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Sensitive and Selective Chromogenic Sensing of Carbon Monoxide by Using Binuclear Rhodium Complexes**

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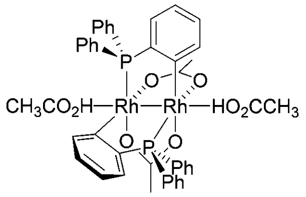
Carbon monoxide is an airborne contaminant that is toxic at low concentration levels and is difficult to detect as it is colorless and odorless. This hazard presents a real danger[1–4] in urban and indoor air, where concentrations of carbon monoxide can reach quite high levels. Typical anthropogenic sources of this pollutant involve combustion engines and improper burning of other fuels. For healthy adults, CO becomes toxic when it reaches a level higher than 50 ppm with continuous exposure over an eight-hour period. Medium exposure (a CO level between 150 ppm to 300 ppm) produces dizziness, drowsiness, and vomiting, whereas extreme exposure (a CO level of 400 ppm and higher) results in unconsciousness, brain damage, and death. Persons with CO poisoning often overlook the symptoms, and undetected exposure can be fatal. Unintentional CO exposure accounts for an estimated 15000 emergency department visits and 500 unintentional deaths in the United States alone each year.[5] Most existing CO sensors use semiconducting metal oxides.[6] As an alternative for certain applications, the development of chromogenic sensing systems that allow the presence of CO at poisonous concentrations to be easily detected with the naked eye may be of interest. However, colorimetric chromogenic probes for the detection of this deadly chemical are still rare. Reported chromogenic systems include the use of oxoacetato-bridged triruthenium cluster complexes,[7] rhodium complexes,[8] polypyrrole functionalized with iron porphyrin derivatives,[9] hybrid materials incorporating a cobalt(III) corrole complex,[10] and iron compounds of diisopropylphosphinodiaminopyridine.[11] Important drawbacks to some of these reported systems involve poor color modulations, CO sensing in solution but not in air, and relatively large detection limits.

Following our interest in the design of novel chromogenic systems,[12] we report herein the development of a colorimetric probe that shows unambiguous color modulations for the sensitive and selective sensing of carbon monoxide.

The chromogenic probe involves the use of binuclear rhodium derivatives, and the sensing function is based on the well-known ability of these complexes to bind in axial sites.[13] Furthermore, it was envisioned that a suitable selection of the bridging ligands in these binuclear derivatives may modulate the electron density of the metals in order to facilitate back donation from metal orbitals to the π* molecular orbital of CO. Moreover, it is also known that axial coordination on binuclear rhodium derivatives may result in color shifts.[13]

After preparing and testing a number of binuclear rhodium derivatives, we finally selected the compound of the formula *cis*-$[Rh_2(C_6H_4PPh_2)_2(O_2CCH_3)_2](HO_2CCH_3)_2$ ($\mathbf{1}\cdot(CH_3CO_2H)_2$) for CO signaling applications (Scheme 1). This product, prepared by Cotton et al. in 1985, was the first dirhodium(II) derivative containing two metalated phosphine ligands in a head-to-tail arrangement.[14]



Scheme 1. The complex $\mathbf{1}\cdot(CH_3CO_2H)_2$.

In a preliminary experiment, air samples containing CO were bubbled into chloroform containing $\mathbf{1}\cdot(CH_3CO_2H)_2$. A remarkable color change of the solutions from violet to orange-yellow was found. These changes are consistent with an axial coordination by CO. To corroborate the binding of carbon monoxide in **1**, crystals suitable for single X-ray diffraction were obtained from CH_2Cl_2 solution of $\mathbf{1}\cdot(CH_3CO_2H)_2$ in the presence of CO to which hexane was layered. Slow evaporation of this solution resulted in different yellow-orange crystals containing mixtures of the species $\mathbf{1}\cdot(CO,CH_3CO_2H)$ and $\mathbf{1}\cdot(CO)_2$ (see the Supporting Information).

