



Palladium complexes based nanogravimetric sensors for carbon monoxide detection



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ABSTRACT

Two palladium complexes, the $[\text{Pd}(\eta^2\text{-ol})(8\text{-}(\text{di-tert-butylphosphinoxy})\text{quinoline})]$ and $[\text{Pd}(\eta^2\text{-ol})(8\text{-}(\text{di-tert-butylphosphinoxy})\text{-2-methylquinoline})]$, have been used as sensing materials to functionalize quartz crystal microbalances (QCM). The developed sensors have been tested to determine carbon monoxide in air. The reversible binding of CO observed in CH_2Cl_2 solution for both complexes is retained in the solid state. The functionalized QCMs showed good reproducibility and sensitivity toward CO detection. While CO detection was not influenced by the presence of molecular hydrogen and methane, the humidity reduced the sensors sensitivity, although the functionalized QCMs were still able to discriminate CO.

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1. Introduction

Carbon monoxide is a real danger pollutant in urban and indoor air, produced by incomplete combustion of organic substances in O_2 deficiency. For humans it is toxic at relatively low concentration levels, starting from 50 ppm over long time exposure, to be lethal over 200 ppm and higher level [1,2]. Although toxic, CO is also produced by human body as signaling molecule and probably this is the reason of the incapacity of humans to recognize its presence in the environment. Carbon monoxide is in fact a colorless, tasteless and odorless gas and for this reason it is the most common type of gaseous poisoning and every year several people die for accidental exposure to this gas. For this reason there is an urgent need of devices able to detect and signal a CO alarm.

Chemical sensors are of course the ideal devices for this kind of application and several examples of CO sensors have been developed [3–5]. Among them, metal oxide semiconductor (MOS) based chemoresistive sensors are probably the most intensively studied [6,7]. These devices are characterized by high sensitivities, but they generally suffer of low selectivity. To modify the selectivity of these devices and to improve sensing characteristics for CO detections, one of the approaches adopted has been the addition of transition

metals (such as Pd, Pt, and Cu, etc.) to the oxide, in order to exploit the binding properties of CO toward transition metals and to take advantage of their catalytic activity [8–13].

Other than these applications, it is quite surprising to note that transition metal complexes have not been intensively studied as sensing materials for CO detection. To the best of our knowledge, transition metal complexes have been generally used as chromogenic receptors for the colorimetric detection of CO [14–16] and only sparse examples of different kind of chemical sensors have been reported [17,18].

From this point of view, in recent years we have been involved in the development of nanogravimetric sensors based on quartz crystal microbalances (QCM) as transducers [19,20]. Using porphyrinoids as sensing materials, we have studied the possibility to develop chemical sensors for CO detection. The sensing mechanism of such a species, however, demonstrated that the metal coordination was not the driving interaction and that the sensitivity observed was mainly due to the CO entrapment inside the porous layer formed by the supramolecular aggregates of porphyrinoids [21,22].

To further explore the possibility to use metal complexes where the CO coordination is the driving interaction, we turned our attention on palladium complexes.

The catalytic application of palladium complexes containing P, N ligands has been recently studied since these complexes are characterized by the presence in the metal coordination sphere of P and N

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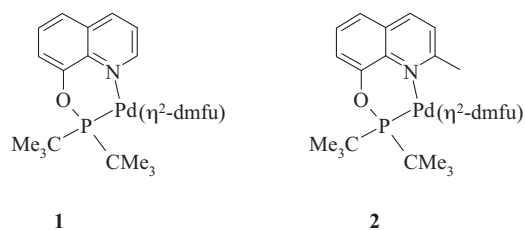


Fig. 1. Molecular structure of the complexes **1** and **2**.

donor atoms which differ in their coordination ability. On the other hand, the complexes appear thermally stable and no decomposition was observed after prolonged time at ambient temperature both in the solid state and in solution [23]. In particular, we have been attracted by complexes **1** and **2**, which both contain the η^2 -bonded olefin dimethylfumarate (DMFU) (Fig. 1).

The stability of these complexes, along with the possible replacement of the olefin by the more π -accepting carbon monoxide, prompted us to use the complexes as sensing materials for CO detection.

In this work, we report the development of QCM functionalized with complexes **1** and **2** and the characterization of their sensing behavior toward carbon monoxide.

2. Experimental

Reagents and solvents (Sigma–Aldrich, Fluka and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Silica gel 60 (70–230 mesh) was used for chromatography.

^1H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). IR spectra were recorded on a Perkin-Elmer, SpectrumOne FT-IR spectrometer.

