Gold(III)-CO and gold(III)-CO$_2$ complexes and their role in the water-gas shift reaction

Dragoş-Adrian Roşca,* Julio Fernandez-Cestau, James Morris, Joseph A. Wright, Manfred Bochmann†

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 $d^9$ 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 $\nu$(CO) frequencies. Key WGS intermediates include the gold-CO$_2$ complex [(C$^N^C$)Au]$\mu$-CO$_2$, which reductively eliminates CO$_2$. The species identified here are in accord with Au(III) as active species and a carboxylate WGS mechanism.

RESULTS

Treatment of (C$^N^C$)AuOAc$^-$ (OAc$^-$ = trifluoroacetate) with B(C$_6$F$_5$)$_3$ in dichloromethane at $-30^\circ$C gave a single product in quantitative yield [by $^1$H NMR (nuclear magnetic resonance) spectroscopy], formulated as [(C$^N^C$)Au]$^+$(C$_2$F$_5$)$_3$BOAc$^-$ (I). This intermediate is sufficiently stable at $-20^\circ$C to permit subsequent reactions with weak donor ligands. Thus, treatment with CO gas cleanly generated [(C$^N^C$)Au–CO]$^+$ (2a), which can be precipitated with light petroleum and was isolated as a yellow microcrystalline solid. The 13C-labeled analog [(C$^N^C$)Au–13CO]$^+$ (2a–13C) was similarly obtained.

The lack of Au(III)–CO complexes is surprising. Au(III) and Pt(II) are isoelectronic $d^9$ ions that typically give isostuctural complexes. Carbonyl complexes of Pt(II) have been known since the 19th century; they were first transition metal–CO complexes ever made (20). Evidently, the platinum-gold analogy, which generally serves well, does not extend to CO adducts. However, although Pt(II) carbonyls show characteristically high $\nu$(CO) frequencies, which suggest electrophilic carbonyl C atoms (21, 22), they have been proven to be stable to the attack of water and do not show WGS-type reactivity (23, 24).

Given the strongly positive redox potential of Au$^{3+}$ ($E_0 = 1.52$ V) and the reducing power of CO, the absence of isolable Au(III) carbonyl derivatives seemed entirely plausible. However, we found that CO complexes of Au(III) are readily accessible through the appropriate choice of stabilizing ligands and report here the synthesis of [(C$^N^C$)Au–CO]$^+$X$^-$ salts, where X is a noncoordinating anion. The cycloometalated C$^N^C$ pincer ligand [(C$^N^C$) = 2,6-bis(4-BuC$_6$H$_4$)$_2$pyridine dianion] had previously enabled the isolation of Au(III) hydride, alkene, and peroxide complexes (25–27). Moreover, these Au(III)–CO complexes show facile WGS-type reactivity, in stark contrast to their Pt(II) congeners.

School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK.
*Present address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany.
†Corresponding author. E-mail: m.bochmann@uea.ac.uk

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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^N^C)AuOAc with [Ph3C][PF6] and CO in CH2Cl2 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 1H 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 13C 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 νCO stretching frequency of 2a is observed at 2167 cm⁻¹, compared to 2143 cm⁻¹ of free 12CO. The νCO stretch of the 13C-labeled version 2a-13C is found at 2143 cm⁻¹. The value found for 2a is close to that of CO bound to Au3⁺ 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^N^C)Pt–CO]+ shows a ν(CO) vibration at 2094 cm⁻¹ (24), that is, substantially lower than that...
of 2 \([\text{N}^\text{N}^\text{N}^\text{C}] = 2 - (\text{C}_6\text{H}_3\text{N}) - 6 - (\text{C}_6\text{H}_2)\text{pyridine}\). 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 \([\text{C}^\text{N}^\text{N}^\text{C}]\text{Au} - \text{CO}\)^+ 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 π-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 π-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 6s, 6p\(_x\), and 6dx\(_{2y}\) molecular orbitals. Support for formulating the Au–CO interaction as a single σ-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: \([\text{C}^\text{N}^\text{N}^\text{C}]\text{Au} - \text{CO}\)^+ 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 cis-PtCl\(_2\)(CO)\(_2\), a complex that shows \(v\)\(_{\text{CO}}\) stretching frequencies of 2178 and 2137 cm\(^{-1}\) (\(v_c\) and \(v_{\text{as}}\), 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-13C in CH\(_2\)Cl\(_2\) were always accompanied by bands at 2338 cm\(^{-1}\) for 13CO\(_2\) and 2273 cm\(^{-1}\) for 13CO\(_2\) (Fig. 2). Because the CO 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°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 (C\(^\text{N}^\text{N}^\text{C}\))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 (C\(^\text{N}^\text{N}^\text{C}\))Au–H instead of 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 (C\(^\text{N}^\text{N}^\text{C}\))AuOH for 30 s at room temperature, followed by the replacement of excess CO by N\(_2\), does indeed generate the hydride (C\(^\text{N}^\text{N}^\text{C}\))AuH, in agreement with reaction steps A and B. This sequence implies the formation of an unstable carboxylate intermediate (C\(^\text{N}^\text{N}^\text{C}\))Au–CO\(_2\), which readily depolymerizes by β-H elimination, to give CO\(_2\) and (C\(^\text{N}^\text{N}^\text{C}\))AuH (Fig. 4).

