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A New Approach for the Detection of Ethylene Using Silica-Supported Palladium Complexes

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The coordination of olefins to square-planar Pd(II) and Pt(II) complexes containing 2,9-dimethylphenanthroline (**L1**) often involves a change of color associated with a change of geometry at the metal center. In order to obtain suitable colorimetric detectors for ethylene gas, a series of new Pd(II) and Pt(II) compounds with a range of 2,9-disubstituted phenanthroline ligands [2,9-di-*n*-butyl-1,10-phenanthroline (**L2**), 2,9-di-*s*-butyl-1,10-phenanthroline (**L3**), 2,9-diphenyl-1,10-phenanthroline (**L4**), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, **L5**)] have been prepared and their reactivity toward ethylene investigated both in solution and after depositing the detector compounds on a variety of solid supports. The Pd(II) complex [$PdCl_2$(**L2**)] supported on silica undergoes a clear color change upon exposure to ethylene, while remaining stable toward air and water, and forms the basis for new simple colorimetric detectors with potential applications in ethylene pipe-leak detection and the monitoring of fruit ripening. Encouragingly, the detector is able to discriminate between fruit at different stages of ripening. The response of the detector to other volatiles was also examined, and specific color changes were also observed upon exposure to aromatic acetylenes. The crystal structures of four new derivatives, including the ethylene−Pt(II) complex [$PtCl_2(C_2H_4)$(**L2**)], are also described.

Introduction

There is a need for inexpensive, fast, simple, and sensitive monitoring devices for the detection of volatile compounds, for example, for the environmental and occupational monitoring of emissions. Optical monitoring based on color changes is one of the simplest approaches to gas monitoring and can be very low-cost and highly analyte-specific.[1] In particular, a visual detector for ethylene would be of interest because it is the largest-volume organic chemical produced worldwide (>70 million tonnes in 2006[2]), is highly flammable, and can form explosive mixtures in the air (explosive limits: 2.7−36 vol % in the air). The laser-based gas detectors currently used industrially are relatively expensive and complicated to use, with monitoring typically taking place once a week. Inexpensive colorimetric leak detectors will therefore have significant safety and economic implications for the industries that produce or use the gas. In addition, ethylene is emitted by climacteric fruit (such as apples, bananas, or tomatoes) as part of the ripening process,[3,4] and visual detectors for ethylene are therefore also of interest as indicators of food ripeness (for example, in "smart packaging"). Permanganate[5] and Pd(II)/molybdate[6] have been put forward as sensor materials for ethylene in the context of fruit ripening. These methods rely on the color-changing reduction of MnO_4^- or Mo^{6+}, but neither of these systems

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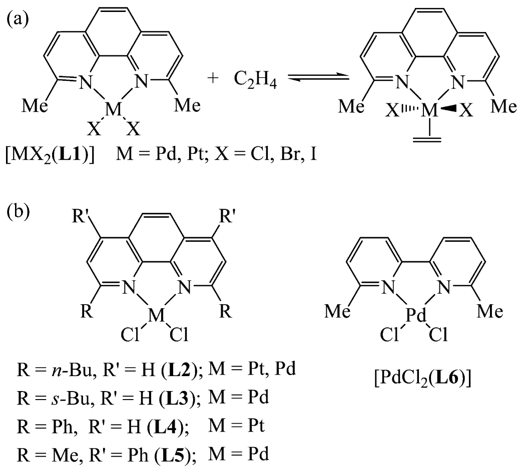

Figure 1. (a) Reversible coordination of ethylene by Fanizzi's complexes, $[MX_2(\mathbf{L1})]$,[7] and (b) analogous compounds used in this work. Complexes $[PdCl_2(\mathbf{L5})]$[11] and $[PdCl_2(\mathbf{L6})]$[10] have been reported previously.

is specific to ethylene. Potassium permanganate is a strong oxidizing agent which also reacts with alcohols and aldehydes. Pd(II)/molybdate mixtures are air-sensitive, and stable sensor films are prepared through a complicated method involving controlled deposition of the mixtures on layers of silica nanoparticles and a polyelectrolyte.[6] Thus, although a number of compounds change color upon reaction with ethylene, establishing a practical chemical basis for such visual detecting still presents significant challenges in terms of both sensitivity (e.g., maxima of 0.1−1 ppm are present in fruit[3]) and selectivity (since oxygen and water as well as other organic species may be present).

As a starting point toward meeting these challenges, we used the work of Fanizzi et al.[7,8] on the reversible binding of olefins by air-stable platinum and palladium complexes of 2,9-dimethylphenathroline (**L1**; Figure 1a). In particular, they observed that compounds $[MX_2(\mathbf{L1})]$ (M = Pd, Pt; X = Cl, Br, I) coordinate ethylene reversibly in solution and generally change color upon the formation of the trigonal-bipyramidal ethylene complex (Figure 1a).[7] The reaction requires a planar bidentate ligand with bulky substituents since steric hindrance around the metal center is then relieved upon formation of the five-coordinate ethylene complex. In order to prepare visual detectors that are practical and easy to use, this solution chemistry had to be transferred to the solid state, for example, by depositing the compounds on solid supports. Here, the suitability of Fanizzi's compounds and of some new analogues for the visual detection of ethylene is studied using a range of solid supports. The chemical basis for a selective ethylene detector is described.

Experimental Section

General. Unless otherwise indicated, all starting materials and volatile compounds were obtained from Aldrich and used as received. ^1H NMR spectra were recorded on a Brüker Advance DPX 300 or a Brüker Advance DPX 500 at room temperature. Chemical shifts (δ) are expressed in parts per million with a typical dispersion of ±0.01 ppm relative to tetramethylsilane for ^1H NMR. Coupling constants (J) are expressed in hertz with a typical dispersion of ±0.1 Hz. CHN elemental analyses and MS/FAB$^+$ spectra were performed by the Analytical Services and Environmental Projects at Queen′s University Belfast. IR spectra were carried out on a Perkin-Elmer Sepctrum-RX or a Perkin-Elmer FTIR Spectrum-One spectrometer, and samples were recorded as Nujol dispersions held between polyethylene sheets (absorptions for Nujol: 2960−2840, 1455, and 1370 cm^{-1}; absorptions for polyethylene: 728 and 718 cm^{-1}). Solid state reactions were carried out in a Mixer Mill type MM 200 from Retsh. Gas chromatography (GC) studies were done using a 5890 Series II gas chromatograph with a porapak column adapted using helium as the mobile phase. X-ray crystal structures were obtained on a Brüker AXS SMART 1000 at the School of Chemistry and Chemical Engineering X-ray facility at Queen′s University Belfast.