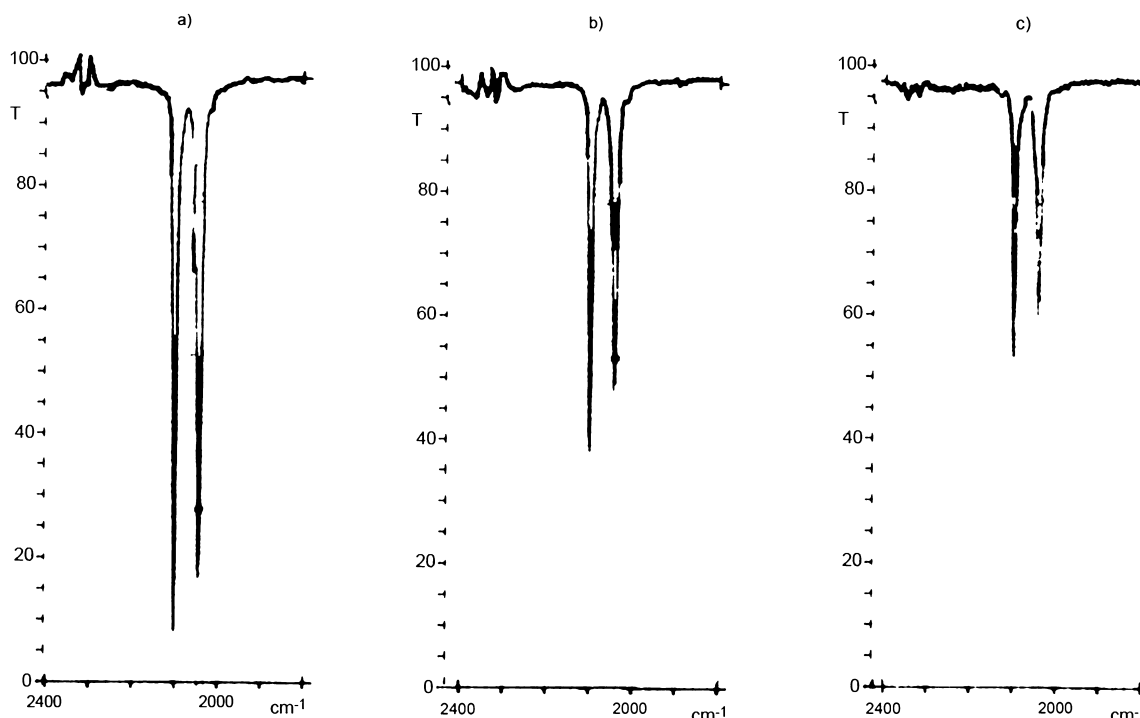


Fig. 2. IR spectra of **1** in CH_2Cl_2 solution: (a) under CO stream; (b) after 30 min of N_2 fluxing; (c) after 60 min of N_2 fluxing.

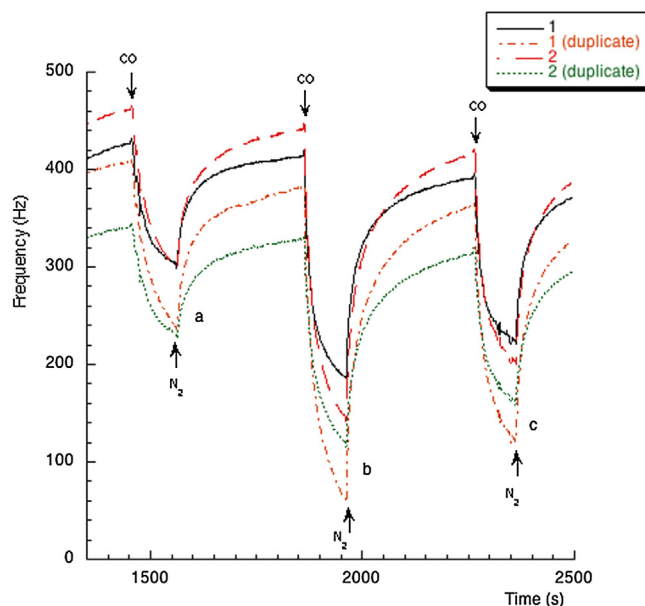


Fig. 3. Response signals of QCM sensors coated with complexes **1** and **2** films exposed to CO [concentrations: 125 ppm (a and c) and 250 ppm (b) in N_2].

2.1. Preparation of the ligand and palladium complexes

The ligands 8-(di-tert-butylphosphinoxy)quinoline and 8-(di-tert-butylphosphinoxy)2-methylquinoline and the palladium derivatives **1** and **2** have been prepared according to previous work [23]. Ligands containing a phosphinito group show high instability, which overcame upon coordination, so that the complexes **1** and **2** appeared thermally stable and no decomposition was observed.

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