# Rhenium(I) and platinum(II) complexes with diimine ligands bearing acidic phenol substituents: hydrogen-bonding, acid-base chemistry and optical properties<sup>†</sup>

Wei Liu and Katja Heinze\*

Received 29th April 2010, Accepted 16th July 2010 DOI: 10.1039/c0dt00393j

Tricarbonylchloro-rhenium(I) (1–4) and catecholato-platinum(II) complexes (6, 7) of diimine ligands bearing phenol and *O*-protected phenol substituents have been prepared and fully characterised including single crystal structure analyses of 1, 4 and 7. The redox behaviour of the catecholato platinum(II) complexes 6 and 7 has been probed by cyclic voltammetry, preparative oxidation and EPR spectroscopy ( $6^{+}$ , 7<sup>+</sup>). Reversible deprotonation of the hydroxy substituted complexes 1, 3 and 6 to 1<sup>-</sup>, 3<sup>-</sup> and 6<sup>-</sup> resulted in significant changes in their electronic spectra. The luminescence properties of the diamagnetic complexes have been investigated using emission spectroscopy. DFT and TD-DFT calculations were invoked to shed some light onto the geometric and electronic structures as well as the experimental spectroscopic properties of the neutral complexes 1–7, the radical cations  $6^{++}$  and  $7^{++}$  and the conjugate bases 1<sup>-</sup>, 3<sup>-</sup> and  $6^{-}$ .

# Introduction

The chemistry of d<sup>6</sup> and d<sup>8</sup> transition metal complexes including Ru<sup>II</sup>, Re<sup>I</sup>, or Pt<sup>II</sup> central atoms has attracted considerable attention in the past two decades,<sup>1</sup> because of their interesting photophysical properties and their possible applications in NLO materials,<sup>2</sup> in solar energy conversion processes,<sup>3</sup> as well as in chemical or biological sensors.<sup>4,5</sup>

Platinum(II) and rhenium(I) complexes incorporating redoxactive and/or photoactive "non-innocent" ligands are particularly intriguing. For potential applications in molecular devices, photocatalysis, energy conversion and information storage<sup>6</sup> their energy and electron transfer properties are actively studied. In this context the diimine type ligand is one of the most widely used bidentate chelating moieties.<sup>7-9</sup>

We have recently discovered that combination of a diimine ligand bearing a remote acidic phenol group with a platinum(II) coordinated catecholato ligand (Scheme 1, top) resulted in the unexpected observation of room temperature luminescence after deprononation. The emission, probably originating from a ligand excited triplet state, appeared to be associated with the planarisation of the phenolate-substituted diimine ligand.<sup>10</sup>

In this respect the anionic complex resembles tetradentate Schiff base platinum(II) complexes. These planar and rigid systems have



Scheme 1 Deprotonation of a phenol-substituted diimine (catecholato)platinum(II) complex<sup>10</sup> (top) and planar platinum(II) complexes with salen-derived  $N_2O_2$  ligands<sup>9</sup> (bottom).

been successfully employed as phosphorescent materials in organic light-emitting devices (OLEDs) (Scheme 1, bottom).<sup>9</sup>

To further investigate this observation and to possibly extract some generalisable rules we replace the unsymmetrical phenol substituted ligand 4-[(pyridine-2-ylmethylene)amino]phenol  $L^1$  by the doubly phenol substituted bis(4-hydroxyphenyl)ethylenediimine

Johannes Gutenberg-University of Mainz, Duesbergweg 10-14, 55128, Mainz, Germany. E-mail: katja.heinze@uni-mainz.de; Fax: + 49-6131-3927277

<sup>†</sup> Electronic supplementary information (ESI) available: Details concerning crystal structure analyses and TD-DFT calculations, Cartesian coordinates of DFT optimised structures, graphical representation of molecular orbitals, UV/Vis/NIR spectra of 1, 2, 3, 4, 6, 7 and Gaussian deconvolution, UV/Vis spectra of 1<sup>-</sup> and 3<sup>-</sup> upon titration with acid, emission spectrum of 4 at 77 K, EPR spectrum of 6<sup>+</sup> and simulation], FD mass spectrum of 1 after the deprotonation/reprotonation sequence. CCDC reference numbers 775540–775542. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00393j

Published on 31 August 2010. Downloaded on 17/08/2013 10:28:26.

ligand  $L^3$  and the Pt(3,6-dbcat) fragment (3,6-dbcat = 3,6-ditert-butyl-1,2-catecholato) by a ReCl(CO)<sub>3</sub> moiety. Rhenium and platinum complexes of the *O*-protected analogues  $L^2$  and  $L^4$  are also investigated for structural and spectroscopic comparison. The geometric and electronic properties of the rhenium(I) and platinum(II) complexes of  $L^1-L^4$  are investigated in the following using experimental and theoretical methods.

# Experimental

# **General considerations**

Standard Schlenk techniques were used in carrying out manipulations under an Ar atmosphere. All solvents were dried with standard methods and freshly distilled under Ar prior to use. Reagents were purchased from commercial sources and used as received. IR spectra were recorded with a BioRad Excalibur FTS 3100 spectrometer using KBr cells in CH<sub>2</sub>Cl<sub>2</sub> and as CsI disks. Absorption spectra were measured on a Varian Cary 5000 UV/Vis/NIR spectrophotometer. Emission spectra were recorded on a Varian Cary Eclipse spectrometer. NMR spectra were measured on a Bruker AM 400 spectrometer at 400.13 MHz (<sup>1</sup>H) and 100.03 MHz (<sup>13</sup>C). Chemical shifts ( $\delta$  (ppm)) were reported with respect to residual solvent peaks as internal standard (<sup>1</sup>H: chloroform,  $\delta = 7.26$  ppm; d<sub>6</sub>-dmso,  $\delta = 2.50$  ppm; <sup>13</sup>C:  $d_{\delta}$ -dmso,  $\delta$  = 39.7 ppm). EPR spectra were acquired on a Magnettech MiniScope MS300 benchtop cw EPR spectrometer (X-band, ~9.4 GHz microwave frequency). EPR simulations were performed using EasySpin 3.1.1.11 Cyclic voltammetry and square wave voltammetry were performed on a BioLogic SP-50 electrochemical analytical instrument, with platinum wires as working and counter electrodes, Ag/AgNO3 as reference electrode, and 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. All potentials are reported relative to Ag/AgNO<sub>3</sub>. FD mass spectra were recorded on a FD Finnigan MAT90 instrument. Elemental analyses were performed by the analytical laboratory of the Chemistry Department, University of Mainz, Germany.

# Synthesis

The ligands 4-[(pyridine-2-ylmethylene)amino]phenol (L<sup>1</sup>), pyridine-2-ylmethylene-(4-trimethylsilanyloxyphenyl)amine (L<sup>2</sup>), N,N'-bis(4-hydroxyphenyl)ethylenediimine (L<sup>3</sup>), N,N'-bis(4methoxyphenyl)ethylenediimine (L<sup>4</sup>), and 3,6-di-*tert*-butyl-1,2benzoquinone (3,6-dbq) were synthesised as described in the literature.<sup>12-14</sup> Tricarbonylchloro[N,N'-bis(4-hydroxyphenyl)ethylenediimine]rhenium(I) (**3**) was prepared according to a reported procedure.<sup>15</sup> The precursor complex Pt(nbe)<sub>3</sub> (nbe = norbornene, bicyclo[2,2,1]heptene) and the platinum(II) complex with ligand L<sup>1</sup> (**5**) were prepared by following known procedures.<sup>10,16</sup>

# ReCl(CO)<sub>3</sub>(L<sup>2</sup>) [tricarbonylchloro(pyridine-2-ylmethylene-(4-trimethylsilanyloxyphenyl)amine)rhenium(1), 2]

All glassware was passivated with  $(CH_3)_3$ SiCl before use. A mixture of ReCl(CO)<sub>5</sub> (322 mg, 1.06 mmol) and L<sup>2</sup> (241 mg, 0.89 mmol) was refluxed in toluene (10 mL) for 1.5 h. The clear orange red solution was allowed to cool to room temperature. The solvent was removed under reduced pressure to afford the crude product. After

washing with diethyl ether and drying *in vacuo* **2** was obtained as an orange red solid. Yield: 241 mg (0.42 mmol; 47%). IR (CsI, cm<sup>-1</sup>): 2022 (s, CO), 1917 (s, CO), 1910 (s, CO). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2026 (s, CO), 1926 (s, CO), 1903 (s, CO). FD-MS: *m*/*z* = 575.7; calcd for C<sub>18</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>4</sub>ReSi 576.0. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 9.03 (d, <sup>3</sup>J<sub>HH</sub> = 5.1 Hz, 1H, H<sup>12</sup>), 8.95 (s, 1H, H<sup>7</sup>), 8.21 (pt, 1H, H<sup>10</sup>), 8.15 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1H, H<sup>9</sup>), 7.69 (pt, 1H, H<sup>11</sup>), 7.49 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 2H, H<sup>2.6</sup>), 7.02 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, H<sup>3.5</sup>), 0.30 (s, 9H, CH<sub>3</sub>). Calcd for C<sub>18</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>4</sub>ReSi (576.10): C, 37.53; H, 3.15; N, 4.86. Found: C, 36.45; H, 2.83; N, 4.61.

