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A chromo-fluorogenic synthetic "canary" for CO detection based on a pyrenylvinyl ruthenium(II) complex

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Supporting Information Placeholder

ABSTRACT: The chromo-fluorogenic detection of carbon monoxide in air has been achieved using a simple, inexpensive system based on ruthenium(II). This probe shows exceptional sensitivity and selectivity in its sensing behavior in the solid state. A color response visible to the naked eye is observed at 5 ppb of CO and a remarkably clear color change occurs from orange to yellow at the onset of toxic CO concentrations (100 ppm) in air. Even greater sensitivity (1 ppb) can be achieved through a substantial increase in turn-on emission fluorescence in the presence of carbon monoxide, both in air and in solution. No response is observed with other gases including water vapor. Immobilization of the probe on a cellulose strip allows the system to be applied in its current form in a simple optoelectronic device to give a numerical reading and/or alarm.

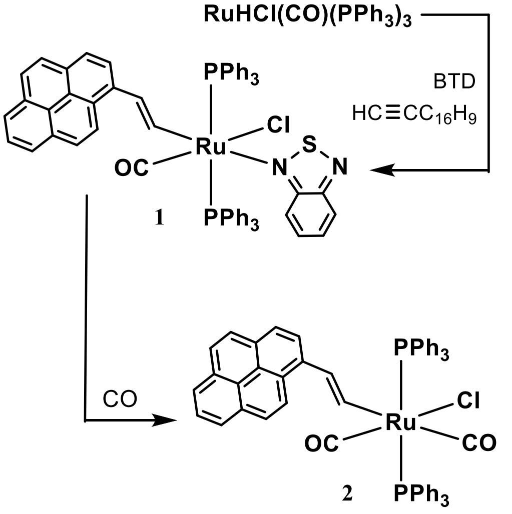
The development of electronic household detectors for harmful gases dates from the 1980s and 90s. Back in 1911, canaries were traditionally used in coal mines as an early detection system against life threatening gases such as carbon dioxide, carbon monoxide and methane. The canary, normally a very songful bird, would stop singing and eventually die in the presence of these gases, signaling to the miners to exit the mine. Although considered as moderately toxic compared to other highly poisonous gases, carbon monoxide (CO) detection has always been of vital importance as it lacks color, odor or taste and it is present in numerous natural and artificial environments.[1] Carbon monoxide is a temporary atmospheric pollutant in some urban areas, mainly arising from the exhaust of internal combustion engines (such as vehicles, portable generators, lawn mowers and power washers), but also from incomplete combustion of other fuels (including wood, coal, charcoal, oil, paraffin, propane, natural gas, and waste). Many technologies and devices (electrochemical,[2] optical,[3] mainly based on metal-oxide semiconductors[4]) have been developed to detect, monitor, and alert the leakage of carbon monoxide. These systems suffer from drawbacks such as false alarms arising due to water vapor or airborne particulates. As an alternative to these systems the design of molecular-based probes for the chromo-fluorogenic recognition of CO is of importance. In particular, colorimetric methods are undemanding, giving advantages such as real-time monitoring and the use of simple and inexpensive instrumentation. Moreover, certain colorimetric changes can be observed "to the naked eye", thus making chromogenic protocols matchless for certain applications.

Although optical detection of carbon monoxide dates back to the late twentieth century when the presence of CO was revealed by a chemically infused paper that turned brown when exposed to the gas; only in the last few years has the number of chromogenic probes for CO detection based on new sensing concepts increased. In this field oxoacetato-bridged triruthenium cluster complexes,[5] glass-immobilized rhodium complexes,[6] iron porphyrin functionalized polypyrroles[7] and a phosphino diaminopyridine iron complex[8] have been reported to display color modulations in the presence of carbon monoxide. More recently the optical detection of CO using bimetallic rhodium complexes has also been reported by some of us.[9] Regardless of several advantages offered by chromogenic sensors, only a few probes for carbon monoxide detection using emission changes have been reported so far involving the use of iron[10] and palladium[11] complexes. However, in some of these reported systems the modulations caused by the presence of carbon monoxide reveal particular shortcomings typically involving poor color or emission changes, sensing in solution but not in air and high detection limits which hamper the use of the probes as viable sensing systems.