Synthesis of Four-Coordinate Complexes. The ligands 2,2′-dipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (**L1**), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, **L5**), and 6,6′-dimethyl-2,2′-dipyridyl (**L6**) were obtained from Aldrich and used without further purification. The phenanthroline ligands 2,9-di-*n*-butyl-1,10-phenanthroline (**L2**), 2,9-di-*s*-butyl-1,10-phenanthroline (**L3**), and 2,9-diphenyl-1,10-phenanthroline (**L4**)[9] as well as $[PdCl_2(\mathbf{L6})]$[10] and all complexes containing **L1**[7] were prepared following reported procedures. Although the structure of $[PdCl_2(\mathbf{L5})]$ has been reported,[11] we have not found a synthetic procedure in the literature, and its preparation is also included here.

$[PtCl_2(L2)]$. A solution of 2,9-di-*n*-butyl-1,10-phenanthroline (**L2**; 1 g, 3.1 mmol) in $CHCl_3$ (10.5 mL) was added to a solution of $K_2[PtCl_4]$ (1.289 g, 3.1 mmol) in water (10 mL). The mixture was heated to reflux for 18 h. The organic fraction was separated and the aqueous phase washed with $CHCl_3$ (3 × 2 mL). The combined organic fractions were dried by stirring with magnesium sulfate, which was then removed by filtration. The filtrate was concentrated to *ca.* 3 mL and added to cold diethyl ether (*ca.* 7 mL) while stirring vigorously. The product precipitated as an orange solid and was collected by filtration. The filtrate was further concentrated and treated with diethyl ether as described above. This procedure was repeated three times to obtain the maximum yield. All of the fractions of the solid thus obtained were combined, washed with diethyl ether, and dried in the air. Yield: 1.219 g, 70%. ^1H NMR ($CDCl_3$): 0.93 [t, 6H, $^3J(HH) = 7.2$ Hz, CH_3], 1.38 [sextuplet, 4H, $^3J(HH) = 7.5$ Hz, CH_2], 1.85 [quintuplet, 4H, $^3J(HH) = 7.5$ Hz, CH_2], 3.72 [t, 4H, $^3J(HH) = 7.8$ Hz, CH_2], 7.55 [d, 2H, $^3J(HH) = 8.7$ Hz, phenH(3, 8)], 7.78 [s, 2H, phenH(5, 6)], 8.39 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(4, 7)] ppm. $\nu(Pt-Cl) = 336$ cm^{-1}(br). Anal. calcd for $C_{20}H_{24}N_2Cl_2Pt$: C, 43.10; H, 4.31; N, 5.03%. Found: C, 43.00; H, 4.33; N, 5.01%. MS/FAB$^+$: 541 (M^+-CH_3), 521 (M^+-Cl), 499 ($M^+-C_4H_9$), 485 (M^+-2Cl), 293 (M^+-2Cl, Pt).

$[PdCl_2(L2)]$. $[PdCl_2(NCPh)_2]$ (0.223 g, 0.58 mmol) was dissolved in $CHCl_3$ (130 mL). The solution was stirred and 2,9-di-*n*-butyl-1,10-phenanthroline (**L2**; 0.268 g, 0.91 mmol) added. After being stirred for 17 h, the solution was concentrated until becoming

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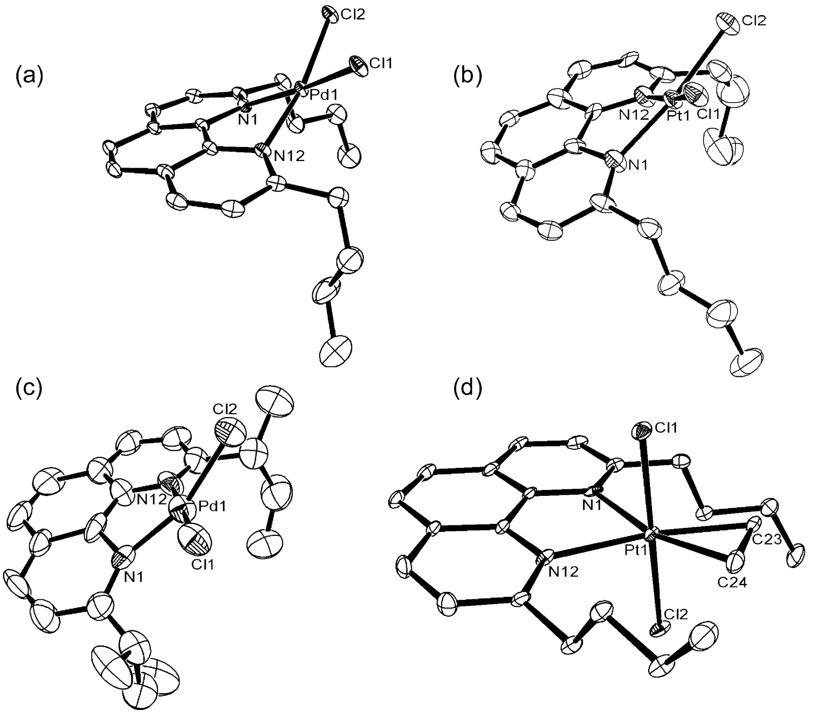