# ReCl(CO)<sub>3</sub>(L<sup>1</sup>) [tricarbonylchloro[4-[(pyridine-2 ylmethylene)amino]phenol]rhenium(1), 1]

**Method 1**: A mixture of  $\text{ReCl}(\text{CO})_5$  (217 mg, 0.6 mmol) and  $L^1$  (99 mg, 0.5 mmol) was refluxed in toluene (10 mL) for 2 h. After solvent evaporation *in vacuo*, washing with diethyl ether and drying 1 was obtained as an orange coloured solid. Yield: 195 mg (0.39 mmol, 77%).

Method 2: To an orange red solution of 2 (127 mg, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added tetra-n-butylammoniumfluoride (TBAF, 85 mg, 0.27 mmol). The mixture was stirred for 2 h at room temperature. Acetic acid (1 mL) was added. The resulting clear orange coloured solution was stirred for 1 h at room temperature. The solvent was evaporated and the residue was filtered and washed with  $CH_2Cl_2$  and  $Et_2O$ . After drying under vacuum an orange coloured powder was obtained. Yield: 99 mg (0.20 mmol, 89%). IR (CsI, cm<sup>-1</sup>): 3259 (m, OH), 2025 (s, CO), 1912 (s, CO), 1894 (s, CO). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2041 (s, CO), 1872 (br, CO). FD-MS: m/z = 503.8; calcd for C<sub>15</sub>H<sub>10</sub>ClN<sub>2</sub>O<sub>4</sub>Re: 504.0. <sup>1</sup>H NMR (400 MHz,  $d_6$ -dmso, ppm):  $\delta = 10.04$  (s, 1H, OH), 9.24 (s, 1H, H<sup>7</sup>), 9.04 (d,  ${}^{3}J_{HH} = 5.6$  Hz, 1H, H<sup>12</sup>), 7.83–8.36 (m, 2H, H<sup>9,10</sup>), 7.79–7.82 (m, 1H, H<sup>11</sup>), 7.45 (d,  ${}^{3}J_{HH} = 9.0$  Hz, 2H, H<sup>2,6</sup>), 6.92 (d,  ${}^{3}J_{\rm HH} = 9.0$  Hz, 2H, H<sup>3,5</sup>). Calcd for C<sub>15</sub>H<sub>10</sub>ClN<sub>2</sub>O<sub>4</sub>Re (503.92): C, 35.75; H, 2.00; N, 5.56. Found: C, 35.57; H, 2.09; N, 5.55.

# ReCl(CO)<sub>3</sub>(L<sup>4</sup>) [tricarbonylchloro[*N*,*N*<sup>'</sup>-bis(4-methoxyphenyl)ethylenediimine]rhenium(1), 4]

A mixture of ReCl(CO)<sub>5</sub> (362 mg, 1 mmol) and L<sup>4</sup> (268 mg, 1 mmol) was refluxed in toluene (15 mL) for 1 h. The solvent was removed *in vacuo* to obtain the crude product. An orange red crystalline solid of **4** was obtained after chromatography on alumina using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield: 498 mg (0.87 mmol, 87%). Red crystals were obtained by slow diffusion of Et<sub>2</sub>O into a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. IR (CsI, cm<sup>-1</sup>): 2022 (s, CO), 1943 (s, CO), 1914 (s, CO). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2036 (s, CO), 1929 (s, CO), 1903 (s, CO). FD-MS: *m*/*z* = 573.6; calcd for C<sub>19</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>5</sub>Re: 574.0. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.58 (s, 2H, H<sup>7,7</sup>), 7.51 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 4H, H<sup>2.6.2'.6'</sup>), 7.00 (d, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, 4H, H<sup>3.5.3'.5'</sup>), 3.89 (s, 6H, OCH<sub>3</sub>). Calcd for C<sub>19</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>5</sub>Re (574.01): C, 39.76; H, 2.81; N, 4.88. Found: C, 39.75; H, 2.95; N, 4.95.

# Pt(dbcat)(L<sup>3</sup>) [(3,6-di-*tert*-butyl-catecholato)[*N*,*N*'-bis(4-hydroxyphenyl)ethylenediimine]platinum(II), 6]

A mixture of  $L^3$  (120 mg, 0.5 mmol), nbe (80 mg, 0.84 mmol) and Pt(nbe)<sub>3</sub> (300 mg, 0.62 mmol) was stirred in THF (18 mL) at room temperature for 3 h. 3,6-Di-*tert*-butyl-1,2-benzoquinone (120 mg, 0.54 mmol) was added as a solid. The mixture was stirred for 20 h at room temperature. The solvent was removed *in vacuo* to afford a dark green solid. The solid was washed with Et<sub>2</sub>O, THF, and CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum. Yield: 157 mg (0.24 mmol, 48%). IR (CsI, cm<sup>-1</sup>): 3421 (br, OH), 2922 (s, CH), 1601 (s), 1514 (s), 1458 (s). FD-MS: m/z = 655.2; calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>Pt: 655.2. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-dmso, ppm):  $\delta = 10.10$  (s, 2H, OH), 9.12 (s, 2H, H<sup>7,7</sup>), 7.92 (d, <sup>3</sup>J<sub>HH</sub> = 9.4 Hz, 4H, H<sup>2,6,2,6</sup>), 6.88–6.91 (m, 4H, H<sup>3,5,3,5</sup>), 6.15 (s, 2H, H<sup>10,10</sup>), 1.29 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>Pt (655.66)×2THF×CH<sub>2</sub>Cl<sub>2</sub>: C, 50.23; H, 5.70; N, 3.17. Found: C, 50.18; H, 6.01; N, 3.04.

# Pt(dbcat)(L<sup>4</sup>) [(3,6-di-*tert*-butyl-catecholato) [*N*,*N*′-bis(4-methoxyphenyl)ethylenediimine]platinum(II), 7]

Complex 7 was prepared by a procedure similar to the one for **6** using L<sup>4</sup> instead of L<sup>3</sup>. Yield: 48%. Dark green crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of 7 in a CH<sub>2</sub>Cl<sub>2</sub>–THF–CH<sub>3</sub>CN mixture. IR (CsI, cm<sup>-1</sup>): 2959 (s, CH), 2867 (m, CH), 1605 (s), 1506 (s), 1453 (s), 1266 (s). FD-MS: *m*/*z* = 683.8; calcd for C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Pt: 683.2. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-dmso, ppm):  $\delta$  = 9.21 (s, 2H, H<sup>7,7</sup>), 8.02 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 4H, H<sup>2,6,27,6'</sup>), 7.09 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 4H, H<sup>3,5,37,5'</sup>), 6.16 (s, 2H, H<sup>10,10'</sup>), 3.88 (s, 6H, OCH<sub>3</sub>), 1.29 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-dmso, ppm) 161.3 (s), 161.2 (s), 160.4 (s), 141.8 (s), 134.0 (s), 126.6 (s), 113.9 (s), 113.1 (s), 55.6 (s), 33.6 (s), 29.4 (s). Calcd for C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Pt (683.72)× $\frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub>: C, 50.45; H, 5.14; N, 3.86. Found: C, 50.00; H, 5.41; N, 3.76.

