[11] Crystal data: $C_{16}H_{32}N_8O_4$, $M_r = 400.48\ \mathrm{g\,mol^{-1}}$, colorless prism, crystal size $0.3 \times 0.1 \times 0.1\ \mathrm{mm^3}$, $a = b = 15.333(3)$, $c = 4.724(1)$ Å, $V = 1110.6(4)$ Å^3, $T = 293$ K, tetragonal, space group $I4$, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.226\ \mathrm{Mg\,m^{-3}}$, $\mu = 0.763\ \mathrm{mm^{-1}}$. Nonius Mach3 diffractometer, $\lambda = 1.54178$ Å. 4293 measured reflections, 1052 unique ($R_{\mathrm{int}} = 0.017$), 953 with $I > 2\sigma(I)$, the structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data to $R_1 = 0.0411$ [$I > 2\sigma(I)$] and $wR_2 = 0.1036$ [$I > 2\sigma(I)$], 93 parameters. CCDC 175843 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] Nonsymmetrical macrocyclic bisureas consisting of one cystine unit and one hexamethylenediamine unit bridged together form tubelike hydrogen-bonded aggregates in the solid state. In this case, the carbonyl groups of the two urea units within the same ring point in opposite directions: D. Ranganathan, C. Lakshmi, I. L. Karle, *J. Am. Chem. Soc.* **1999**, *121*, 6103–6107.

[13] A different packing is observed in the structure of the β-peptide cyclo(β^3-HAla)$_4$ with *S,S,S,S* configuration. Although all C=O and N−H bonds point, respectively, in the same direction in each tubular stack, neighboring tubes are arranged in opposite directions. See reference [5a].

Drastic Luminescence Response to Carbon Monoxide from a Ru$^{\mathrm{II}}$ Complex Containing a Hemilabile Phosphane Pyrene Ether[**]

Cerrie W. Rogers and Michael O. Wolf[*]

The rapid, reversible nature of the coordinative bonding between metals and Lewis-basic small molecules makes molecular chemosensors based on this phenomenon quite promising. Indeed, recent reviews contain numerous reports of sensors based on metal–ligand interactions.[1–3] Of particular potential are metal complexes designed such that the analyte-binding event changes the luminescence properties of an intramolecular lumophore. One approach is to use a modular design in which a metal-based analyte receptor is covalently linked to a separate lumophore. The emission of the lumophore is influenced by the binding of the analyte, usually through On–Off switching of energy- or electron-transfer quenching mechanisms.[1, 2, 4] Pyrene, which emits intense indigo-blue fluorescence in dilute solution[5] and blue-green excimer emission in concentrated solution,[5, 6] is a popular lumophore for such molecule-based sensors, particularly those based on photoinduced electron transfer (PET) processes.[2, 7] Switching between pyrene monomer and excimer emission has also been used to obtain a sensor response, whereby the ability of pyrene moieties to interact with one another is influenced by the binding of analyte to the receptor.[2, 8]

We used a [RuCl$_2$(POR-*P,O*)$_2$] complex (where POR is an ether-substituted phosphane) as the basis for a modular molecular sensor. This type of complex reacts rapidly and reversibly with numerous Lewis-basic small molecules, including CO,[9–11] a small-molecule analyte for which effective new sensor materials may be useful, by displacement of the labile ether moiety. Incorporation of a pyrene group in the hemilabile ligand leads to metal-based reactivity towards small molecules and pyrene-based luminescence. Here a Ru$^{\mathrm{II}}$ complex containing the hemilabile phosphane ether ligand 4-{2-(diphenylphosphanyl)phenoxy}butylpyrene (POC4Pyr) is described. The complex [RuCl$_2$(POC4Pyr-*P,O*)$_2$] (**1**, see Scheme 1) reacts with carbon monoxide to produce a significant luminescence response in which monomer-to-excimer emission switching is observed. This is the first example of the use of the hemilabile-ligand approach to obtain a molecular sensor with a room-temperature luminescence response, although we have previously reported a Ru bipyridyl complex containing a hemilabile ligand that exhibits small-molecule-dependent luminescence at low temperature.[12]

Complex **1** was prepared by reaction of POC4Pyr with RuCl$_3 \cdot x$H$_2$O in boiling deaerated ethanol/toluene. The burgundy-pink complex is mildly sensitive to oxidation by air, both in solution and as a solid. The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data of **1** (Tables 1 and 2) are analogous to those of [RuCl$_2$(POMe-*P,O*)$_2$] (POMe = (2-methoxyphenyl)diphenylphosphane), which has been crystallographically characterized[9] and found to contain two *P,O*-coordinated phosphane ether ligands with the phosphane moieties *cis* to each other.