The structure of $\mathbf{1}\cdot(CO,CH_3CO_2H)$ consists of a binuclear dirhodium core bridged by cisoid acetate groups, two ortho-metalated triphenylphosphines, and axial sites occupied by acetic acid and carbon monoxide (Figure 1).[15] This complex

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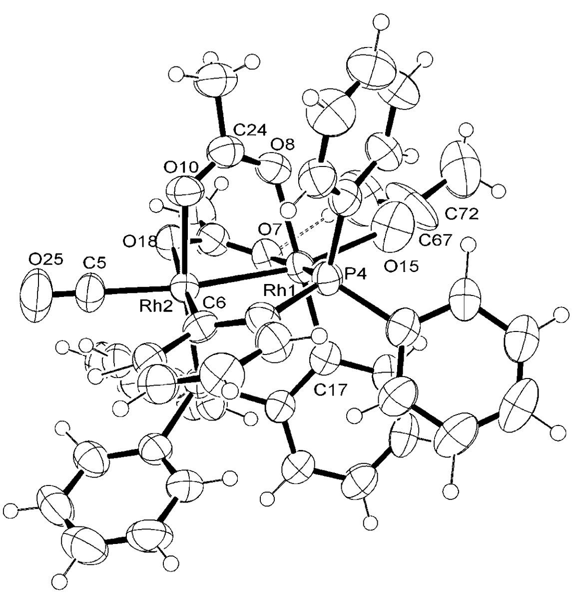


Figure 1. ORTEP of the crystal structure of **1**·(CO, CH_3CO_2H); ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Rh1–Rh2 2.5424(6), Rh1–P4 2.2118(12), Rh2–P3 2.2385(14), Rh1–O15 2.358(24), Rh2–C5 1.981(6), C5–O25 1.112(7); Rh2-C5-O25 178.1(5).

is the first reported crystal structure of a binuclear rhodium derivative containing two different axial ligands. The isolation of this asymmetric compound **1**·(CO,CH_3CO_2H) can be explained by considering the inductive effect of the first CO coordination, which is effectively transferred through the metal–metal bond to weaken the Lewis acidity of the second center. Furthermore, in this case, the ability of the axial ligand to behave as a π acceptor must also play an important role in the stability of the mono substituted adduct.

Further characterization of the **1**·(CO,CH_3CO_2H) complex demonstrated the existence of a C–O stretching frequency of 2028 cm^{-1}, which is considerably lower than the C–O stretching frequency of the free carbon monoxide (2143 cm^{-1}) suggesting a relatively high level of M→CO π back-bonding interaction. Additionally, the ^{13}C NMR spectrum exhibited a resonance at $\delta = 128.4$ ppm assigned to the coordinated carbon monoxide ligand.

Motivated by the favorable chromogenic sensing features observed in chloroform by **1**·$(CH_3CO_2H)_2$ in solution, we took a step forward towards the potential use of this compound for the detection of CO in air. With this idea in mind, compound **1**·$(CH_3CO_2H)_2$ was adsorbed on silica gel, resulting in a modified gray-violet solid. In a typical test, this colored silica support containing the rhodium probe was exposed to air containing different concentrations of carbon monoxide. A remarkable color modulation from violet to orange-yellow was observed after few minutes of exposure. Moreover, a more detailed look at the titration process, using an increasing concentration of carbon monoxide, clearly revealed that two products are formed. Thus, the visible diffuse reflectance spectrum of silica gel containing **1**·$(CH_3CO_2H)_2$ shows a unique band at 554 nm. The presence of air containing a large excess of CO resulted in the appearance of a new band at 398 nm, whereas at intermediate concentrations of CO, a band at 475 nm was observed (Figure 2). These changes are consistent with an axial coordination by CO and the formation of the derivatives **1**·$(CO)_2$ and **1**·(CO, CH_3CO_2H) (Scheme 2). Figure 3 shows a calibration curve using changes in the band at 554 nm of **1**·$(CH_3CO_2H)_2$ adsorbed on silica gel in the presence of increasing concentrations of CO in air. A linear dependence on CO concentration between 2 and 100 ppm was observed.