Figure 2. Crystal structures of (a) [$PdCl_2$(**L2**)], (b) [$PtCl_2$(**L2**)], (c) [$PdCl_2$(**L3**)]$\cdot$$CHCl_3$, and (d) [$PtCl_2(C_2H_4)$(**L2**)]. Hydrogen atoms and solvent molecules have been omitted for clarity. Ortep representations (ellipsoids probability 30%) have been done using Ortep-3 for Windows.[19]

Table 1. Crystal Data

	[$PdCl_2$(**L2**)]	[$PdCl_2$(**L3**)]$\cdot$$CHCl_3$	[$PtCl_2$(**L2**)]	[$PtCl_2(C_2H_4)$(**L2**)]
formula	$C_{20}H_{24}Cl_2N_2Pd$	$C_{21}H_{25}Cl_5N_2Pd$	$C_{20}H_{24}Cl_2N_2Pt$	$C_{22}H_{28}Cl_2N_2Pt$
M	469.71	589.08	558.40	586.45
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a/Å	13.7330(18)	11.29(13)	13.9102(18)	9.0953(14)
b/Å	10.2556(13)	12.04(11)	10.4746(14)	10.9734(17)
c/Å	14.5380(19)	17.80(14)	14.6778(19)	12.0763(18)
U/Å^3	1916.4(4)	2420(40)	2010.8(5)	1103.3(3)
T/K	153(2)	298(2)	153(2)	153(2)
Z	4	4	4	2
μ(Mo Kα)/mm^{-1}	1.252	1.330	7.249	6.610
reflns measured	21008	10794	14839	12114
unique reflns (R_{int})	4331 (0.0356)	4206(0.1288)	3229(0.0536)	4843(0.0634)
R ($I > 2\sigma(I)$)	0.0386	0.1215	0.0448	0.0581
$wR(F^2)$ (all data)	0.1074	0.3423	0.1441	0.1483

cloudy and diethyl ether (*ca.* 10 mL) added to give an orange solid. The solid was collected by filtration, washed with diethyl ether, and dried in the air. Yield: 0.256 g, 93%. ^1H NMR ($CDCl_3$): 0.97 [t, 6H, $^3J(HH) = 7.4$ Hz, CH_3], 1.42 [sextuplet, 4H, $^3J(HH) = 7.4$ Hz, CH_2], 1.86 [quintuplet, 4H, $^3J(HH) = 7.7$ Hz, CH_2], 3.71 [t, 4H, $^3J(HH) = 8.0$ Hz, CH_2], 7.55 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(3, 8)], 7.85 [s, 2H, phenH(5, 6)], 8.35 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(4, 7)] ppm. ν(Pd−Cl) = 336 cm^{-1} (br). Anal. calcd for $C_{20}H_{24}N_2Cl_2Pd\cdot{}^1/_5CHCl_3$: C, 49.26; H, 4.91; N, 5.69%. Found: C, 49.34; H, 4.68; N, 5.81%. MS/FAB$^+$: 453 (M^+-CH_3), 433 (M^+-Cl), 411 ($M^+-C_4H_9$), 397 (M^+-2Cl), 293 (M^+-2Cl, Pd).

[$PdCl_2$(L3)]. To a solution of [$PdCl_2(NCPh)_2$] (0.05 g, 0.13 mmol) in $CHCl_3$ (5 mL) was added 2,9-di-*s*-butyl-1,10-phenanthroline (**L3**; *ca.* 0.02 g, *ca.* 0.07 mmol). The solution was stirred for 19 h and filtered through Celite. The filtrate was concentrated to *ca.* 1.5 mL and added dropwise to cold diethyl ether (*ca.* 3 mL) with vigorous stirring. A brown solid precipitated, which was collected by filtration, washed with diethyl ether, and dried in the air. Yield: 0.011 g, *ca.* 32%. ^1H NMR ($CDCl_3$): isomer 1, 0.97 [t, 6H, $^3J(HH) = 7.4$ Hz, CH_3], 1.53 [d, 6H, $^3J(HH) = 6.9$ Hz, CH_3], 1.88−1.66 [m, 2H, CH_2], 4.36 [sextuplet, 2H, $^3J(HH) = 8.0$ Hz, CH], 7.58 [d, 2H, $^3J(HH) = 8.7$ Hz, phenH(3, 8)], 7.86 [s, 2H, phenH(5, 6)], 8.39 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(4, 7)] ppm; isomer 2, 0.75 [t, 6H, $^3J(HH) = 7.4$ Hz, CH_3], 1.37 [d, 6H, $^3J(HH) = 6.9$ Hz, CH_3], 1.88−1.66 [m, 2H, CH_2], 4.35 [sextuplet, 2H, $^3J(HH) = 8.0$ Hz, CH], 7.58 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(3, 8)], 7.85 [s, 2H, phenH(5, 6)], 8.38 [d, 2H, $^3J(HH) = 8.4$ Hz, phenH(4, 7)] ppm. ν (Pd−Cl) = 326 cm^{-1} (br). Anal. calcd for $C_{20}H_{24}N_2Cl_2Pd$: C, 51.14; H, 5.15; N, 5.96%. Found: C, 51.07; H, 5.27; N, 5.94%. MS/FAB$^+$: 437 (M^+-Cl), 415 ($M^+-C_4H_9$), 397 (M^+-2Cl), 293 (M^+-2Cl, Pd).