Within this context, we have taken advantage of the well-known ability of alkenyl-ruthenium(II) complexes to react with small donor ligands such as carbon monoxide[12] to explore their use as potential colorimetric probes for CO sensing. The organometallic probe, $[Ru(CH=CHPyr\text{-}1)Cl(CO)(BTD)(PPh_3)_2]$ (**1**) (Scheme 1), consists of a Ru(II) metal center bonded to a fluorogenic pyrenylvinyl (CH=CH-Pyr-1) ligand *trans* to a 2,1,3-benzothiadiazole (BTD) molecule that acts as an emission quencher (vide infra). The coordination sphere in **1** is completed by two triphenylphosphine ligands, a chloride and a CO moiety. The probe was designed to express a dual chromo- and fluorogenic response to carbon monoxide. Thus, the presence in the complex of a pyrene donor group and a BTD acceptor was expected to result in a ligand-to-ligand charge transfer band that would inhibit the fluorescence emission from pyrene. The interchange of the labile quencher BTD by CO to give **2** was envisaged to induce both a revival of the pyrene fluorescence and a color change due to the modification of the coordination sphere of the Ru(II) atom.

Probe **1** was prepared in 96% yield following the simple and extensively developed synthesis of alkenyl ruthenium complexes through hydroruthenation of a hydride complex by a suitable terminal alkyne.[13] This process consists of a regio- and stereospecific insertion of a terminal alkyne into the Ru-H bond. In particular the brightly colored σ-alkenyl 18-electron adduct **1** (see Scheme 1) was readily synthesized by reaction of the hydride [RuHCl(CO)(PPh$_3$)$_3$][14] with 1-ethynylpyrene and BTD[15] in dichloromethane at room temperature.

Scheme 1. Formation of complex [Ru(CH=CHPyr-1)Cl(CO)(BTD) (PPh$_3$)$_2$] 1 and complex [Ru(CH=CHPyr-1)Cl(CO)$_2$(PPh$_3$)$_2$] 2.



X-ray quality crystals of **1** were obtained by recrystallization of the complex via vapor diffusion of diethyl ether onto a dichloromethane solution of **1**. Figure 1 provides a plot of the complex showing the atomic numbering scheme. In the structure, the Ru(II) center adopts a distorted octahedral coordination environment with two triphenylphosphine ligands in axial positions and four ligands (Cl, CO, BTD and vinylpyrene) occupying the equatorial sites.

The electronic spectrum of a methanol solution of complex **1** in the visible region is dominated by low intensity band at ca. 500 nm attributed to a π-π* pyrenylvinyl-to-BTD ligand-to-ligand charge transfer transition and a moderately intense absorption band at 390 nm due to a pyrene π-π* transition.[16]

In a preliminary test, air samples containing CO were bubbled into methanol solutions of **1** and an instantaneous and remarkable color change from red to yellow was observed. This color modulation is concomitant with significant reduction in intensity of the broad band at 390 nm which additionally reveals the typical absorption bands of the pyrene group at 339 and 355 nm.[17]

All these changes are consistent with a displacement of the BTD ligand by CO and the formation of complex [Ru(CH=CHPyr-1)Cl(CO)$_2$(PPh$_3$)$_2$] (**2**) (Scheme 1). Suitable crystals of **2** for X-ray single-crystal diffraction studies were obtained by diethyl ether diffusion onto a dichloromethane solution of **1** under an atmosphere of CO. Figure 2 shows a plot of **2** which reveals the presence of a CO molecule *trans* to the pyrenylvinyl ligand due to the displacement of the BTD group, supporting the proposed mechanism.