## Crystal structure determinations

The data were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo-K<sub>a</sub> ( $\lambda =$ 0.71073 Å) radiation using a  $\omega$ -2 $\theta$  scan mode at 173 K. The highly redundant datasets were reduced using SAINT<sup>17</sup> and corrected for Lorentz and polarization effects. Absorption corrections were applied using MULABS.<sup>18</sup> The structures were solved by direct methods and refined by full-matrix leastsquares methods on  $F^2$  using SHELXTL-97.<sup>19</sup> All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of  $U_{iso}$ .

# **Computational details**

All calculations were carried out with Gaussian03 programs.<sup>20</sup> Density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed with the B3LYP hybrid functional without symmetry constraints imposed on the molecules.<sup>21</sup> The calculations were carried out using a 6-31G\* basis set for C, H, N, O and Cl atoms and effective core potentials (LANL2DZ) for Re and Pt atoms. All geometries were characterised as minima by frequency analysis ( $N_{imag} = 0$ ). For solvent modeling the integral equation formalism polarisable continuum model (IEFPCM) was employed. All computational results are summarised in the Supporting Information.<sup>†</sup>

# **Results and discussions**

# Synthesis and characterisation

The unsymmetrical and symmetrical OR-substituted diimine ligands  $L^1$ ,  $L^3$  and  $L^4$  (R = H, CH<sub>3</sub>) employed in this study were prepared by previously reported routes using Schiff base condensation methods in high yields (Scheme 2). The trimethylsilyl protected ligand  $L^2$  was obtained by silylation of the hydroxo group of  $L^1$  with trimethylsilyl chloride and triethylamine as base.<sup>12</sup>



Scheme 2 Syntheses of diimine rhenium(I) and platinum(II) complexes and atom numbering for NMR assignments.

Coordination of  $\text{ReCl}(\text{CO})_5$  to  $L^1-L^4$  in refluxing toluene under CO substitution gave the orange coloured Re<sup>1</sup> complexes **1–4** (Scheme 2). The hydroxo-substituted complex **1** can also be obtained from the trimethylsilyl derivative **2** by desilylation with fluoride ions in high yield. Although the synthesis of complex **3** has been reported previously,<sup>15</sup> its acid/base chemistry and electronic structure properties have not yet been analysed and discussed. Thus, **3** is additionally included for comparative studies.

The catecholato diimine platinum(II) complexes **6** and **7** were prepared by coordination of the diimine ligand  $L^3$  or  $L^4$  to Pt(nbe)<sub>3</sub> (nbe = norbonene). Subsequent oxidative addition of the  $C_{2v}$ -symmetrical 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-dbq) gave the symmetrical green complexes **6** and **7** similar to a reported

Empirical formula	$C_{15}H_{10}ClN_2O_4Re$	$C_{19}H_{16}ClN_2O_5Re$	$C_{30}H_{36}N_2O_4Pt$
$M_{\rm r}$	503.90	573.99	683.70
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\overline{1}$	C2/c
a/Å	12.4274(8)	7.08950(10)	23.3474(5)
b/Å	9.1175(6)	11.2851(2)	9.2838(2)
c/Å	14.0330(9)	12.3164(2)	26.4446(5)
$\alpha$ (°)	90.00	97.4140(10)	90.00
β(°)	100.057(4)	97.2240(10)	107.1440(10)
$\gamma$ (°)	90.00	94.2410(10)	90.00
$V/Å^3$	1565.60(18)	965.31(3)	5477.2(2)
Ζ	4	2	8
$\rho_{\rm c}/{\rm g~cm^{-3}}$	2.138	1.975	1.658
F(000)	952	552	2720
$\mu(Mo-K_{\alpha})/mm^{-1}$	7.952	6.466	5.161
Index ranges	$-15 \le h \le 15$	$-9 \le h \le 9$	$-30 \le h \le 30$
-	$-11 \le k \le 11$	$-14 \le k \le 14$	$-12 \le k \le 12$
	$-17 \le l \le 17$	$-16 \le l \le 16$	$-34 \le l \le 34$
$\operatorname{GOF}(F^2)$	1.044	1.057	0.946
$R_{1},^{a} w R_{2}^{b}$	0.0236, 0.0664	0.0150, 0.0346	0.0206, 0.0441
$(I > 2\sigma(I))$			
$R_1$ , <sup><i>a</i></sup> $wR_2^{b}$ (all data)	0.0253, 0.0675	0.0166, 0.0351	0.0288, 0.0458
${}^{a}R_{1} = \Sigma   F_{o}  -$	$ F_{\rm c}  /\Sigma F_{\rm o} .^{b} wR_{2} =$	$[\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w]$	$(F_{o}^{2})]^{1/2}.$

4

7

1

procedure using L<sup>1</sup> as ligand giving unsymmetrical **5** (Scheme 2).<sup>10</sup> The acid/base chemistry of **5** has been reported previously by us<sup>10</sup> and the results are also included here for comparison.

The new complexes were characterised by IR and NMR spectroscopy, mass spectrometry and elemental analysis. All complexes feature in their <sup>1</sup>H NMR spectra sharp singlet resonances in the range of  $\delta = 8.58$ –9.24 ppm for the imine proton H<sup>7</sup> of the coordinated dimine ligands. The resonances of the OH protons of **1**, **3** and **6** are observed around 10 ppm. Compared with the respective uncoordinated ligands L<sup>1</sup>/L<sup>2</sup> the proton resonances of the pyridyl rings (H<sup>9</sup>–H<sup>12</sup>) of **1** and **2** are shifted to higher frequency due to coordination of the metal. The proton resonances of the coordinated dioxolene ligand in **6** and **7** appear at expected positions and with correct intensities [ $\delta = 6.15$  (2H), 1.29 (18H) ppm].<sup>10</sup> Mass spectra and elemental analyses confirm the proposed compositions of the new complexes **1**, **2**, **4**, **6** and **7**.

### Crystal structure descriptions

The molecular structures of 1, 4, and 7 in the crystal were determined by single crystal X-ray diffraction. Crystallographic and data collection parameters are given in Table 1, selected bond lengths and angles are listed in Table 2.

Orange red coloured crystals of the phenol-substituted rhenium(1) complex 1 were obtained by slow diffusion of diethyl ether into a solution of the trimethyl silyl-protected complex 2 in  $CH_2Cl_2$  under a non-inert atmosphere. Under these conditions the trimethyl silylether is slowly hydrolysed to the hydroxyl group.

The rhenium(I) atom of complex 1 adopts a distorted octahedral coordination geometry with three carbonyl ligands occupying *facial* positions (Fig. 1). A five-membered ring is formed by the bidentate diimine ligand and the rhenium centre. The N1–Re1–N2 angle amounts to  $74.62(10)^\circ$  similar to other previously

**Table 2** Selected experimental and calculated bond lengths/Å and angles/° for 1, 4, and 7 together with DFT calculated metrical data for 1, 4, 7 and anions  $1^-$ ,  $3^-$  and  $6^-$ 