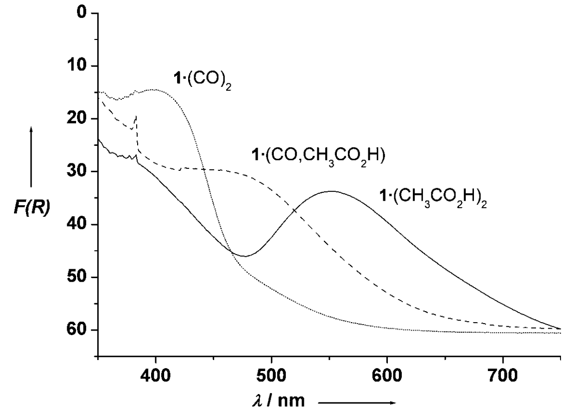
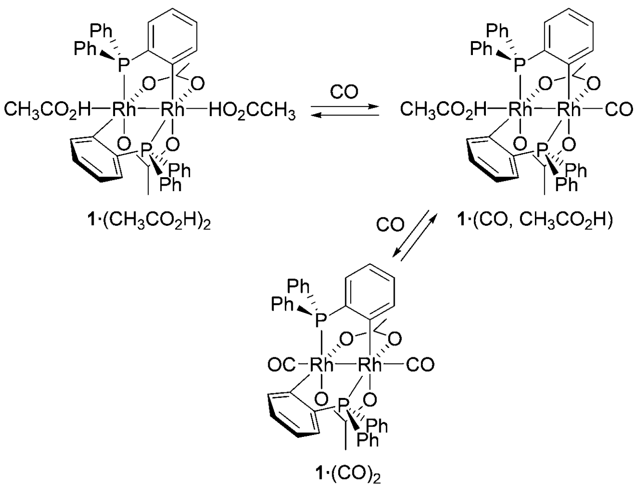


Figure 2. Diffuse reflectance spectra of **1**·$(CH_3CO_2H)_2$ adsorbed on silica gel (——) and the changes observed in the presence of CO to give the derivatives **1**·(CO,CH_3CO_2H) (-----) and **1**·$(CO)_2$ (•••••).



Scheme 2. **1**·$(CH_3CO_2H)_2$ and the products **1**·(CO, CH_3CO_2H) and **1**·$(CO)_2$ obtained upon coordination of carbon monoxide at axial positions.

From further additional studies, a detection limit as low as 0.5 ppm of CO in air was obtained using a conventional UV/Vis spectrophotometer and **1**·$(CH_3CO_2H)_2$ adsorbed on silica gel. A remarkable feature of this system is that for concentrations of CO in air at which it starts to become toxic (50 ppm) are able to induce a very clear and remarkable color change from violet to orange (see Figure 4).

This system is highly selective toward CO. For example, no reaction was found in the presence of CO_2, N_2, O_2, or Ar.

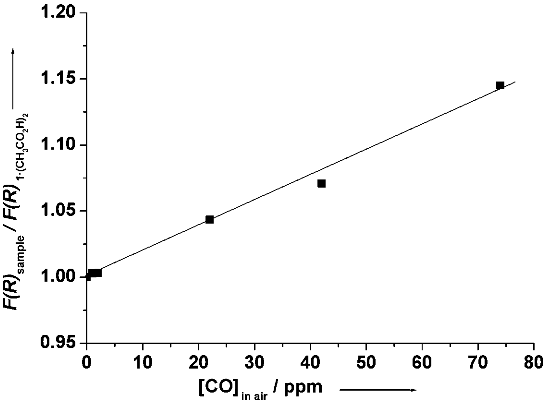


Figure 3. Intensity of the band in the diffuse reflectance spectrum in Figure 2 centered at 554 nm versus the concentration of CO in air for $\mathbf{1}\cdot(CH_3CO_2H)_2$ adsorbed on silica gel.