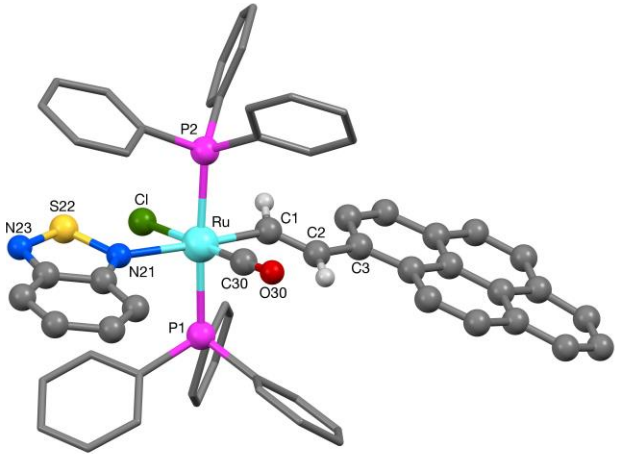


Figure 1. Crystal structure of [Ru(CH=CHPyr-1)Cl(CO)(BTD) (PPh$_3$)$_2$] (**1**). Selected bond lengths [Å] and angles [°]: Ru-C30 1.824(3), Ru-C1 2.048(3), Ru-N21 2.238(3), Ru-P1 2.4064(7), Ru-P2 2.4099(6), Ru-Cl 2.4663(7); O30-C30-Ru 178.2(3), C30-Ru-P1 92.25(8), N21-Ru-P2 92.35(6), C30-Ru-Cl 178.60(8), C1-Ru-N21 171.45(11).

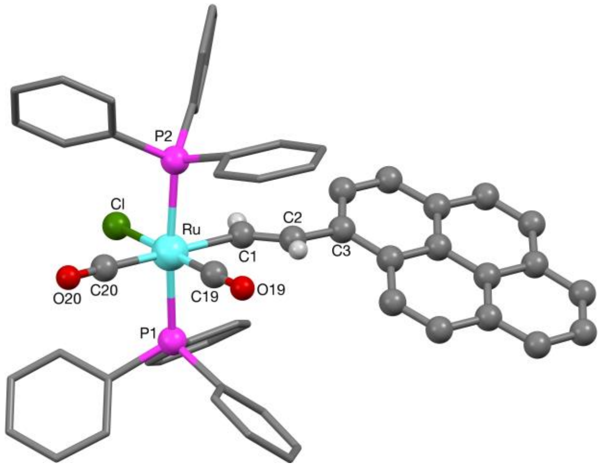


Figure 2. Crystal structure of [Ru(CH=CHPyr-1)Cl(CO)$_2$ (PPh$_3$)$_2$] (**2**). Selected bond lengths [Å] and angles [°]: Ru-C19 1.857(2), Ru-C20 1.957(2), Ru-C1 2.104(2), Ru-P1 2.4126(5), Ru-P2 2.4060(5), Ru-Cl 2.4472(5); O19-C19-Ru 177.95(19), O20-C20-Ru 175.49(19), C19-Ru-P1 92.49(6), C19-Ru-Cl 175.94(6), C20-Ru-C1 178.37(8), C20-Ru-P2 93.09(6).

Moreover, the displacement of the BTD ligand by CO also results in the recovery of the fluorescence emission of the pyrene group. Thus, whereas **1** is very weakly fluorescent in methanol (λ_{exc} = 355 nm, λ_{em} = 458 nm) formation of **2** results in a remarkable 36-fold increase in emission. This can be seen in Figure 3 which shows the effect of bubbling increasing volumes of CO through a methanolic solution of compound **1**. Further experiments demonstrated that a similar chromo-fluorogenic response from **1** in the presence of CO was observed in methanol:water 1:1 v/v solutions (complex **1** is not soluble in higher proportions of water). Titration experiments with carbon monoxide in methanol:water 1:1 v/v allowed the determination of a limit of detection (LOD) as low as 1 ppb. The turn-on fluorescence is tentatively explained by the fact that BTD displacement eliminates the electron transfer between pyrenylvinyl and BTD ligands in **1** resulting in an emission revival.