Hydrolysis of the gold(III) hydride, with liberation of H\(_2\) and regeneration of (C\(^\text{N}^\text{N}^\text{C}\))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 (C\(^\text{N}^\text{N}^\text{C}\))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 (C\(^\text{N}^\text{N}^\text{C}\))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 (C\(^\text{N}^\text{N}^\text{C}\))Au(μ-κC\(_3\)O-CO\(_2\))Au(C\(^\text{N}^\text{N}^\text{C}\)-C\(_6\)H\(_6\)) (3-C\(_6\)H\(_6\)). The formation can be explained by the reaction of (C\(^\text{N}^\text{N}^\text{C}\))AuOH with C\(_2\)O\(_2\) 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 [(C\(^\text{N}^\text{N}^\text{C}\))Au]_2(μ-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\(_6\)H\(_6\) confirmed the presence of a bridging CO\(_2\) ligand that adopts a μ-κC\(_3\)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 \([2,6-\text{C}_6\text{H}_3\text{P} (\text{Pr})_2]_2\text{Au}(\mu-\text{CO})_2\) (31). The Au–C bond to CO\(_2\), 2.11(1) 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 (C\(^\text{N}^\text{N}^\text{C}\))AuEt and (C\(^\text{N}^\text{N}^\text{C}\))Au(C\(_6\)H\(_4\)F)(OAc\(_2\)) are 2.042(8) and 2.029(7) Å, respectively (32]). The short C=O (1.18 Å) and long C–O (1.29 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 [(C\(^\text{N}^\text{N}^\text{C}\))Au(CO)]\(^+\) as simulated by DFT. None of the lower-lying occupied orbitals shows any π-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 \((\text{C}^N\text{C})\text{AuOMe}\) (30), which gives the methyl carboxylate \((\text{C}^N\text{C})\text{AuOC(O)H}\) (4) as a white crystalline solid. Compound 4 is thermally stable, and there is no reaction of 4 with excess \((\text{C}^N\text{C})\text{AuO}\) 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, \(\Delta H = -4 \text{kJ mol}^{-1}\)).

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 back-donation 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 \(v_{\text{CO}}\) 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) carbonyls. 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. \((\text{C}^N\text{C})\text{AuOH}\) (30), \((\text{C}^N\text{C})\text{Au(OAc)}^2\) (30), \([\text{C}(\text{N}^\text{C})\text{Au}]_2\)O (27), \((\text{C}^N\text{C})\text{AuH}\) (25), \([\text{C}(\text{N}^\text{C})\text{Au}]_2\) (25), \([\text{C}(\text{N}^\text{C})\text{Au}(\text{n}^\text{2}-\text{C}_2\text{H}_4)]\text{[B(C}_6\text{F}_5)_3\text{(OAc)}^2]\) (26), and \(\text{B(C}_6\text{F}_5)_3\) (34) were prepared using literature methods. [Ph₃C][PF₆] (Sigma) was used.
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as purchased. Natural abundance CO (BOC) and 13CO (Euriso-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 solvents were dried over CaH2, degassed by three freeze-pump-thaw cycles, and stored on 4 Å molecular sieves before use.