[$PtCl_2$(L4)]. To a stirred suspension of [$PtCl_2(dmso)_2$] (0.133 g, 0.32 mmol) in $CHCl_3$ (35 mL) was added 2,9-diphenyl-1,10-phenanthroline (**L4**; 0.110 g, 0.33 mmol). The suspension was heated to reflux for 24 h. The solid dissolved after 40 min, and the resulting solution became orange after a further 20 min. A suspension formed after 90 min at reflux. The solid was collected by filtration, washed with diethyl ether, and dried in the air. Yield: 0.155 g, 81%. ^1H NMR (dmso-d$_6$): 7.20−7.09 [m, 2H, phen], 7.70−7.45 [m, 5H, phen], 8.20−7.72 [m, 3H, phen+Ph], 8.27 [d, 1H, $^3J(HH) = 8.7$ Hz, phen], 8.43 [d, 1H, $^3J(HH) = 8.4$ Hz, phen], 8.51 [d, 1H, $^3J(HH) = 7.2$ Hz, Ph], 8.62 [d, 1H, $^3J(HH) = 8.4$ Hz,

Table 2. Selected Bond Distances (Å) and Angles (deg)

	$[PdCl_2(\mathbf{L2})]$	$[PdCl_2(\mathbf{L3})]\cdot CHCl_3$	$[PtCl_2(\mathbf{L2})]$	$[PtCl_2(C_2H_4)(\mathbf{L2})]$
M−Cl1	2.2779(8)	2.258(17)	2.340(3)	2.328(2)
M−Cl2	2.2944(8)	2.259(17)	2.330(3)	2.318(2)
M−N1	2.074(3)	1.97(2)	2.080(9)	2.266(8)
M−N12	2.051(2)	1.96(3)	2.082(9)	2.242(7)
Pt−C23				2.073(8)
Pt−C24				2.086(10)
C23−C24				1.464(14)
N1−M−Cl1	170.41(7)	97.5(9)	98.3(2)	88.38(17)
N12−M−Cl2	169.45(7)	92.6(9)	94.5(2)	90.49(18)
Cl1−M−Cl2	86.76(3)	87.1(8)	85.98(9)	178.85(8)
N1−M−N12	80.62(9)	82.1(10)	80.3(3)	74.6(3)
N1−M−Cl2	97.08(6)	162.0(6)	172.1(3)	92.54(17)
N12−M−Cl1	94.00(7)	177.7(7)	171.1(2)	89.10(18)
C23−Pt−C24				41.2(4)
C23−Pt−Cl2				90.0(3)
C24−Pt−Cl2				89.8(3)

phen], 8.77 [d, 1H, ^3J(HH) = 8.4 Hz, phen], 8.86 [d, 1H, ^3J(HH) = 8.7 Hz, phen] ppm. ν (Pt−Cl) = 304 and 341 cm^{-1}. Anal. calcd for $C_{24}H_{16}N_2Cl_2Pt$: C, 48.17; H, 2.69; N, 4.68%. Found: C, 47.85; H, 3.25; N, 4.46%. MS/FAB$^+$: 562 (M$^+$−Cl), 526 (M$^+$−2Cl), 333 (M$^+$−2Cl, Pt).

$[PdCl_2(\mathbf{L5})]$. Bathocuproine (**L5**; 0.08 g, 0.2 mmol) was added to a solution of $[PdCl_2(NCPh)_2]$ (0.09 g, 0.2 mmol) in $CHCl_3$ (25 mL) while stirring. After being stirred for 20 h, the solution was filtered through Celite. The filtrate was concentrated to *ca.* 5 mL, and diethyl ether was added to precipitate an orange solid, which was collected by filtration, washed with diethyl ether, and dried in the air. Yield: 0.102 g, 86%. ^{1}H NMR ($CDCl_3$): 3.30 [s, 6H, CH_3], 7.48−7.82 [m, 14H, phen+Ph] ppm. ν (Pd−Cl) = 304, 342 cm^{-1}.

Reactions with Ethylene in Solution. Each complex (*ca.* 0.02 mmol) was dissolved in *ca.* 3.5 mL of $CDCl_3$ or dmso-d$_6$ ($[PtCl_2(\mathbf{L4})]$) and placed in a flask. Ethylene gas was bubbled directly into the solution through a needle while it was stirred for 90 min. Significant changes of color were observed only in the case of **L1** derivatives, in agreement with a study previously reported.[7] The ^{1}H NMR spectra of the resulting solutions were taken. Complete conversion to the corresponding five-coordinate complex was observed for **L1** complexes[7] and $[PtCl_2(\mathbf{L2})]$. The ethylene derivative of the latter was isolated and fully characterized (see below). Partial coordination occurred for $[PdCl_2(\mathbf{L2})]$ and $[PdCl_2(\mathbf{L3})]$, and no reaction was observed for any of the complexes containing **L4**−**L6**. The ^{1}H NMR data for the ethylene derivatives of $[PdCl_2(\mathbf{L2})]$ and $[PdCl_2(\mathbf{L3})]$, as shown by the NMR spectra of the mixtures, are as follows.

$[PdCl_2(C_2H_4)(\mathbf{L2})]$. ^{1}H NMR ($CDCl_3$): 1.09 [t, 6H, ^3J(HH) = 7.5 Hz, CH_3], 1.68 [sextuplet, 4H, ^3J(HH) = 7.5 Hz, CH_2], 2.14 [quintuplet, 4H, ^3J(HH) = 7.8 Hz, CH_2], 4.00 [t, 4H, ^3J(HH) = 8.2 Hz, CH_2], 4.94 [s, 4H, $CH_2{=}CH_2$], 7.77 [d, 2H, ^3J(HH) = 8.5 Hz, phenH(3,8)], 7.82 [s, 2H, phenH(5,6)], 8.32 [d, 2H, ^3J(HH) = 8.5 Hz, phenH(4,7)] ppm. $[PdCl_2(C_2H_4)(\mathbf{L3})]$: ^{1}H NMR ($CDCl_3$): isomer 1, 0.95 [t, 6H, ^3J(HH) = 7.4 Hz, CH_3], 1.52 [d, 6H, ^3J(HH) = 6.6 Hz, CH_3], 1.95−1.58 [m, 2H, CH_2], 4.32 [sextuplet, 2H, CH], 4.92 [s, 4H, $CH_2{=}CH_2$], 7.57 [d, 2H, ^3J(HH) = 8.7 Hz, phenH(3,8)], 7.86 [s, 2H, phenH(5,6)], 8.41 [d, 2H, ^3J(HH) = 8.7 Hz, phenH(4,7)] ppm; isomer 2, 0.73 [t, 6H, ^3J(HH) = 7.2 Hz, CH_3], 1.35 [d, 6H, ^3J(HH) = 6.9 Hz, CH_3], 1.95−1.58 [m, 2H, CH_2], 4.32 [sextuplet, 2H, CH], 4.92 [s, 4H, $CH_2{=}CH_2$], 7.56 [d, 2H, ^3J(HH) = 8.7 Hz, phenH(3,8)], 7.85 [s, 2H, phenH(5,6)], 8.40 [d, 2H, ^3J(HH) = 8.7 Hz, phenH(4,7)] ppm.