The absorption spectrum of complex **1** is essentially a combination of those of [RuCl$_2$(POMe-*P,O*)$_2$] and the pyrenyl ligand POC4Pyr. The color of the complex is caused by a weak

Table 1. Summary of ^{13}C{^{1}H} NMR spectroscopic data[a] for **1**–**3**.

Complex	δ/ppm (multiplicity) [*J*/Hz] CO	 *ortho*[b]	 *ipso*	 *ipso′*
1	–	161.7 (t) [5.2]	134.1 (d) [25.3]	ND[c]
2	197.6 (t) [13.5]	160.5 (t) [2.3]	132.8 (t) [24.4]	118.8 (t) [23.9]
3	193.7 (t) [10.9]	159.0 (t) [2.3]	131.8 (t) [24]	119.3 (t) [23.5]

[a] In CD$_2$Cl$_2$. [b] Phenyl C atom bound to oxygen. [c] ND = not determined.

Table 2. Comparison of **1**–**3** with analogous POMe complexes.[a]

Complex	Color	δ(^{31}P{^{1}H})/ppm	$\tilde{\nu}$(C=O)/cm^{-1}
tcc-**1**	red	63.7[b]	–
ttt-**2**	greenish yellow	27.1[b]	2005[c]
cct-**3**	greenish yellow	13.9[b]	2005, 2058[c]
tcc-[RuCl$_2$(POMe-*P,O*)$_2$]	red	62.7[d]	–
ttt-[RuCl$_2$(CO)$_2$(POMe-*P*)$_2$]	yellow	26.7	1962
cct-[RuCl$_2$(CO)$_2$(POMe-*P*)$_2$]	white	10.6	2000, 2060

[a] From ref. [9]; ^{31}P{^{1}H} NMR spectra measured in CDCl$_3$ solution; IR spectra measured in mineral-oil mulls. [b] In CD$_2$Cl$_2$. [c] In CHCl$_3$. [d] In CDCl$_3$.

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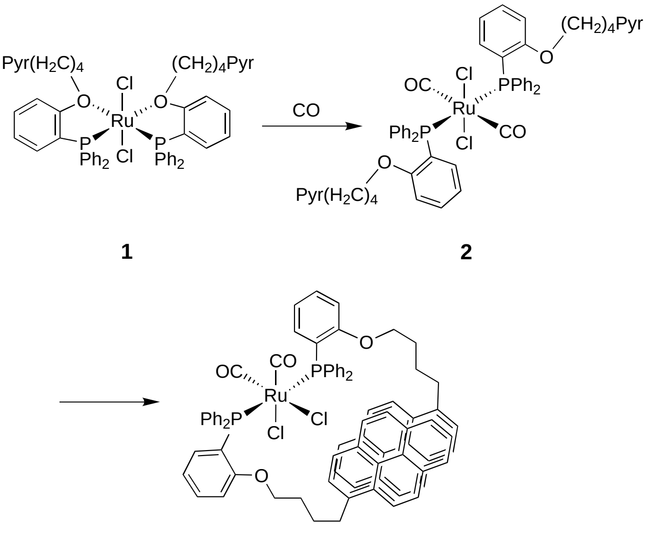
[**] This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. C.W.R. thanks NSERC and UBC for graduate fellowships.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

metal-based absorption band ($\varepsilon_{519} = 490\,\text{M}^{-1}\,\text{cm}^{-1}$ in cyclohexane), similar to that of [$RuCl_2$(POMe-*P,O*)$_2$] ($\varepsilon_{517} = 550\,\text{M}^{-1}\,\text{cm}^{-1}$ in $CHCl_3$).[13] The peaks in the emission spectrum of complex **1** (measured in air-saturated solution) appear at energies similar to those of free POC4Pyr. However, the emission from the complex is significantly diminished in intensity, presumably because of some intramolecular quenching of pyrene emission by the metal.