	X-ray 1	DFT 1	DFT 1-
Re1-N1	2,182(3)	2 213	2.285
Re1_N2	2.102(3) 2.172(3)	2.213	2 202
Re1_C11	2.172(3) 2 4887(10)	2.212	2.202
Rel-Cl	1.962(5)	1 922	1 915
Re1_C2	1.932(4)	1.932	1.915
Re1-C3	1.932(4)	1.928	1 911
N1-C10	1.917(3) 1.438(4)	1.926	1 375
C13-O4	1.362(5)	1.362	1 248
$N1_Re1_N2$	74.62(10)	74.3	75.2
C9-N1-C10-C15	-50 2(6)	50.7	22.9
	50.2(0)	50.7	
	X-ray 4	DFT 4	DFT 3 <sup>-</sup>
Re1–N1	2.1689(18)	2.200	2.302
Re1–N2	2.1911(18)	2.202	2.204
Re1–Cl1	2.4785(5)	2.519	2.537
Re1–C1	1.906(2)	1.923	1.913
Re1–C2	1.919(2)	1.936	1.929
Re1–C3	1.929(2)	1.936	1.914
N1-C13	1.437(3)	1.422	1.365
N2-C4	1.434(3)	1.419	1.413
C16–O5	1.367(3)	1.358	1.246
C7–O4	1.365(3)	1.358	1.375
N1–Re1–N2	74.35(7)	74.4	75.3
C12-N1-C13-C18	49.1(5)	49.2	19.6
C11-N2-C4-C9	37.1(4)	44.1	46.0
	X-ray 7	DFT 7	DFT 6-
Pt1-N1	1.992(2)	2.025	2.095
Pt1–N2	1.990(2)	2.023	2.046
Pt1–O1	1.9748(17)	1.997	2.025
Pt1–O2	1.9741(16)	1.996	2.008
O1C1	1.359(3)	1.343	1.353
O2–C6	1.359(3)	1.343	1.351
C1–C2	1.415(3)	1.420	1.415
C2–C3	1.396(3)	1.393	1.401
C3–C4	1.399(4)	1.405	1.346
C4–C5	1.390(3)	1.393	1.401
C5–C6	1.415(3)	1.420	1.416
C6-C1	1.409(3)	1.422	1.417
N1-C19	1.427(3)	1.416	1.411
N2-C24	1.428(3)	1.417	1.368
C27–O3	1.369(3)	1.360	1.247
C16-O4	1.371(3)	1.361	1.375
N1-Pt1-N2	78.80(9)	79.1	79.8
O1-P1-O2	82.07(7)	80.7	80.9
C22-N1-C19-C20	40.5(7)	-41.3	-16.2
C23-N2-C24-C25	-37.7(2)	-42.6	-48.9

reported metal complexes with this ligand.<sup>22–25</sup> As expected the five-membered chelate ring is almost coplanar with the pyridine ring, while a torsional angle C9–N1–C10–C15  $\alpha = -50.2(6)^{\circ}$  is formed with the phenol substituent (Fig. 1).

As shown in Fig. 2 and Table S1<sup>†</sup> close intermolecular hydrogen contacts are formed between the hydroxy group O4–H4A as hydrogen atom donor and the coordinated chloride Cl1 of an adjacent molecule as hydrogen atom acceptor (O4–H4A… Cl1  $102^{\circ}$ ; O4… Cl1 3.129(3) Å). These hydrogen contacts connect the molecules along the crystallographic *b* axis to give rise to infinite one-dimensional chains. The same basic motif has been previously observed in allyl chloro dicarbonyl molybdenum(II) complexes of ligand L<sup>1</sup>.<sup>24b</sup> These OH… Cl linked chains are



Fig. 1 ORTEP view of 1 and atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

further supported by OH  $\cdots$  OC contacts (O4–H4A  $\cdots$  O2=C2; O4–H4A  $\cdots$  O2 142°; O4 $\cdots$  O2, 3.240(5) Å) giving bifurcated hydrogen contacts from H4A to Cl1 and to O2 (Fig. 2). Further contacts from CH groups of the diimine ligand to equatorial carbonyl groups of neighbouring molecules (C5–H5A  $\cdots$  O2=C2 and C9–H9A  $\cdots$  O3=C3) further cross-link the chains. Together with the bifurcated OH  $\cdots$  Cl/O hydrogen contact a threedimensional architecture is generated (Fig. 2, Fig. 3).



Fig. 2 Crystal packing of complex 1; view onto the *ab* plane;  $O-H \cdots X$  hydrogen contacts are indicated by dashed lines.

The molecular structure of **4** is basically similar to that of **1** (Fig. 4). The N1–Re1–N2 angle amounts to 74.35(7)° and the torsion angles C12–N1–C13–C18 and C11–N2–C4–C9 between the five-membered chelate ring and the two phenol substituents are  $\alpha = 49.1(5)^{\circ}$  and 37.1(4)°, respectively. Complex **4** features intermolecular C–H···X contacts to the chloro ligand and to the equatorial carbonyl ligands in the crystal (C12–H12A···Cl1, C18–H18A···O2=C2, C10–H10A···O3=C3). Again, a three-dimensional network is formed (Fig. S1 and Table S1, Supporting Information†).

The central platinum(II) atom in complex 7 adopts a nearly square planar coordination geometry (Fig. 5). The N1–Pt1–N2 angle amounts to  $78.80(9)^{\circ}$  and the O1–Pt1–O2 angle to  $82.07(7)^{\circ}$  while the N1–Pt1–O1 and N2–Pt1–O2 angles are correspondingly larger with 99.2(4)° and 99.9(1)° resulting in an angular sum around the metal centre of  $360^{\circ}$ . The two *p*-anisyl substituents of the diimine ligand are tilted relative to the N–Pt–N-chelate



Fig. 3 Crystal packing diagram of complex 1; view onto the *ac*-plane.  $CH \cdots O$  contacts are indicated by dashed lines.



**Fig. 4** ORTEP view of complex **4** and atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

plane with torsional angles C22–N1–C19–C20 and C23–N2–C24– C25 of  $\alpha = 40.5(7)^{\circ}$  and  $-37.7(2)^{\circ}$ , respectively. The coordinated dioxolene ligand is well described as dianionic catecholate with balanced C–C bond lengths and C–O single bonds (Table 2 and Table S2, Supporting Information†).



**Fig. 5** ORTEP view of complex 7 and atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

#### Infrared studies

Hydrogen bonding in the solid state is conveniently probed by infrared spectroscopy. Undisturbed OH groups absorb above 3500 cm<sup>-1</sup> while strong OH···X hydrogen bonds are indicated by vibrational energies well below 3350 cm<sup>-1</sup>. The hydroxy substituted complexes **1**, **3** and **6** display signals due to OH stretching vibrations below 3500 cm<sup>-1</sup> which indicates some OH···X interaction in the solid state in all cases. For **1**  $v_{OH}$  = 3259 cm<sup>-1</sup> is observed confirming the strong OH····Cl/OH···O hydrogen bonds in the solid state (*vide supra*). For **3** weaker OH···X hydrogen bonds are indicated ( $v_{OH} = 3354 \text{ cm}^{-1}$ ) while for **6** only very weak OH···X contacts are observed ( $v_{OH} = 3421 \text{ cm}^{-1}$ ). Similar observations (OH···O<sub>carbonyl</sub> and OH···Cl hydrogen bonds) have been described previously with carbonyl molybdenum(0) and molybdenum(II) complexes of ligand L<sup>1</sup><sup>23,24</sup> as well as with water hydrogen-bonded to the OH group of PtCl<sub>2</sub>(L<sup>1</sup>) ( $v_{OH} = 3109 \text{ cm}^{-1}$ ).<sup>22</sup>

All tricarbonyl complexes 1–4 display three CO absorptions in their IR spectra as expected for fac-M(CO)<sub>3</sub> fragments lacking threefold symmetry (Experimental Section). In Mo<sup>II</sup>(allyl)(Cl)(CO)<sub>2</sub>(L<sup>1</sup>) complexes hydrogen bonds to the axial chloro ligand result in a bathochromic shift of the asymmetrical *cis*-Mo(CO)<sub>2</sub> stretching vibration of  $\Delta v_{\rm CO} \sim 10$  cm<sup>-1</sup> (solution  $\rightarrow$  solid).<sup>24</sup> Similarly, in the chloro rhenium(I) complex 1 the hydrogen bond to the axial chloro ligand shifts the " $A_1$ " fac-Re(CO)<sub>3</sub> stretching vibration by  $\Delta v_{\rm CO} = 16$  cm<sup>-1</sup> to lower energy (solution  $\rightarrow$  solid).

## **Electrochemical properties**

The redox properties of complexes 1–7 were studied in  $CH_2Cl_2$  by cyclic voltammetry (CV) and square wave voltammetry (SWV). Unfortunately, due to the very poor solubility of complexes 3 and 6 (and also of  $5^{10}$ ) no interpretable redox waves could be observed.

For 1, 2 and 4 an irreversible Re<sup>1</sup>/Re<sup>II</sup> oxidation is observed in the cyclic voltammograms at  $E_{ox} = 0.97, 0.99, 1.01$  V, respectively, in a typical range for complexes of this type.<sup>26,27</sup> The catecholato platinum(II) complex 7 displays a reversible redox couple at  $E_{1/2} = 0.26$  V. This redox process is ascribed to the oxidation of the catecholato moiety 3,6-dbcat to the respective coordinated semiquinone 3,6-dbsq (Fig. 6).<sup>10,28</sup>



Fig. 6 Square wave voltammogram (top) and cyclic voltammogram (bottom) of 7 ( $5 \times 10^{-4}$  M) in CH<sub>2</sub>Cl<sub>2</sub> (*E vs.* Ag/Ag<sup>+</sup>).