$[PtCl_2(C_2H_4)(\mathbf{L2})]$. A solution of $[PtCl_2(\mathbf{L2})]$ (0.098 g, 0.18 mmol) in $CHCl_3$ (4 mL) was prepared in a Schlenk tube and stirred. The air was removed and the tube connected to a rubber balloon containing ethylene. The solution was stirred for 22 h. Diethyl ether was added to the solution to form a yellow solid, which was collected by filtration, washed with diethyl ether, and dried in the air. Yield: 0.008 g, 8%. ^{1}H NMR ($CDCl_3$): 1.07 [t, 6H, ^3J(HH) = 7.5 Hz, CH_3], 1.63 [sextuplet, 4H, ^3J(HH) = 7.8 Hz, CH_2], 2.07 [quintuplet, 4H, ^3J(HH) = 7.8 Hz, CH_2], 3.91 [t, 4H, ^3J(HH) = 8.1 Hz, CH_2], 3.66 [m, 4H, $CH_2{=}CH_2$, $J(^{195}$Pt−H) = 69 Hz], 7.82 [d, 2H, ^3J(HH) = 8.4 Hz, phenH(3,8)], 7.86 [s, 2H, phenH(5,6)], 8.36 [d, 2H, ^3J(HH) = 8.1 Hz, phenH(4,7)] ppm. ν (Pt−Cl) = 340 cm^{-1}. Anal. calcd for $C_{22}H_{28}N_2Cl_2Pt$: C, 45.06; H, 4.81; N, 4.78%. Found: C, 44.54; H, 4.67; N, 4.57%. MS/FAB$^+$: 587 (M$^+$), 551 (M$^+$−Cl), 521 (M$^+$−C_2H_4Cl), 485 (M$^+$−C_2H_4, 2Cl).

Crystal Structures. Single crystals of $[MCl_2(\mathbf{L2})]$ (M = Pt, Pd), $[PdCl_2(\mathbf{L3})]\cdot CHCl_3$, and $[PtCl_2(C_2H_4)(\mathbf{L2})]$ suitable for X-ray studies were obtained by the slow evaporation of $CHCl_3$ or CH_2Cl_2 solutions of the compounds. Each crystal was mounted onto the diffractometer at low temperatures under nitrogen at *ca.* 120 K (253 K for $[PdCl_2(\mathbf{L3})]\cdot CHCl_3$). The structures were solved using direct methods and refined with SHELXTL.[12] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were added at idealized positions with a riding model and fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded). The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

Experiments on Solid Supports. Preparation of Detector Plates. Six types of supports were used for the experiments: silica gel $60F_{254}$ on aluminum obtained from Merck; reverse-phase silica plates, KC2F ethyl reverse-phase, and K2F cellulose obtained from Whatman; cellulose on polyester obtained from Aldrich; and Polygram Alox N/UV$_{254}$ obtained from Macherey-Nagel. To ensure consistency, reference color cards were used to monitor any changes of color. All of the detectors were prepared following the same procedure: Solutions of each metal complex were prepared in two concentrations, 2.5 and 5 mM, in $CHCl_3$. In the case of $[PtCl_2(L4)]$, a few drops of dimethylsulfoxide were added to dissolve the solid completely. Seven drops of each solution (ca. >0.24 mL) were applied to the support to create a spot. The plate was placed in a desiccator jar in an oil bath and dried under a vacuum at 50 °C over 1 h. The dry plates were stored under a vacuum until used. At this point, the colors of the spots were similar to those of the corresponding complexes and ranged from yellow to light-brown or gray/green.

Control Experiments. To monitor any changes of color of the detector plates toward water, each plate was placed on a frit above water (ca. 20 mL) in a closed desiccator jar for 14 days. To monitor any changes of color due to the air, the plates were left open to the air for 14 days. Changes of color were monitored every 24 h.

Exposure to Ethylene or Propene. Each plate was placed in a Schlenk tube. The air was removed, and an ethylene- or propene-filled balloon was connected. The gas atmosphere was maintained for one week, and the color changes were monitored approximately every hour during the first 12 h, and then every 24 h. Most plates significantly changed color within the first 24 h, with no further changes observed afterward.

Exposure to Volatile Liquids. The plates were placed in a Schlenk tube (open to the atmosphere). In an adjacent Schlenk tube, equipped with a rubber septum, the corresponding volatile was

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(12) Sheldrick, G. *SHELXTL*, version 6.10; Brüker AXS: Madison, WI, 2000.

placed, and the Schlenk tubess were connected *via* a rubber tube. A dinitrogen flow was bubbled into the volatile liquid using a needle through the septum and passed through the Schlenk tube containing the plate. The flow was maintained for 1 h, during which color changes were monitored.

Experiments with Fruit. Silica plates spotted with a 5 mM solution of [PdCl$_2$(**L2**)] in chloroform, as described above, were placed in desiccator jars containing bananas. In the first experiment, green bananas in a very early ripe stage were used. The detector plates exposed to these changed color from orange to green/gray after 4 days. In a second experiment, already ripened yellow bananas were used. In this case, the bananas were kept for 12 days, until rotten. After this time, only a very slight darkening of the detector plates was observed.

