CD$_2$Cl$_2$.

Fig. S10. $^1$H NMR spectra of a solution of $[(C^N^C)Au]_2$ in CD$_2$Cl$_2$ under 2 bar of CO at room temperature at different reaction times.

Fig. S11. Aromatic and hydride regions of the $^1$H NMR spectra of a solution of $[(C^N^C)Au]_2$ in CD$_2$Cl$_2$ and after CO addition for 30 s.

Fig. S12. $^1$H NMR spectra in CD$_2$Cl$_2$ at room temperature of the aromatic region of $[(C^N^C)Au]_2$ before and after its exposure to 2 bar of CO in the solid state.

Fig. S13. Superposition of the IR spectra of $[(C^N^C)Au]_2$ in the solid state and after exposure to 2 bar of CO for 8 hours.

Fig. S14. $^1$H NMR spectrum of 4 (CD$_2$Cl$_2$, 25°C).

Fig. S15. Superposition of the IR spectra of $[(C^N^C)Au]_2$ and $[(C^N^C)Au]_2$ in the blue state.
REFERENCES AND NOTES


21. The 13C NMR signal of coordinated CO in 2a, b is observed at 51 167.6 (cf. 51 184 for free CO); this value falls within the range observed, for example, for [Au(CO)]2+ and [Au(CO)]2+ in superacidic solution (51 158 to 172) and is minimally influenced by the d5 vs. d10 electron configuration of the metal center; see (16).


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