To substantiate the assumption of ligand centered oxidations 6 and 7 were treated with silver(1) triflate (AgOTf) as oxidant in THF. The resulting red-brown species  $6^{++}$  and  $7^{++}$  have a reasonable lifetime at room temperature which enables to characterise the radical cations  $6^{++}$  and  $7^{++}$  by EPR spectroscopy (Fig. 7, Fig. S10, Supporting Information<sup>†</sup>). Isotropic EPR spectra are obtained



**Fig.** 7 Experimental (bottom) and simulated (top) EPR spectra of 7<sup>++</sup> (10<sup>-3</sup> M) in a mixture of THF–CH<sub>3</sub>CN (v/v, 9/1) at room temperature, 9.421862 GHz, g = 1.9975,  $A_{iso}$ (<sup>195</sup>Pt) = 24 G,  $A_{iso}$ (2×<sup>1</sup>H) = 3.7 G.

showing signals with *g*-values around 2.0 and superhyperfine coupling to two protons with  $A_{iso}(2\times^{1}\text{H}) = 3.3$ , 3.7 G (6<sup>•+</sup>, 7<sup>•+</sup>). Platinum satellite subspectra (<sup>195</sup>Pt;  $I = \frac{1}{2}$ ; 33.8%) with  $A_{iso}(^{195}\text{Pt}) = 23$ , 24 G (6<sup>•+</sup>, 7<sup>•+</sup>) indicate that the unpaired electron is largely localised on the semiquinonato ligand and only delocalised onto the platinum diimine moiety to a minor extend. This is similar to the electron spin distribution in the previously reported radical 5<sup>•+</sup>.<sup>10</sup>

## **Optical properties**

The diimine rhenium complexes 1 and 2 display a complex structured absorption band around 370–380 nm in THF (Fig. S2–S3, Supporting Information†). For complexes 3 and 4 this band is found bathochromically shifted around 440 nm (Fig. S4–S5, Supporting Information†). These bands can be deconvoluted to (at least) three bands [328, 370, 424, 430 nm (1); 338, 368, 412 nm (2); 413, 435, 448 nm (3); 419, 442, 461 nm (4), Supporting Information†]. All these absorptions are tentatively attributed to  $d_{\pi}(\text{Re}) \rightarrow \pi^*(\text{diimine})$  and to  $\pi(\text{C}_6\text{H}_4\text{-OR}) \rightarrow \pi^*(\text{diimine})$  transitions.

For the catecholato platinum(II) complexes 6–7 intense absorption bands are found at the low and high energy side of the visible spectral region with maxima at 898, 639, 442 nm (6) and 898, 820 (sh), 650 (sh), 439 nm (7) (Fig. 8, Fig. S6, Supporting Information). The solvatochromic low-energy bands [898 nm (THF), 892 nm (CH<sub>2</sub>Cl<sub>2</sub>), 802 nm (CH<sub>3</sub>CN) (7), Fig. 8] are assigned to  $\pi$ (3,6-dbcat)  $\rightarrow \pi^*$ (dimine) LLCT absorptions<sup>10</sup> while the 440 nm band might arise from d<sub>\pi</sub>(Pt)  $\rightarrow \pi^*$ (dimine) and  $\pi$ (C<sub>6</sub>H<sub>4</sub>–OR)  $\rightarrow \pi^*$ (dimine) transitions, in analogy to the Re(I) complexes 1–4. These data



Fig. 8 UV/Vis/NIR absorption spectra of 7 in  $CH_3CN$ ,  $CH_2Cl_2$  and THF.

are fully compatible with those reported for the unsymmetrical platinum complex **5**.<sup>10</sup>

Deprotonation of 1 with  $P_1$ - $tBu^{29}$  ( $P_1$ -tBu = tert-butyliminotris(dimethylamino)phosphorane) results in the decline of the band at 377 nm and in the appearance of a new band at 589 nm  $(\varepsilon = 8900 \text{ M}^{-1} \text{ cm}^{-1})$  responsible for the pale blue colour (Fig. 9; cuvette c). Two isosbestic points at 328 and 454 nm indicate a simple equilibrium between complex 1 and its conjugate base 1<sup>-</sup>. Addition of acetic acid practically reverses the optical changes indicating a reversible behaviour. Only the original 377 nm band is now observed at lower energy (419 nm; Fig. S7, Supporting Information<sup>†</sup>) possibly due to the now different salt concentration, polarity and availability of hydrogen donors (cf. Fig. 2; hydrogen contacts to Cl and CO ligands). In fact, addition of a premixed equimolar mixture of  $P_1$ -*t*Bu/HCl corresponding to the salt  $[P_1$ tBu-H]Cl) to a solution of 1 results in a similar bathochromic shift (Fig. S11, Supporting Information<sup>†</sup>). Furthermore, the FD mass spectrum of 1 after the deprotonation/reprotonation sequence reveals a  $[1+H]^+$  peak at m/z = 505 instead of the original  $[1]^+$ peak at m/z = 504 (Fig. S12, Supporting Information<sup>†</sup>). This proves the stability of 1 and 1<sup>-</sup> and additionally suggests hydrogen bonding interactions with acidic reagents. The new absorption band of 1<sup>-</sup> at 589 nm might arise from an intraligand  $\pi$ - $\pi$ \* charge transfer from the phenolate moiety to the tricarbonyl-rhenium(I) coordinated diimine unit. Deprotonation of L<sup>1</sup> coordinated to an electron-rich dichloro platinum(II) fragment  $PtCl_2(L^1)$  has resulted only in unremarkable changes in the optical spectra.<sup>22</sup> It is thus tempting to assume that the intraligand CT only occurs if an electron-accepting ML<sub>n</sub> fragment is coordinated to deprotonated  $L^1$ . The electron accepting power of  $Re(CO)_3$  is seen by changes of the CO stretching vibrations of 1 upon deprotonation of the



**Fig. 9** UV/Vis/NIR absorption spectra of **1** in THF upon addition of phosphazene base  $P_{1}$ -*t*-Bu (top); titration plot observed at 589 nm and solution of **1** in THF (4 × 10<sup>-5</sup> M) upon addition of  $P_{1}$ -*t*-Bu (a $\rightarrow$ c) and re-acidification with acetic acid (c $\rightarrow$ d $\rightarrow$ e) (bottom).

remote OH group to give  $1^-$ . Especially the totally symmetric " $A_1$ " stretch is bathochromically shifted from 2041 cm<sup>-1</sup> to 2019 cm<sup>-1</sup> in THF indicating stronger  $\pi$ -backbonding of rhenium(I) to the CO ligands.

More dramatically, orange yellow coloured 3 is deprotonated to the turquoise anion  $3^-$  (Fig. 10; cuvette b). The 436 band decreases in intensity and an intense "blue band" at 673 nm ( $\varepsilon$  = 32730 M<sup>-1</sup> cm<sup>-1</sup>) appears. The latter band is much more intense than the corresponding band of  $1^-$  and accordingly the visible colour change from 3 to  $3^{-}$  is much more pronounced (Fig. 10; cuvettes a and b). Isosbestic points for the  $3/3^-$  pair occur at 346 and 528 nm. No further changes are observed upon addition of a second equivalent of base. Thus, the doubly charged  $3^{2-}$  is not accessible under these conditions. Re-protonation of  $3^-$  with acetic acid qualitatively restores the original electronic spectrum. However, the original 436 nm band is now found at 489 nm due to the now different salt concentration, polarity and presence of hydrogen donors analogous to the  $1/1^-$  case (Fig. S8, Supporting Information<sup>†</sup>) resulting in a red solution (Fig. 10; cuvette d). Similar to the  $1/1^-$  acid/base pair the IR band for the symmetric "A<sub>1</sub>" CO stretching vibration of **3** is shifted from 2022 cm<sup>-1</sup> to 2013 cm<sup>-1</sup> in THF upon deprotonation to 3<sup>-</sup>.