Synthesis of [(C^N^C)Au][B(C6F5)3OAcF] (1) (C^N^C)AuOAcF (100 mg, 0.16 mmol) and B(C6F5)3 (62 mg, 23.6 µmol) were charged into a J. Young NMR tube and cooled to −78°C. The sample was inserted into an NMR spectrometer probe head precooled to −40°C. 1H NMR (fig. S1, 300 MHz, CD2Cl2, −25°C) δ 7.88 (t, J = 8.0 Hz, 1H, H1), 7.41 to 7.33 (m, 5H), 7.23 (d, J = 10.0 Hz, 2H, H2), 7.12 (s, 18H, H11 or 11), 7.04 (d, J = 8.0 Hz, 1H, H1 or 1), 1.20 (s, 18H, H11 or 11). 13C{1H} NMR (75 MHz, CD2Cl2, −25°C) δ 163.92 (C2), 157.65 (C7), 144.65 (C4), 144.42 (C2), 127.14 (C6), 126.57 (C5), 118.05 (C2), 35.69 (C10), 30.54 (C11). Resonances for C9, C13, and the B(C6F5)3OAcF anion were not observed because of the short acquisition time. 19F NMR (282 MHz, CD2Cl2, −40°C) δ −76.68 (s, 3F, OAcF), −133.56 (br s, 3F, o-C6F5), −159.36 (br s, 3F, p-C6F5), −164.86 (br s, 6F, m-C6F5). IR (CH2Cl2 solution): ν(12CO) 2143 cm−1.

Synthesis of [(C^N^C)AuOAc][B(C6F5)3] (2a) Method 1. (C^N^C)AuOAcF (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][B(C6F5)3OAcF] (2a-13C) Method 3. In a J. Young NMR tube, [(C^N^C)Au][B(C6F5)3OAcF] (15 mg, 23.6 µmol) with B(C6F5)3 (12 mg, 23.6 µmol) at −50°C. The 1H NMR spectrum of 1 was then recorded at −40°C. 13CO or 13CO was bubbled through the solution for a few seconds, and the sample was injected into the NMR spectrometer precooled to −40°C. The conversion from 1 to 2a could be monitored over the course of 2 hours at −20°C (figs. S3 to S5).

Synthesis of [(C^N^C)Au][B(C6F5)3] (2b) (C^N^C)AuOAcF (100 mg, 0.16 mmol) and [Ph3C][PF6] (62 mg, 0.16 mmol) were charged into a J. Young NMR tube and cooled to −78°C. The sample was then left to stand in the dark for 20 hours, yielding 2a as a bright yellow powder.

Sample preparation for IR spectroscopy: an aliquot of a CH2Cl2 solution of 2a was injected into a liquid IR cell that was precooled with dry ice. The IR spectrum was recorded immediately (fig. S2).

Method 2. In a J. Young NMR tube, [(C^N^C)Au][B(C6F5)3OAcF] (1) was generated as described above by mixing (C^N^C)AuOAcF (15 mg, 23.6 µmol) with B(C6F5)3 (12 mg, 23.6 µmol) at −50°C. The 1H NMR spectrum of 1 was then recorded at −40°C. 13CO or 13CO was bubbled through the solution for a few seconds, and the sample was injected into the NMR spectrometer precooled to −40°C. The conversion from 1 to 2a could be monitored over the course of 2 hours at −20°C (figs. S3 to S5).

Synthesis of [(C^N^C)Au][B(C6F5)3] (2a) (C^N^C)AuC2H4 (30.5 mg, 0.16 mmol) and B(C6F5)3 (12 mg, 23.6 µmol) at −50°C. The 1H NMR spectrum of 1 was then recorded at −40°C. Ethylene was then added to generate [(C^N^C)Au(C2H4)][B(C6F5)3], and the mixture was treated with CO gas for a few seconds at −40°C. The solution was transferred into the NMR spectrometer probe precooled to −20°C, and the conversion of [(C^N^C)Au(C2H4)]+ to [(C^N^C)Au(CO)]+ was monitored (fig. S6).

IR (CH2Cl2 solution): ν(13CO) 2167 cm−1.