When a solution of **1** is treated with 1 atm of CO, the raspberry-red color changes immediately to greenish yellow, as is typical of [$RuCl_2$(POR-*P,O*)$_2$] complexes.[9, 10] Analysis of the samples by $^{31}P\{^1H\}$ NMR spectroscopy immediately after the reaction revealed quantitative formation of the new complex **2** ($\delta = 27.1$). Removal of the CO atmosphere from **2** leads to geometric isomerization with formation of **3** ($\delta = 13.9$); samples kept under CO atmosphere are almost entirely inert to this isomerization. The mechanism of this isomerization has not yet been established, but it appears to involve dissociation of CO, as is common for [$RuCl_2(CO)_2(PR_3)_2$] complexes.[14] The combinations of spectroscopic properties for complexes **1**–**3** (color, NMR chemical shifts, IR bands) are similar to those of the analogous POMe complexes[9] (Table 2).

Complex **2** was identified as a dicarbonyl complex on the basis of the triplet $^{31}P\{^1H\}$ signal of samples prepared with ^{13}CO; furthermore, the triplet carbonyl $^{13}C\{^1H\}$ signal indicates that the two equivalent CO moieties in **2** are coupled to two equivalent ^{31}P nuclei. The magnitude of the $^{13}C,^{31}P$ coupling constant (ca. 13 Hz) is typical of [$RuCl_2(CO)_2(PR_3)_2$] complexes with phosphanes *cis* to the carbonyl ligands ($^2J_{P,C} < 20$ Hz).[9] From these data and the NMR and IR spectroscopic data listed in Tables 1 and 2, **2** is identified as *trans,trans,trans*-[$RuCl_2(CO)_2$(POC4Pyr-*P*)$_2$]. Similarly, **3** contains two equivalent phosphane groups, and the ^{13}CO-labeled complex has a triplet ^{31}P NMR signal in accord with the presence of two equivalent carbonyl ligands. The spectroscopic data are consistent with assignment of the thermodynamically favored dicarbonyl complex **3** as *cis,cis,trans*-[$RuCl_2(CO)_2$(POC4Pyr-*P*)$_2$]. Scheme 1 shows the proposed reaction of **1** with CO and the further isomerization of the kinetic product **2** to the thermodynamically favored isomer **3**.



3

Scheme 1. Reaction of **1** with CO and further isomerization of the kinetic product **2** to the thermodynamically favored isomer **3**.

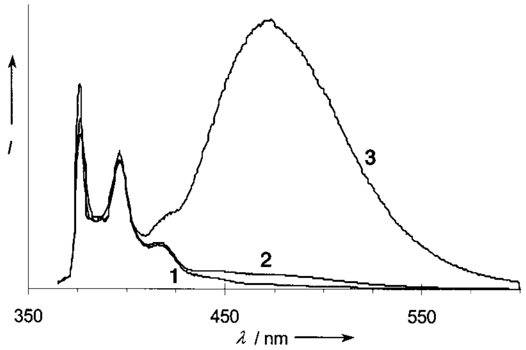


Figure 1. Comparison of the emission from dilute solutions of **1**–**3**. According to excimer band intensity *I*: highest: [**3**] = 3.4×10^{-6} M; middle: [**2**] = 1.8×10^{-6} M; lowest: [**1**] = 1.4×10^{-6} M; in air-saturated CH_2Cl_2 solution at RT; $\lambda_{ex} = 350$ nm; excitation path 10 mm, emission path 2 mm.

In the context of chemical sensing, the change in the luminescence properties on reaction of **1** with CO is of greater interest than the color change associated with the reaction because superior detection limits are achievable for measurements based on luminescence than on absorption. When concentrated solutions of **1** (ca. 10^{-2} M) were treated with CO under UV irradiation, the dim blue pyrene emission from **1** switched to strong blue-green excimer emission from **2**. Displacement of the ether from the metal center increases the conformational freedom of the alkylpyrene moiety by further lengthening the tether between the pyrene ring and the metal atom. This increased conformational freedom influences the ability of the pyrene moieties to interact with one another, and these interactions are manifested as excimer emission. It is noteworthy that in dilute solution ([**2**] = 1.8×10^{-6} M), a trace of excimer emission persists, as is evident from the spectra in Figure 1. This implies that excimers can also form intramolecularly, since intermolecular excimer emission from pyrene is typically insignificant for concentrations below about 10^{-3} M.[5]

After isomerization of **2** to **3**, strong excimer emission is observed, even in dilute solution. Thus, the pyrene moieties in the thermodynamically preferred complex **3** must be readily able to interact with each other to form intramolecular excimers. Although both complexes have *trans* phosphane groups, the *cis* disposition of both the carbonyl and chloro ligands in **3** evidently favors π stacking of the pyrene rings. Interactions between the pyrene rings are possibly involved in the isomerization process and stabilize a geometry in the purported five-coordinate intermediate that favors formation of the *cis,cis,trans* isomer **3**.