**Fig. 10** UV/Vis/NIR absorption spectra of **3** in THF upon addition of phosphazene base  $P_{1}$ -*t*-Bu (top); titration plot observed at 673 nm and solution of **1** in THF (4 × 10<sup>-5</sup> M) upon addition of  $P_{1}$ -*t*-Bu (a $\rightarrow$ b) and re-acidification with acetic acid (b $\rightarrow$ c $\rightarrow$ d) (bottom).

The absorption spectra of the  $Pt(3,6-dbcat)(L^3)$  complex **6** upon titration with  $P_1$ -*t*-Bu are depicted in Fig. 11. The solution remains dark green so no changes are observed with the naked eye. However, the electronic spectra reveal significant changes with an increasing 639 nm band (final maximum at 659 nm). This observation is in qualitative agreement with the results previously obtained for the  $5/5^-$  pair showing a decrease of a 733 nm (5) and a development of a 570 nm band ( $5^-$ ).<sup>10</sup> Beginning precipitation



Fig. 11 UV/Vis/NIR absorption spectra of 6 in THF upon addition of phosphazene base  $P_1$ -*t*-Bu (top); titration plot observed at 639 nm (bottom).

of charged  $6^-$  results in less well-defined isosbestic points and hampers clean generation of doubly deprotonated  $6^{2^-}$ .

The rhenium complexes 1–4 are practically non-emissive at room temperature in fluid solution. In a frozen THF matrix (77 K) weak emission bands with vibrational fine structure are observed for the *O*-protected complexes 2 and 4 (Fig. 12, Fig. S9, Supporting Information†) while the OH-substituted complexes 1 and 3 are non-luminescent even at 77 K. Probably the OH oscillator and hydrogen bonding interactions (*vide supra*) provide radiationless deactivation pathways. The weak emissions of 2 and 4 (437 nm,  $\Phi_{\rm em} \ll 10^{-3}$ ) are attributed to ligand based <sup>1</sup>( $\pi$ – $\pi^*$ ) emissions, following assignments of ReCl(CO)<sub>3</sub> complexes of analogous 1-pyridylimidazo[1,5-*a*]pyridine ligands (428–456 nm, respectively).<sup>30</sup>



Fig. 12 Emission spectrum of 2 (THF matrix, 77 K,  $\lambda_{exc} = 388$  nm,  $10^{-7}$  M).

The platinum(II) complexes 5–7 are also non-luminescent both at room temperature and at 77 K. For the anion 5<sup>-</sup> a roomtemperature emission at 512 nm (CH<sub>2</sub>Cl<sub>2</sub>) has been reported.<sup>10</sup> This emission has been assigned to a  ${}^{3}(\pi-\pi^{*})$  state. This emissive state is not completely depopulated by radiationless deactivation through the phenolate torsion around the C–N bond as the deprotonation has restricted this intramolecular rotation. However, for anion 6<sup>-</sup>, with the monodeprotonated ligand L<sup>3</sup> coordinated to platinum, no emission is observed at room temperature. This could be due to the presence of an OH oscillator or the unrestricted torsional motion of the remaining phenol moiety. In order to get a deeper understanding of these spectroscopic observations DFT calculations have been performed on 1–7, the cations 6<sup>++</sup> and 7<sup>++</sup> and the anions 1<sup>-</sup>, 3<sup>-</sup> and 6<sup>-</sup>.

#### **Computational studies**

The geometries of all complexes mentioned were optimised using DFT methods (B3LYP functional; 6-31G\* basis set for C, H, N, O, and Cl atoms; effective core potentials (LANL2DZ) for Re and Pt atoms; gas phase).

The DFT optimised bond lengths and angles of 1, 4 and 7 agree sufficiently well with the experimentally observed ones (Table 2). Even the absolute values of the torsional angles  $|\alpha|$  with a rather shallow energy potential are reproduced reasonably well. The practically non-alternating calculated C–C bond lengths of the catecholato ligand in 7 are also in good agreement with the experiment.

The CO stretching vibrations of **2** and **4** are calculated (scaled by  $0.9614^{31}$ ) and compared with the experimental ones in solution (absence of hydrogen bonding). The symmetric " $A_1$ " stretching mode is reproduced very well [**2**/**4**: calcd 2025/2029 cm<sup>-1</sup>; exp. 2026/2036 cm<sup>-1</sup>]. The two vibrations involving mainly the equatorial CO ligands are calculated at slightly higher energy by some 30 cm<sup>-1</sup> [**2**/**4**: calcd 1956,1934/1966,1937 cm<sup>-1</sup>; exp. 1926,1903/1929,1903 cm<sup>-1</sup>] but are still in reasonably good agreement with the experiment. Deprotonation of **1** to **1**<sup>-</sup> and of **3** to **3**<sup>-</sup> results in a calculated, scaled shift of the CO stretching vibrations from 2025, 1958, 1935 to 2006, 1927, 1909 cm<sup>-1</sup> (**1**/**1**<sup>-</sup>) and from 2030, 1967, 1939 to 2005, 1928, 1910 cm<sup>-1</sup> (**3**/**3**<sup>-</sup>), respectively, in accordance with the experimentally observed trend (*vide supra*). Thus, the calculations sufficiently reproduce the experimental geometries and vibrational frequencies.

UV/Vis/NIR spectra of 1-4 were calculated using timedependent density functional theory (TD-DFT). Exemplarily, the calculated electronic absorption spectrum of 1 and the dominantly involved orbitals (#86, #87  $\rightarrow$  #90) are depicted in Fig. 13 (for spectra of 2-4 see Supporting Information, Table S3). The structured absorption band at 377/371 nm (1/2) and 440 nm (3/4) is composed of several transitions with significant oscillator strength (details are summarised in the Supporting Information, Table S3). The centres of the bands (with Lorentzian line broadening, FWHM 100 cm<sup>-1</sup>) are estimated at 406 nm (f =0.25), 422 nm (f = 0.27), 459 nm (f = 0.40) and 469 nm (f = 0.40) 0.43) for 1-4 in reasonable agreement with the corresponding experimental values of 377 nm ( $\varepsilon = 7860 \text{ M}^{-1} \text{ cm}^{-1}$ ), 371 nm ( $\varepsilon =$ 12590 M<sup>-1</sup> cm<sup>-1</sup>), 436 nm ( $\varepsilon = 12760$  M<sup>-1</sup> cm<sup>-1</sup>) and 442 nm ( $\varepsilon =$ 17530  $M^{-1}$  cm<sup>-1</sup>). The calculated most intense transitions for 1 and 2 correspond to HOMO–2/HOMO–3  $\rightarrow$  LUMO electron



Fig. 13 Experimental (top) and calculated (bottom) optical spectrum of 1 and relevant molecular orbitals involved in the most intense transition (417 nm, f = 0.1712) (contour value 0.06 a.u.).

excitations. The involved occupied orbitals are composed of the  $\pm$  combination of phenol- $\pi$  and Re(CO<sub>eq</sub>)<sub>2</sub> ( $d_{xy}$ ) contributions while the LUMO possesses largely pyridine/diimine  $\pi^*$  character. Basically the same holds for complexes **3** and **4**. Thus, these absorptions are correctly attributed to mixed  $\pi$ (Re-d<sub>xy</sub>/CO)  $\rightarrow \pi^*$ (diimine) and  $\pi$ (C<sub>6</sub>H<sub>4</sub>–OR)  $\rightarrow \pi^*$ (diimine) transitions.

The two most intense absorptions of the catecholato platinum(II) complexes at around 640 and 890 nm are reasonably well reproduced by the TD-DFT calculations. Exemplarily, the calculated UV/Vis/NIR absorption spectrum of 6 is shown in Fig. 14 together with the experimental one. The two main absorptions are assigned to quite pure  $\pi(C_6H_4-OR) \rightarrow \pi^*(\text{diimine})$ and  $\pi$ (catecholato)  $\rightarrow \pi^*$ (diimine) transitions, respectively.<sup>10</sup> The transition calculated at 511 nm is mainly due to the  $\pi$ (C<sub>6</sub>H<sub>4</sub>–OR,  $\#130) \rightarrow \pi^*$ (diimine, #133) electronic excitation and the 809 nm band is due to the dbcat-HOMO (#132)  $\rightarrow \pi^*$ (diimine, #133) excitation. The solvatochromic behaviour of these absorption bands has been probed experimentally with complex 7 (Fig. 8). Gratifyingly, the experimental trend for the low-energy band (802 nm, 892 nm, 898 nm in CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, THF) is reproduced by TD-DFT/IEFPCM calculations (815 nm, 829 nm, 830 nm; Table S3, Supporting Information<sup>†</sup>).