Monitoring of Ethylene Production Using Gas Ghromatography. Ethylene at a concentration of 10 ppm was used as a reference. Volumes of 0.1−0.5 mL were taken directly from an ethylene cylinder at two different pressures (0.5 and 1 bar) and injected into a GC *via* syringe. The retention times for the reference ethylene samples were in the range 0.630−0.646 min. Bananas and a silica-[PdCl$_2$(**L2**)] detector plate were introduced in a headspace with a septum adapter in the upper part. The container was closed and left to equilibrate for 2 h. Samples (0.5 mL) were taken daily through the septum and injected into the GC. In a first experiment, three green, unripe bananas were used. The bananas remained green for 7 days. During this time, no ethylene was detected by GC, and the detector plate did not change color significantly. In a second experiment, one yellow and two unripe bananas were left in the headspace for 4 days. Ethylene was detected by GC every day from the first day, and the detector plate clearly changed color after 2 days. A second plate was introduced on the third day that also changed color after 24 h.

Results and Discussion

Synthesis and Characterization of Four-Coordinate Complexes. In addition to Fanizzi's complexes (Figure 1a),[7] a series of new four-coordinate platinum and palladium compounds containing 2,9-disubstituted phenanthroline ligands (**L2**−**L5**, Figure 1b) were prepared. For comparison, the Pd derivative of the more flexible 2,2′-dimethyl-6,6′-dipyridyl, [PdCl$_2$(**L6**)],[10] was also included in the study (Figure 1b).

The only unusual features with regard to the spectroscopic data of these compounds are found in [PtCl$_2$(**L4**)]. Its ^{1}H NMR spectrum in dmso-d$_6$ shows asymmetry of the phenanthroline ligand, which may be due to restricted rotation in solution of the bulky Ph substituents, and potentially the formation of a Cl···H−C(Ph) interaction. All complexes show in their IR spectra either one broad band or two bands in the region 325−345 cm^{-1}, compatible with a *cis*-MCl$_2$ (M = Pt, Pd) geometry[13] (see the Experimental Section and Supporting Information). However, [PtCl$_2$(**L4**)] exhibits an additional low-frequency band at 304 cm^{-1}, which supports the involvement of one of the Cl atoms in H bonding.[14]

The crystal structures of three new phenathroline complexes, [MCl$_2$(**L2**)] (M = Pt, Pd) and [PdCl$_2$(**L3**)]·CHCl$_3$, were obtained (Figure 2a−c, Tables 1 and 2). They all show the expected distortions arising from the bulky chelating phenanthroline ligand, in particular, the bending of the phenanthroline backbone and the displacement of the Cl atoms from the N−metal−N plane.[7,8] Complexes [MCl$_2$(**L2**)] (M = Pt, Pd) form layered structures in which layers of interdigitated *n*-Bu chains alternate with layers of $\pi-\pi$ stacked (3.2−3.4 Å) phenanthroline groups. A number of inter- and intralayer CH···Cl hydrogen-bonding interactions are also present (see Figure 3 and the Supporting Information). In contrast, complex [PdCl$_2$(**L3**)]·CHCl$_3$ does not form layers but exhibits an extended H-bonded structure involving the solvent molecules (see the Supporting Information). The ^{1}H NMR spectrum of [PdCl$_2$(**L3**)] shows a *ca.* 1:1 mixture of the RR/SS and RS/SR diastereomers, although the crystal used for X-ray studies shows only the meso (RS) isomer.

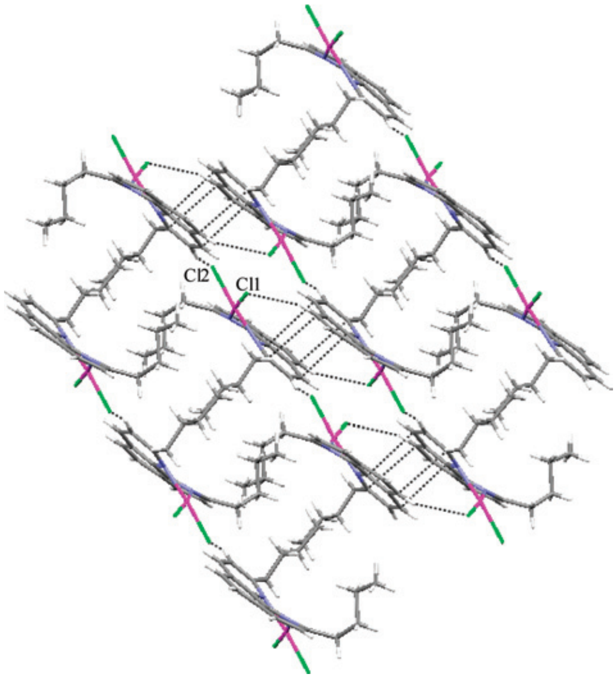

Figure 3. Crystal packing for [PtCl$_2$(**L2**)] showing its layered structure with molecules connected through $\pi-\pi$ (3.22, 3.35 Å) and Cl···H−C interactions (Cl1···H6A, 2.837 Å; Cl1−C6, 3.734 Å; Cl1···H6A−C6, 158°; Cl2···H3A, 2.815 Å; Cl2−C3, 3.688 Å; Cl2···H3A−C3, 152°).

Reactions with Ethylene in Solution. The reactions of the complexes with excess ethylene in solution were monitored by ^{1}H NMR spectroscopy. Complete conversion into the five-coordinate species was observed for Fanizzi's **L1** complexes, as previously reported,[7] and for [PtCl$_2$(**L2**)], whereas only partial coordination of ethylene was observed in the cases of [PdCl$_2$(**L2**)] and [PdCl$_2$(**L3**)]. However, significant changes of color were observed only for CDCl$_3$ solutions of [PdCl$_2$(**L1**)] (orange to yellow), [PtBr$_2$(**L1**)] (red to orange), and [PdI$_2$(**L1**)] (gray to brown).

The ^{1}H NMR resonances corresponding to the five-coordinate derivatives [MCl$_2$(C$_2$H$_4$)(**L2**)] (M = Pt, Pd) and [PdCl$_2$(C$_2$H$_4$)(**L3**)] were similar to those of the analogous **L1** complexes,[7] with coordinated ethylene appearing at *ca.* 4.9 ppm for [PdCl$_2$(C$_2$H$_4$)(**L2**)] or [PdCl$_2$(C$_2$H$_4$)(**L3**)], and at 3.66 ppm [$J(^{195}$Pt−H) = 69 Hz] for [PtCl$_2$(C$_2$H$_4$)(**L2**)].