The rapid CO-induced switching from weak pyrene monomer fluorescence to strong excimer emission makes **1** an attractive candidate for further study as a molecule-based sensor. The luminescence response to CO occurs within seconds at room temperature, and the response is easily observed by the naked eye in concentrated solutions (ca. 10^{-2} M), as shown in Figure 2; the reaction is also evidenced by a color change that is readily observed under ambient lighting.

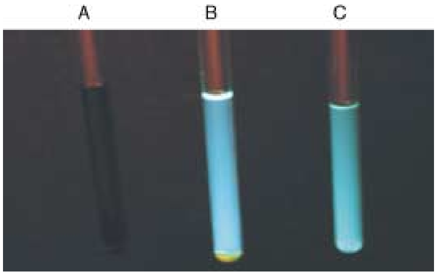


Figure 2. Concentrated solutions (ca. 10^{-2} M) of A) **1**, B) **2** and C) **3** under UV light (366 nm).

Furthermore, exposure of a solution (ca. 10^{-6} M) of **1** to an atmosphere containing 0.05% (ca. 850 ppm) CO results in a detectable change in emission (not shown), and studies are ongoing to determine the detection range for this sensor complex. Investigations are also underway to determine whether the intensely emissive excimer of **3** can be observed immediately when the reaction with CO occurs at elevated temperature.[14] This would result in a substantial difference in emission intensity from the sensor material before and after CO exposure. Importantly, the drastic difference in behavior of **2** and **3** suggests that luminescence changes may be triggered by subtle changes in the bonding environment at the metal atom. This is significant because it indicates that it may be possible to design sensors based on this approach in which differences in response result not only from selectivity for specific analytes by tuning the reactivity of the metal, but also from steric and electronic considerations which favor or disfavor the formation of pyrene excimers.

Experimental Section

Full experimental and characterization details for POC4Pyr and complexes **1**–**3** are available in the Supporting Information.

Received: November 5, 2001
Revised: March 1, 2002 [Z18161]

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Shape-Persistent, Fluorescent Polyphenylene Dyads and a Triad for Efficient Vectorial Transduction of Excitation Energy[**]

Tanja Weil, Erik Reuther, and Klaus Müllen[*]

Plants and some bacteria have the unique ability to convert sunlight into chemically bound energy, thus opening up a nearly unlimited energy source.[1] Since supplies of fossil fuels are expected to become exhausted in the near future, there has been an increasing interest in the synthesis of novel organic and polymeric molecules for the efficient harvesting of solar energy as well as for the conversion of solar radiation into electrical energy.[2a–d] The geometry of linear chain macromolecules is not ideal for efficient energy transfer; in particular, it is difficult to achieve an energy gradient for a vectorial transduction of light energy.[3] Not surprisingly, therefore, dendrimers have received great interest. Their globular shape provides a large surface area that can be decorated with chromophores, which thus results in a large absorption cross section and enables efficient capturing of photons.[4] Balzani et al. have synthesized light-harvesting dendrimers that bear an osmium complex in the center and several ruthenium complexes at the periphery.[5] In the phenylacetylene dendrimers reported by Moore and coworkers, a focal perylene chromophore acts as a light-harvesting antenna and there is an energy gradient from the periphery towards the center.[6] For light-harvesting dendrimers based on a flexible scaffold[7a–d] the investigation of energy transfer is often complicated because conformational mobility leads to undesired chromophore interactions such as aggregation, excimer formation, and dye self-quenching.[8, 9] Other drawbacks are often the very limited photostability[9] and low fluorescence quantum yields of the chosen chromophores.

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[**] This research was supported by the TMR European Research Program through the SISITOMAS project, the Volkswagen-Stiftung, and the Bundesministerium für Bildung and Forschung. We also thank S. Spang and C. Beer for support in the synthetic work.