Oxidation of 5–7 with silver triflate leads to EPR active radical cations (*vide supra* and ref. 10 for 5<sup>++</sup>). In accordance with the EPR spectra and the calculated largely dbcat centered HOMOs of the catecholato complexes 5–7 the spin density of the radical cations  $5^{++}-7^{++}$  is calculated to reside essentially on the semiquinonato ligand with small contributions from the platinum centre and the diimine (see Fig. 15 for a spin density map of 7<sup>++</sup>). Thus, the spectroscopic properties of 1–7 and 5<sup>++</sup>–7<sup>++</sup> are well reproduced by the calculations.



**Fig. 14** Experimental (top) and calculated (bottom) optical spectrum of **6** and relevant orbitals involved in the most intense transitions (511 nm, f = 0.2159; 809 nm, f = 0.2216) (contour value 0.06 a.u.).



Fig. 15 Calculated spin density map of 7<sup>++</sup> (contour value 0.001 a.u.).

Deprotonating the hydroxy substituted complexes 1, 3, 5 and 6 results in anionic complexes  $1^-$ ,  $3^-$ ,  $5^{-10}$  and  $6^-$ . For anion  $5^$ the DFT calculations have predicted an iminoquinoid structure of the phenolate substituent (C=O 1.286; C=C 1.380; C-C 1.437/1.460; C=N 1.389 Å).<sup>10</sup> The phenolate substituent is oriented coplanar to the diimine moiety (torsion angle  $\alpha = 0^{\circ}$ ) and a substantial rotation barrier has been calculated for  $5^{-10}$ . The corresponding rhenium(I) complex 1- also shows iminoquinoid character for the substituent (C=C 1.366/1.368; C-C 1.459/1.463/1.434/1.429 Å; and Table 2). The phenolate torsion angle  $\alpha = 22.9^{\circ}$  is smaller than that calculated for the corresponding acid 1 ( $\alpha = 50.7^{\circ}$ ), but significantly distinct from zero. Due to the small bite angle of the dbcat chelate the O1-Pt1-O2 angles in the platinum complexes ( $\sim 80^{\circ}$ ) are smaller than the C2-Re1-C3 angles in the rhenium complexes (~90°). Obviously, steric interaction of the equatorial carbonyl ligand C2-O2 with the



CH group prevents full planarization of the ligand in the carbonyl

Scheme 3 Calculated metrical data of anions  $1^-$ ,  $3^-$ ,  $5^-$  and  $6^-$  relevant to planarisation.

The same arguments apply to the carbonyl rhenium complex  $3^{-}$  (Scheme 3). The anionic moiety displays some iminoquinoid character (C=C 1.363/1.365; C-C 1.465/1.460/1.440/1.433 Å; and Table 2), but is twisted relative to the diimine ( $\alpha = 19.6^{\circ}$ ). The phenol part of  $3^{-}$  remains essentially undisturbed ( $3/3^{-}$ :  $\alpha = 43.9/46.0^{\circ}$ ). Thus, the non-rigid diimine ligand (together with the presence of an OH oscillator in  $3^{-}$ ) might impede the observation of luminescence for  $1^{-}$  and  $3^{-}$  due to efficient deactivation pathways.

Similar to 3<sup>-</sup> the platinum complex 6<sup>-</sup> possesses a substituent with some iminoquinoid character (C=C 1.364/1.366; C-C 1.439/1.431/1.465/1.459 Å) and phenol/phenolate substituents with  $\alpha = -41.9/-16.2^{\circ}$ , respectively (Scheme 3). Thus, the nonplanarity, the non-rigidity and the presence of an OH oscillator in 6<sup>-</sup> could be responsible for the absence of emission.

Finally, the optical spectra of the anions  $1^-$ ,  $3^-$  and  $6^-$  were calculated using TD-DFT. For  $1^-$  a low-energy band is calculated at 539 nm which is essentially composed of electron excitations

from the three highest occupied molecular orbitals to the  $\pi^*$  LUMO and LUMO+1 of the chelate ligand. The highest occupied molecular orbitals are  $\pi$ -orbitals of the chelate ligand and the Re(CO)<sub>3</sub> fragment. A second high-intensity band is calculated at 441 nm also involving molecular orbitals of  $\pi$ -symmetry of the chelate and the ML<sub>n</sub> fragment (Table S3, Supporting Information†). The calculations are in qualitative agreement with the experiment (377/589 nm, Fig. 9). Analogous transitions are calculated for **3**<sup>-</sup> at 481 and 571 nm (exp. 449/673 nm, Fig. 10). For **6**<sup>-</sup> intense  $\pi$ - $\pi^*$  transitions are calculated at 506 and 859 nm (exp. 639/898 nm). Gratifyingly, the calculated absorption band positions do not change much for the **6**/**6**<sup>-</sup> pair, while the intensity of the former one increases from **6** to **6**<sup>-</sup> as found experimentally (Fig. 11; Table S3, Supporting Information†)).

Thus, the theoretical analyses coincide nicely with the experimental data and provide confidence for our interpretations.

## Conclusions

Tricarbonylrhenium(I) (1-4) and catecholato-platinum(II) complexes (6, 7) of diimine ligands bearing phenol and O-protected phenol substituents have been prepared and fully characterised including single crystal structure analyses of 1, 4 and 7. The catecholato platinum complexes 6 and 7 can be oxidised to the semiquinonato complexes  $6^{+}$  and  $7^{+}$  as shown by EPR spectroscopy and DFT calculations. The hydroxy substituted complexes 1, 3 and 6 feature intermolecular  $OH \cdots X$  hydrogen bonds/contacts in the solid state. Deprotonation of these complexes to  $1^-$ ,  $3^-$  and  $6^-$  results in significant changes in the optical spectra which are reproduced by TD-DFT calculations. The ligand moieties of the deprotonated complexes  $1^-$ ,  $3^-$  and  $6^-$  acquire some iminoquinoid character as found for  $5^-$  but are not fully coplanar to the imine unit (as found for  $5^{-}$ ) (Scheme 3). In the carbonyl rhenium complexes  $1^-$  and  $3^-$  steric hindrance prevents planarisation (Scheme 3; CH<sub>ortho</sub> ··· C<sub>carbonyl</sub> contacts; green). The slight bending of the dbcat relative to the diimine in the coordination plane (5<sup>-</sup>: N-Pt-O 93°/105°; 6<sup>-</sup>: N-Pt-O 97°/103°) seems to be hampered due to the presence of the other phenol substituent which inhibits full planarisation of  $6^-$  (Scheme 3).

As a planar rigid structure appears to be a premise for room temperature ligand triplet emission  $1^-$ ,  $3^-$  and  $6^-$  are nonluminescent due to the non-planar substituted diimine ligand. We are currently investigating sterically less demanding ML<sub>n</sub> fragments in combination with diimine ligands bearing only a single phenol/phenolate unit like L<sup>1</sup>. This could allow base-induced planarisation of the diimine ligands with phenol/phenolate substituents and could eventually support acid/base sensitive, *i.e.* switchable room temperature ligand based triplet emission similar to 5<sup>-</sup> and covalently permanently rigidified complexes (Scheme 1).

## Acknowledgements

Regine Jung-Pothmann is acknowledged for collection of the X-ray data.

# Notes and references

1 (a) H. Tsubaki, A. Sekine, Y. Ohashi, K. Koike, H. Takeda and O. Ishitani, J. Am. Chem. Soc., 2005, 127, 15544; (b) S. Y. Reece and D. G. Nocera, J. Am. Chem. Soc., 2005, 127, 9448 and references therein.