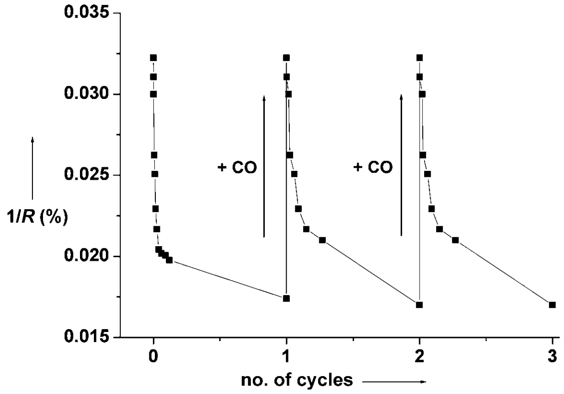


Figure 5. Reflectance changes in the band at 400 nm of silica containing $\mathbf{1}\cdot(CH_3CO_2H)_2$ upon exposure to CO and regeneration with a stream of air (900 min at room temperature).

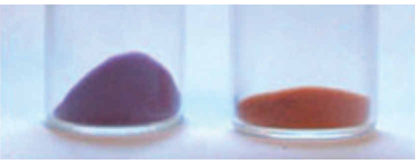


Figure 4. Photograph showing silica gel containing adsorbed $\mathbf{1}\cdot(CH_3CO_2H)_2$ in contact with air in the absence (left) and the presence of 50 ppm of CO (right).

Furthermore, no color change was observed in the presence of vapors of volatile organic compounds (VOCs), such as chloroform, hexane, ethanol, acetone, methane, toluene, xylene, or formaldehyde. Studies with coordinating species, such as SO_2, NO, and NO_2 were also carried out; in these cases, no reaction between SO_2 and $\mathbf{1}\cdot(CH_3CO_2H)_2$ adsorbed on silica gel was observed. The presence of the nitrogen oxides NO and NO_2 did induce a color modulation of the binuclear rhodium complex to yellow that is similar to that observed in the presence of CO but only when a very high concentrations of NO or NO_2 were used (1320 ppm and 3450 ppm, respectively). The $\mathbf{1}\cdot(CH_3CO_2H)_2$ complex gave no response to water-saturated air.

In the course of these experiments, it was also observed that the binding of CO in this system was fully reversible. Figure 5 shows plots of the changes in intensity of the band at 400 nm in the diffuse reflectance spectrum of probe $\mathbf{1}\cdot(CH_3CO_2H)_2$ adsorbed on silica gel upon exposure to CO and CO-free air. This cyclic process was repeated at least 10 times without significant degradation of the sensing ability of the material.

Finally, to assess the effect that the metalated phosphines in complex $\mathbf{1}\cdot(CH_3CO_2H)_2$ have in the chromogenic sensing of carbon monoxide, the tetraacetate dirhodium complex $[Rh_2(O_2CCH_3)_4]$ was used as control. In this case, even relatively high concentrations of CO resulted in no significant color variation, thus indicating poor or no coordination of the carbon monoxide molecule on the tetraacetate derivative.[16] This result is in agreement with the observation that bis-cyclometalated dirhodium complexes show a higher ability for back donation to axial ligands than dirhodium tetracarboxylate, making the metalated derivative **1** more suitable for CO coordination. These comparative studies point to the importance of the selection of the bridging ligands in relation to the final chromogenic response observed.

In summary, we have demonstrated the use of a metalated binuclear rhodium complex as a chromogenic system for carbon monoxide sensing. Color modulations are due to coordination of CO at axial positions. The probe shows remarkable sensing properties, such as a clear color change to the naked eye at concentrations at which the carbon monoxide start to become toxic (50 ppm). As additional features, the system is selective and fully reversible. These results suggest that this or similar systems could have a potential application as efficient chemosensors for the simple colorimetric detection of this colorless and odorless hazard.

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