Incomplete conversion into the ethylene complex in the cases of [PdCl$_2$(**L2**)] and [PdCl$_2$(**L3**)] is not unexpected, since

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[13] Sakai, K.; Tomita, Y.; Ue, T.; Goshima, K.; Ohminato, M.; Tsubomura, T.; Matsumoto, K.; Ohmura, K.; Kawakami, K. *Inorg. Chim. Acta* **2000**, *297*, 64.

[14] Spaniel, T.; Gorls, H.; Scholz, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1862–1865.

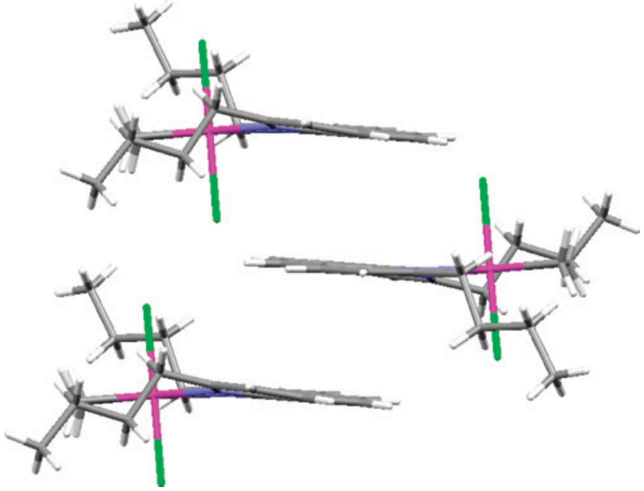

Figure 4. Crystal packing for [$PtCl_2(C_2H_4)$(**L2**)] showing $\pi-\pi$ stacking (i.e., shortest $\pi-\pi$ distance is ca. 3.45 Å).

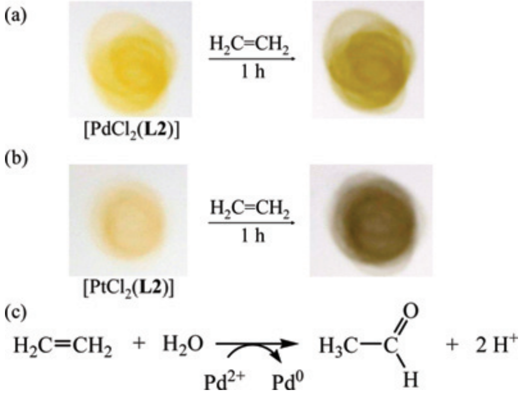

Figure 5. Silica plate impregnated with (a) [$PdCl_2$(**L2**)] or (b) [$PtCl_2$(**L2**)] before and after exposure to ethylene gas. (c) Proposed mechanism for the formation of Pd black and the darkening of the sensor in the presence of ethylene.

olefin coordination has been shown to be less favored in palladium than in platinum complexes.[7] Even in the presence of a large excess of ethylene, the ^{1}H NMR spectra of these mixtures showed four- and five-coordinate species together with free ethylene. The latter appeared as an intense singlet at 5.4 ppm. In the case of [$PdCl_2(C_2H_4)$(**L3**)], signals corresponding to the RR/SS and RS/SR diastereomers were also identified.

Derivatives with **L4** or **L5** did not react with ethylene, presumably due to the electron-withdrawing phenyl substituents. In addition, no reaction with ethylene was observed for the more flexible dipyridyl derivative [$PdCl_2$(**L6**)].

The crystal structure of [$PtCl_2(C_2H_4)$(**L2**)] was obtained (Figure 2d, Tables 1 and 2) and shows the expected trigonal-bipyramidal geometry at the metal center, with the equatorial positions occupied by the nearly planar phenanthroline ligand and the olefin. Extended $\pi-\pi$ stacking involving the phenanthroline moieties is also observed (Figure 4).

Reactions of Supported Complexes with Ethylene. To investigate ethylene coordination in the solid state, samples of each compound were deposited on a variety of solid supports, including silica, reverse-phase silica, cellulose, and alumina. The potential detectors were prepared by depositing *ca*. 0.24 cm^3 of a chloroform solution (2.5×10^{-3} or 5×10^{-3} M) of each compound over each of the solid supports. The plates were then dried and exposed to ethylene gas. Most complexes underwent significant changes of color within a few hours of exposure to ethylene, and on more than one type of support. Interestingly, there was no direct correlation with their reactivities in solution. The changes were irreversible and generally consisted of darkening to brown or dark gray, suggesting partial decomposition to palladium or platinum black (Figure 5a,b). Control experiments to assess the stability of the samples toward air or water vapor were also performed. During these control tests, color changes were observed in many cases, but the final colors were often different from those obtained upon ethylene exposure. For example, the colors of the plates generally became lighter when left in the air. The plates prepared using 2.5×10^{-3} M solutions of the complexes generally kept their original color for longer periods when exposed to the air or water vapor than those prepared using 5×10^{-3} M solutions. However, the lower loadings also tended to show less significant color changes upon exposure to ethylene. In general, the platinum derivatives were more affected by water and/or air than the palladium analogues. Although further research is needed to fully understand the role of the support, it is interesting to note that the response to ethylene was specific to the type of support used, with selective responses to ethylene observed mainly on silica or reverse-phase silica preparations (see the Supporting Information for a summary of the color changes observed).

From the above studies, various complex−support combinations were identified as promising detectors; that is, the detector's color was visually stable when exposed to the air and water but gave an easily detectable change of color upon exposure of ethylene. From these, [$PdCl_2$(**L2**)] on silica was chosen as the optimum system for further studies because it gave one of the clearest color changes (from very light orange to green, Figure 5a) at a low loading within 1 h, and because of the high solubility and ease of preparation of the metal complex itself.