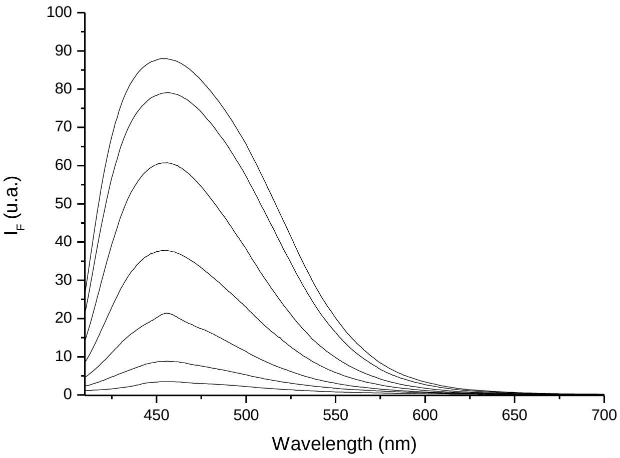


Figure 3. Turn-on fluorescence response (λ_{ex} = 355 nm) of a 1 x 10^{-4} mol dm^{-3} methanol solution of **1** upon addition of increasing volumes of CO (0, 0.03, 0.08, 0.2, 0.5, 0.7, 1 mL).

Motivated by the favorable chromo-fluorogenic sensing features of **1** observed in solution, the system was developed with a view to exploiting the potential use of this compound for CO detection in air. With this aim in mind, compound **1** was adsorbed on silica gel resulting in an orange solid. In a typical test, this colored silica support containing the ruthenium probe was exposed to air containing different concentrations of carbon monoxide. An instantaneous and remarkable modulation of color from orange to yellow was observed, consistent with the formation of **2** (Figure 4). From further titration studies a detection limit as low as 0.6 ppb of CO in air was obtained. Furthermore, a visual color change to the naked eye from orange to yellow was observed for CO concentrations in air as low as 5 ppb. At concentrations of ca. 100 ppm, which is the concentration at which CO becomes toxic for short-term exposure to humans, the color change is extremely clear (see Figure 4).

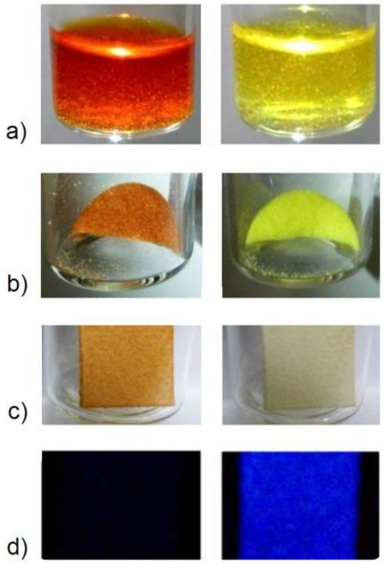


Figure 4. Summary of the visual color and/or fluorescence changes observed by the naked eye in the absence (left) and in the presence of 100 ppm of CO (right) for compound **1** when a) in methanol aqueous solution, b) adsorbed on silica gel, c) deposited on cellulose paper and, d) fluorescence emission under UV irradiation at 355 nm on cellulose paper.

Furthermore, the chromogenic response to CO in air using **1** absorbed on silica gel was found to be highly selective over other gases tested. For instance no color changes were found in the presence of Ar, N_2, O_2, CO_2, H_2S, coordinating gases such as SO_2 and NO_x, nor in the presence of common volatile organic compounds such as chloroform, formaldehyde, acetone, ethanol, toluene or hexane. Only acetonitrile induced some evident color change to yellow, but only at concentrations of ca. 5000 ppm. Importantly in terms of potential applications (where steam may be present), exposure of **1** to water-saturated air did not trigger any chromogenic response.

