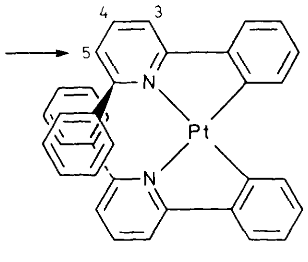
A New Type of 'Square Planar' Platinum(II) Complex showing Helical Chirality

Christine Deuschel-Cornioley,[a] Helen Stoeckli-Evans,[b] and Alex von Zelewsky*[a]

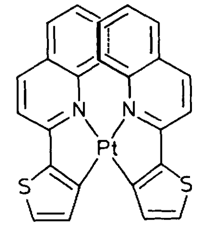
[a] *Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland*
[b] *Institute of Chemistry, University of Neuchâtel, Av. Bellevaux, CH-2000 Neuchâtel, Switzerland*

The *X*-ray structure of *cis*-bis(2,6-diphenylpyridinato-$N,C^{2'}$)platinum(II) shows the first example of helical chirality for a 'square planar' co-ordination compound with nonchiral ligands; ^{1}H NMR investigations indicate no racemization of the compound in solution on the NMR time scale.

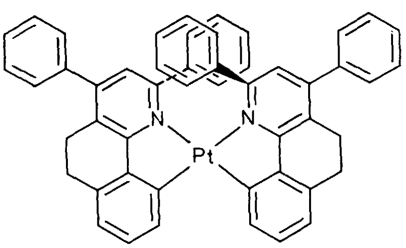
In the present paper we describe the molecular structure of the first 'square planar' co-ordination compound showing helical chirality. It is the bis-homoleptic cyclometallated platinum(II) complex (**1**).† In general, the chirality of 'square planar' complexes is due either to chiral ligands[1] or to specially chosen nonplanar ligands.[2] In our case, the chirality is a consequence



(**1**)



(**2**)



(**3**)

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† The synthesis is accomplished by reacting PtCl$_2$(SEt$_2$)$_2$ with the monolithiated ligand (prepared *in situ* from diphenylpyridine with LiBu in diethyl ether).

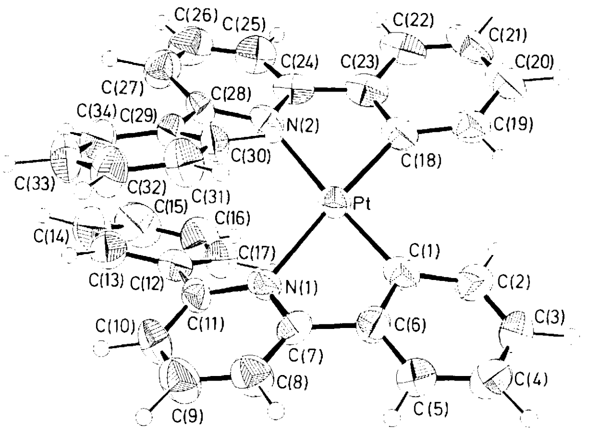

Figure 1. ORTEP[4d] plot of (**1**) showing the crystallographic atomic numbering scheme and the vibrational ellipsoids (50% probability level). Important bond distances (Å) and angles (°): Pt(1)–N(1) 2.152(8), Pt(1)–N(2) 2.163(7), Pt(1)–C(1) 2.009(10), Pt(1)–C(18) 1.965(10); N(1)–Pt(1)–N(2) 102.6(3), N(1)–Pt(1)–C(1) 78.5(4), N(2)–Pt(1)–C(18) 79.4(4), C(1)–Pt(1)–C(18) 100.0(4).

of ligand–ligand interactions causing a conformation of the ligands similar to that of the helicenes.[3] The *X*-ray structure‡ (Figure 1) shows clearly the deviations from planarity. Platinum and the ligand atoms form, however, an almost planar PtC_2N_2 moiety. The space group indicates the formation of racemic crystals. Experiments for separating the enantiomers by chromatographic methods are in progress.

^{1}H NMR investigations, using one enantiomer of 'Pirkle's reagent,' [2,2,2-trifluoro-1-(9-anthryl)ethanol],[5] show a doubling of several proton signals, particularly evident for H–C(5), indicating no racemization of the compound in solution on the NMR time scale (Figure 2). Two other complexes, (**2**) and (**3**), with the same structural characteristics have been prepared, showing the general tendency of these bis-cyclometallated complexes to form *cis*-compounds even in cases where very strong interligand steric interactions occur.

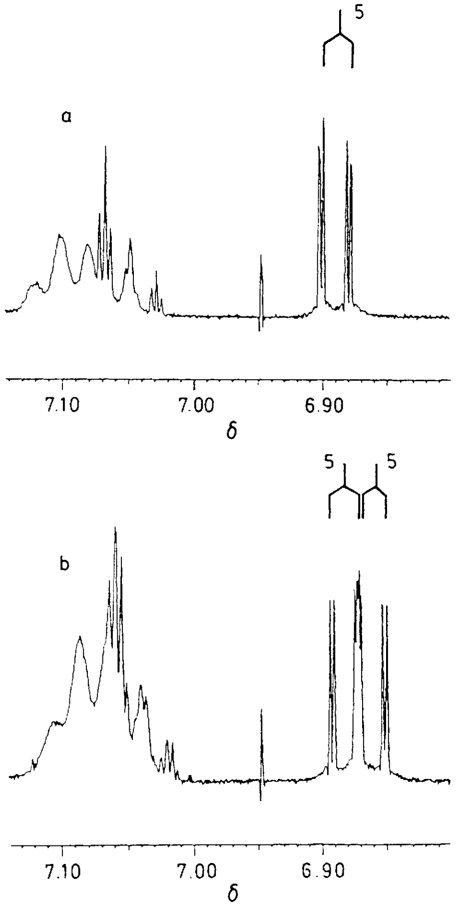

Figure 2. Part of the ^{1}H NMR spectra (360 MHz, $CDCl_3$) of (a) (**1**) and (b) (**1**) mixed with ten equivalents of 'Pirkle's reagent.' Peaks indicated by 5, corresponding to the signal of the H–C(5) protons in spectrum (a), are split in spectrum (b).

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‡ *Crystal data* for (**1**): $C_{34}H_{24}N_2Pt$, $M = 655.1$, orthorhombic, space group *Pbna*, $a = 9.272(2)$, $b = 17.581(3)$, $c = 30.779(4)$ Å, $U = 5017.3$ Å^3, $Z = 8$, $D_c = 1.739$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.71073$ Å), 3266 unique reflections measured with a STOE-SIEMENS AED2 four-circle diffractometer. Accurate cell parameters were obtained from $\pm\omega$ values of 20 reflections ($2 < 2\theta < 30°$) and their Friedel pairs. There was 1% intensity variation of 4 standard reflections measured every hour. A numerical absorption correction was applied to the data.[4a] The structure was solved using SHELXS-86,[4b] refinement and all further calculations were carried out using SHELXS-76.[4a] Final residuals of $R = 0.035$ and $R_w = 0.026$ for 2191 reflections with $F_o > 5\,\sigma(F_o)$. H-atoms were included in idealized positions as 'riding atoms,' with an overall refinable isotropic thermal parameter for each half of the molecule (final values 0.056 and 0.082 Å^2). Non-H atoms were refined anisotropically by weighted full-matrix least-squares. Complex neutral-atom scattering factors not included in ref. 4a were taken from ref. 4c. A final difference map revealed a small amount of residual density in the region of the Pt atom. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.