It is likely that the mechanism of the reduction involves a Wacker-type oxidation of ethylene in the presence of traces of water (Figure 5c). However, due to the small quantities of product released against the large ethylene background concentration, and the extended period over which the reaction takes place, it has not been possible to confirm this by identifying the byproduct of the reaction.

The first step of a Wacker process is the formation of an ethylene−Pd(II) complex, which in the present case may involve a species analogous to the five-coordinate species formed in solution. In contrast to that observed in the solid−gas reaction, decomposition to Pd black has not been observed for the five-coordinate ethylene−Pd(II) complexes in solution, but this may be due to the lability of the olefin ligand under these conditions (see above). Further work is planned in order to identify the intermediates and fully understand the mechanism of the reaction between the supported complexes and ethylene.

To assess the influence of the bidentate ligand on the response to ethylene, the derivatives containing nonsubsti-

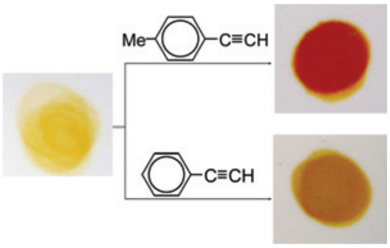

Figure 6. Color changes observed for [PdCl$_2$(**L2**)]−silica detectors upon exposure to *p*-tolylacetylene and phenylacetylene.

tuted ligands [PdCl$_2$(1,10-phenanthroline)] and [PdCl$_2$(2,2′-dipyridyl)][15] were also tested after deposition on silica, together with [PdCl$_2$(NCPh)$_2$]. Upon exposure to ethylene, air, or water, neither of the former two complexes underwent significant color changes, whereas [PdCl$_2$(NCPh)$_2$] darkened significantly in all cases. From this, it appears that the complexes with nonsubstituted bidentate ligands are too stable and are unresponsive, while in the absence of a stabilizing chelating ligand, [PdCl$_2$(PhCN)$_2$] very quickly decomposes to Pd black. With 2,9-disubstituted bidentate ligands, the complexes are sufficiently stable toward water and air, but still reactive toward ethylene.

We extended the investigation to see if detectors of this type would respond differently to fruit at different stages of ripeness. Experiments with fruit were performed with [PdCl$_2$(**L2**)]−silica. When placed in a sealed vessel with green, preclimacteric bananas for 24 h, a similar color change to that seen upon exposure to ethylene occurred (light-orange to green/gray). Significantly, when exposed to already-ripe bananas under the same conditions, no response was observed. These results are consistent with the known emission profile for ethylene from climacteric fruit, in which an ethylene "spike" is observed during the climacteric itself, from which point ripening accelerates.[3,16] In complementary experiments, ethylene production from the fruit was monitored by GC. No ethylene was detected from the green bananas, and detector plates placed next to the fruit did not change color. However, when a yellow banana was added to the experiment to induce ripening, ethylene was detected by GC at 24 and 48 h after addition of the yellow banana, and a clear color change of the detector was observed after 2 days.

Reactions of Supported Complexes with Other Volatiles. In order to assess the selectivity of the detectors, the responses of silica-supported [PdCl$_2$(**L2**)] or [PtCl$_2$(**L2**)] toward other organic volatiles were studied. [PtCl$_2$(**L2**)] underwent significant darkening (to brown) in most cases, whereas the response of the Pd detector was more selective. Thus, [PdCl$_2$(**L2**)]−silica detectors did not change color upon exposure to alkenes such as 1-decene, 1-dodecene, styrene, cyclopentene, cyclooctene, 1,3-butadiene, or acrylonitrile. Slight color changes were observed upon exposure to aromatic compounds (toluene, pyridine, and benzonitrile) and to some terminal alkynes, such as 2-butyne and (4-pentylphenyl)acetylene, whereas significant darkening to brown or red was observed upon exposure to propene, phenylacetylene, and *p*-tolylacetylene (Figure 6). However, these other analytes are not relevant in the context of fruit ripening or ethylene pipe-leak detection because they are not expected to be present at significant amounts. Moreover, other fruit volatiles, such as hexylalcohol, 3-methyl-1-butanol, and 2-pentanone did not produce a color change. This is important because alcohols and carbonyl compounds are also emitted by climacteric fruit at various stages but may not be reliable indicators of ripening.[17]

Conclusions

In summary, we report a simple system consisting of a palladium complex on a silica support which shows a clear visible response to ethylene and, therefore, represents a chemical basis for visual ethylene detection that can be applied in pipe-leak detection and the monitoring of fruit ripening. Although the detectors have also been found to respond to propene and terminal aromatic acetylenes, these volatiles are not significant in the context of the mentioned applications. Encouragingly, discrimination between fruit at different stages of ripening has also been observed. Overall, [PdCl$_2$(**L2**)]−silica detectors are easy to prepare and use, and they show improved specificity and stability compared with previous visual sensors (*i.e.*, those based on permanganate or Pd(II)/molybdate). It is interesting to note that the color change (to red) upon exposure to *p*-tolylacetylene is specific for this volatile.

With regard to cost, it should be noted that an effective detector requires only 0.5−1 mg of [PdCl$_2$(**L2**)]; that is, starting from 1 g of PdCl$_2$, it is possible to prepare over 2000 detectors, and therefore cost is unlikely to be prohibitive. The system can clearly also be varied with regard to the types of coligands present, so that the visible response may be tuned. In addition, color-changing detectors of this type can be incorporated into low-cost optical devices that allow remote wireless detection,[18] with important potential applications including the detection of ethylene leaks from pipelines. Work is currently underway in this area.

Acknowledgment. We are grateful to the European Social Fund and the Questor Centre, Belfast, for funding.

Supporting Information Available: Summary of color changes upon exposure to ethylene and control experiments, IR data, additional figures of the crystal packing of complexes [PdCl$_2$(**L2**)] and [PdCl$_2$(**L3**)]·CHCl$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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