These data show silica to be a simple and effective support for the chromogenic detection of CO in air using complex **1**. However, the fluorogenic response observed for **1** in the presence of carbon monoxide was relatively poor when using silica as the support. In contrast, **1** was found to display a clear turn-on emission enhancement at 495 nm in the presence of carbon monoxide when adsorbed on strips of cellulose paper. This support also offers many practical benefits as it avoids the need for silica and is easier to handle. It is also compatible with simple optoelectronic devices which can convert color changes into numerical readings.[9c] Using cellulose paper the response of the probe was studied by monitoring the emission changes upon exposure to increasing concentrations of CO and a remarkable LOD of 0.7 ppb was calculated. A clear optical response to the naked eye can also be observed for concentrations of ca. 90 ppm (see Figure 4) using a conventional UV lamp. Complex **1** is also highly selective to CO on this support and it was confirmed that no changes in color or in emission were observed in the presence of Ar, N_2, O_2, CO_2, SO_2, NO_x, H_2S and common volatile organic compounds (e.g. chloroform, formaldehyde, acetone, ethanol, toluene or hexane).

In summary, we report the design and use of a ruthenium(II) complex (**1**) for the simple, selective chromo-fluorogenic detection of carbon monoxide. To our knowledge, this is the first complex capable of either chromogenic or fluorogenic sensing of CO in air. In addition, the combination of two sensing modalities allows both simple visible detection as well as greater sensitivity when desired. The probe shows a color change visible to the naked eye at CO concentrations of 5 ppb and a remarkably clear change from orange to yellow at CO concentrations of 100 ppm in air. This serves as a clear warning at levels which become toxic on prolonged exposure to the gas. Moreover, **1** also displays a turn-on fluorescence emission in the presence of carbon monoxide. Both the color and turn-on emission modulations observed are highly selective and due to a displacement of the BTD ligand in **1** by CO to yield complex **2**. This exceptionally high selectivity for CO over water vapor is of crucial importance in the potential application of this system in a domestic setting where steam is present (a shortcoming of commercial devices). The high-yielding and straightforward synthetic procedure used to prepare **1** in air, coupled with the commercial availability and relatively low cost of ruthenium and other reagents render compound **1** both accessible and inexpensive. These attributes make this system suitable for implementation in an easy-to-use portable optoelectronic device,[9c] allowing **1** to be applied as an efficient chemosensor for the simple chromo-fluorogenic detection of this colorless and odorless killer.

ASSOCIATED CONTENT

Supporting Information

General considerations. Instrumentation. Synthesis of [Ru(CH=CHPyr-1)Cl(CO)(BTD)(PPh$_3$)$_3$] (**1**). Silica gel immobilization of complex **1**. Preparation of cellulose probe of **1**. Reactivity of **1** with CO. Crystallographic data and structure of **1** and **2**. Selected geometric data for compounds **1** and **2** at 173 K. Fluorescence calibration curve to **1** aqueous methanol solution response upon addition of CO. Sensitivity studies with **1** adsorbed on silica upon addition of CO. Selectivity studies with **1** adsorbed on silica. Sensitivity studies with **1** deposited on cellulose strip upon addition of CO. This material is available free of charge via the Internet at http://pubs.acs.org.

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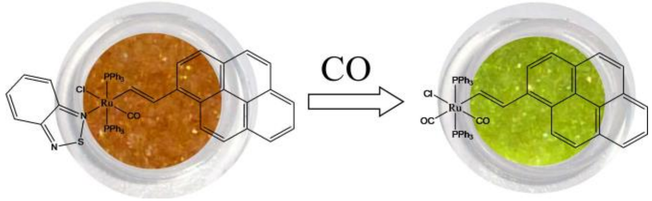

Table of Contents