- 2 J. Zyss, Ed. Molecular Nonlinear OpticsAcademic Press Boston, MA, 1993.
- 3 (a) M. S. Wrighton and G. L. Geoffroy, Organometallic Photochemistry, Academic Press, New York, 1979; Chapter 2; (b) M. K. Nazeeruddin, C. Klein, P. Liska and M. Grätzel, Coord. Chem. Rev., 2005, 249, 1460; (c) A. S. Polo, M. K. Itokazu, K. M. Frin, A. O. de Toledo Patrocínio and N. Y. Murakami Iha, Coord. Chem. Rev., 2006, 250, 1669 and references therein.
- 4 (a) P. D. Beer, V. Timoshenko, M. Maestri, P. Passaniti and V. Balzani, *Chem. Commun.*, 1999, 1755; (b) A. J. Di Bilio, B. R. Crane, W. A. Wehbi, C. N. Kiser, M. M. Abu-Omar, R. M. Carlos, J. H. Richards, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 2001, **123**, 3181; (c) K. K. W. Lo, W. K. Hui, D. C. M. Ng and K. K. Cheung, *Inorg. Chem.*, 2002, **41**, 40; (d) S. S. Sun, A. J. Lees and P. Y. Zavalij, *Inorg. Chem.*, 2003, **42**, 3445; (e) T. Lazarides, T. A. Miller, J. C. Jeffery, T. K. Ronson, H. Adams and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2005, 528.
- 5 (a) D. B. MacQueen and K. S. Schanze, J. Am. Chem. Soc., 1991, 113, 6108; (b) D. I. Yoon, C. A. Berg-Brennan, H. Lu and J. T. Hupp, Inorg. Chem., 1992, 31, 3192; (c) Y. Shen and B. P. Sullivan, Inorg. Chem., 1995, 34, 6235; (d) J. D. Lewis, I. P. Clark and J. N. Moore, J. Phys. Chem. A, 2007, 111, 50; (e) K. K. W. Lo, K. H. K. Tsang and N. Zhu, Organometallics, 2006, 25, 3220.
- 6 (a) V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, Chem. Rev., 1996, 96, 759; (b) C. Lauterbach and J. Fabian, Eur. J. Inorg. Chem., 1999, 1995; (c) J. van Slageren, D. J. Stufkens, S. Záliš and A. Klein, J. Chem. Soc., Dalton Trans., 2002, 218; (d) W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger and R. Eisenberg, Coord. Chem. Rev., 1998, 171, 125; (e) M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings and R. Eisenberg, Coord. Chem. Rev., 2000, 208, 115.
- 7 (a) S. Huertas, M. Hissler, J. E. McGarrah, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2001, **40**, 1183; (b) S. D. Cummings and R. Eisenberg, *Inorg. Chem.*, 1995, **34**, 2007; (c) W. Paw and R. Einsenberg, *Inorg. Chem.*, 1997, **36**, 2287.
- 8 (a) C. G. Pierpont and A. S. Attia, *Collect. Czech. Chem. Commun.*, 2001, **66**, 33; (b) D. Herebian, E. Bothe, E. Bill, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 10012; (c) D. N. Hendrickson and C. G. Pierpont, *Top. Curr. Chem.*, 2004, **234**, 63; (d) K. M. C. Wong, W. P. Li, K. K. Cheung and V. W. W. Yam, *New J. Chem.*, 2005, **29**, 165.
- 9 (a) Y.-Y. Lin, S.-C. Chan, M. C. W. Chan, Y.-J. Hou, N. Zhu, C.-M. Che, Y. Liu and Y. Wang, *Chem.-Eur. J.*, 2003, **9**, 1263; (b) C.-M. Che, S.-C. Chan, H.-F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Commun.*, 2004, 1484; (c) C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu and H. Yersin, *Chem.-Eur. J.*, 2010, **16**, 233.
- 10 K. Heinze and S. Reinhardt, Chem.-Eur. J., 2008, 14, 9482.
- 11 S. Stoll, *Easyspin, Version 3.1.1*, University of California, Davis, USA, 2009; available at http://www.easyspin.org(a) S. Stoll and A. Schweiger, J. Magn. Reson., 2006, **178**, 42; (b) S. Stoll and R. D. Britt, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6614.
- 12 K. Heinze, Chem.-Eur. J., 2001, 7, 2922.
- 13 J. M. Kliegman and R. K. Barnes, J. Org. Chem., 1970, 35, 3140.
- 14 L. A. Paquette, G. J. Hefferon, R. Samodral and Y. Hanzawa, J. Org. Chem., 1983, 48, 1262.
- 15 S. H. Chan, L. S. M. Lam, C. W. Tse, K. Y. K. Man, W. T. Wong, A. B. Djurišić and W. K. Chan, *Macromolecules*, 2003, 36, 5482.
- 16 (a) L. E. Crascall and J. L. Spencer, *Inorg. Synth.*, 1990, 28, 126; (b) M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 271.

- 17 SAINT-Plus, Bruker Analytical X-ray System, Madison, WI, 1999.
- 18 (a) B. Blessing, Acta Crystallogr., Sect. A: Found. Crystallogr., 1995, 51, 33; (b) A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.
- 19 G. M. Sheldrick, SHELXTL-97, Universität of Göttingen, Göttingen, Germany, 1997.
- 20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, revision D.01, Gaussian, Inc. Wallingford, CT, 2004.
- 21 (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; (b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
- 22 S. Reinhardt and K. Heinze, Z. Anorg. Allg. Chem., 2006, 632, 1465.
- 23 (a) K. Heinze and J. D. B. Toro, *Eur. J. Inorg. Chem.*, 2004, 3498; (b) K. Heinze and V. Jacob, *J. Chem. Soc., Dalton Trans.*, 2002, 2379.
- 24 (a) K. Heinze, J. Chem. Soc., Dalton Trans., 2002, 540; (b) K. Heinze, V. Jacob and C. Feige, Eur. J. Inorg. Chem., 2004, 2053.
- 25 J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez and P. Gómez-Sal, *Organometallics*, 2006, 25, 3876.
- 26 (a) S. A. Moya, J. Guerrero, R. Pastene, R. Schmidt, R. Sariego, R. Sartori, J. Sanz-Aparicio, I. Fonseca and Martinez-Ripoll, *Inorg. Chem.*, 1994, 33, 2341; (b) B. J. Coe, N. R. M. Curati, E. C. Fitzgerald, S. J. Coles, P. N. Horton, M. E. Light and M. B. Hursthouse, *Organometallics*, 2007, 26, 2318; (c) R. Lin, Y. Fu, C. P. Brock and T. F. Guarr, *Inorg. Chem.*, 1992, 31, 4346.
- 27 (a) W. Liu, Y. Chen, X. H. Zhou, J. L. Zuo and X. Z. You, Organometallics, 2008, 27, 2990; (b) W. Liu, J. Xiong, Y. Wang, R. Wang, X. H. Zhou, J. L. Zuo and X. Z. You, Organometallics, 2009, 28, 755; (c) Z. Si, J. Li, B. Li, F. Zhao, S. Liu and W. Li, Inorg. Chem., 2007, 46, 6155.
- 28 (a) K. Heinze and S. Reinhardt, *Organometallics*, 2007, 26, 5406; (b) J. A. Weinstein, M. T. Tierney, E. S. Davies, K. Base, A. A. Robeiro and M. W. Grinstaff, *Inorg. Chem.*, 2006, 45, 4544; (c) N. M. Shavaleev, E. S. Davies, H. Adams, J. Best and J. A. Weinstein, *Inorg. Chem.*, 2008, 47, 1532.
- 29 (a) R. Schwesinger, Nachr. Chem. Technol. Lab., 1990, 38, 1212; (b) R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E. M. Peters, K. Peters and H. G. von Schnering, Angew. Chem., Int. Ed. Engl., 1993, 32, 1361.
- 30 (a) L. Salassa, C. Garino, A. Albertino, G. Volpi, C. Nervi, R. Gobetto and K. I. Hardcastle, *Organometallics*, 2008, **27**, 1427; (b) C. Garino, T. Ruiu, L. Salassa, A. Albertino, G. Volpi, C. Nervi, R. Gobetto and K. I. Hardcastle, *Eur. J. Inorg. Chem.*, 2008, 3587.
- 31 W. Koch and M. Holthausen, A Chemist's Guide to Density Functional Theory, Wiley-VCH Verlag GmbH, 2001.