Synthesis of [(C^N^C)Au][B(C6F5)3OAcF] (2a-13C) (2b) (C^N^C)AuOAcF (100 mg, 0.16 mmol) and [Ph3C][PF6] (62 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.
168.06 (C^N^C)Au, 154.99 (C^N^C)Au), 143.26 (C^N^C)Au, 141.79 (C^N^C)Au, 134.41 (C^N^C)Au, 131.65 (C^N^C)Au, 124.68 (C^N^C)Au, 124.65 (C^N^C)Au, 124.14 (C^N^C)Au, 123.45 (C^N^C)Au, 116.19 (C^N^C)Au, 115.81 (C^N^C)Au, 35.17 (C^N^C)Au, 35.04 (C^N^C)Au, 31.08 (C^N^C)Au, 30.93 (C^N^C)Au.

**Method 2.** CO gas was bubbled for 30 s through a solution of [(C^N^C)Au]2(O)2 (20 mg, 0.017 mmol) in CD2Cl2 (2 ml) for 10 min at −30°C (fig. S7). Further, CD2Cl2 was added to restore the evaporation losses. The mixture was subjected to three freeze-pump-thaw cycles, stored under N2, and monitored by 1H and 13C NMR spectroscopy. The 1H NMR spectrum shows a pattern identical to 4, but the signal at 3.93 ppm appeared as a 13C-coupled doublet. In addition, because of the difficulty of drying 13CO as thoroughly as 12CO, the complex appeared mixed with 3 and [(C^N^C)Au]2, because of the hydrolysis of [(C^N^C)AuOMe], which generates CH3OH and (C^N^C)AuOH and opens the path to CO2 elimination (figs. S17 and S18).

**Attempted hydrolysis of [(C^N^C)AuCO2Me]4**

A high-pressure NMR tube was charged with [(C^N^C)Au]2(O)2 (5 mg, 9 μmol) in CD2Cl2 (5 ml), pressurized with 4 bar of H2, and warmed to 60°C. No formation of methyl formate was detectable after 1 week.

**Synthesis of (C^N^C)AuCO2Me 4**

CO gas was bubbled through a solution of (C^N^C)AuOMe (5 mg, 9 μmol) in CD2Cl2 (2 ml) for 10 min at −30°C (fig. S16). 1H NMR (300 MHz, CD2Cl2, 20°C): 6.73 (t, J = 8.0 Hz, 1H, H1), 7.73 (d, J = 2.0 Hz, 2H, H2), 7.55 (d, J = 8.2 Hz, 2H, H3), 7.45 (d, J = 8.0 Hz, 2H, H4), 7.30 (dd, J = 8.2, 2.0 Hz, H5), 3.93 (s, 3H, Me, COOCH3), 1.34 (s, 18H). 1H NMR: 13CO gas was bubbled through a solution of (C^N^C)AuOMe (10 mg, 9 μmol) in CD2Cl2 (5 ml), pressurized with 4 bar of H2, 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/11/e1500761/DC1

Text

Fig. 1. 1H NMR (CD2Cl2, −25°C) spectrum of 1.
Fig. 2. Superposition of the IR spectra of [(C^N^C)Au(13CO)][BC6F5(OAc)2]+ at 20°C (2a) and [(C^N^C)Au(13CO)][BC6F5(OAc)2]+ at 10°C.
Fig. 3. 2a NMR spectrum of CD2Cl2 (20°C).
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Fig. 9. Monitoring by 1H and 13C NMR spectroscopy of the thermolysis of complex 3-13C in CD2Cl2.
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Fig. 11. Superposition of the IR spectra of [(C^N^C)Au][BC6F5(OAc)2]+ before and after its exposure to 2 bar of CO in the solid state.
Fig. 12. Superposition of the IR spectra of [(C^N^C)Au][BC6F5(OAc)2]+ before and after its exposure to 2 bar of CO in the solid state.
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Fig. 15. Superposition of the IR spectra of [(C^N^C)Au][BC6F5(OAc)2]+ before and after its exposure to 2 bar of CO in the solid state.
REFERENCES AND NOTES


17. The 14C NMR signal of coordinated CO in 2a,b is observed at 167.6 (cf. 184 for free CO); this value falls within the range observed, for example, for [Au(CO)]+ and [Au(CO)]2− in superacidic solution (δ 158 to 172) and is minimally influenced by the δd versus δd15 electron configuration of the metal center; see (16).


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Gold(III)-CO and gold(III)-CO₂ complexes and their role in the water-gas shift reaction
Dragos-Adrian Rosca, Julio Fernandez-Cestau, James Morris, Joseph A. Wright and Manfred Bochmann

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