Cis–trans isomerism in a square-planar platinum(II) complex bearing bulky fluorinated phosphane ligands

Sylvain Bernès[a]*, Francisco J. Meléndez[b] and Hugo Torrens[c]

[a]Instituto de Física, Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico

[b]Laboratorio de Química Teórica, Facultad de Ciencias Químicas, Universidad Autónoma de Puebla, Edif. 105-I, Ciudad Universitaria, 72570 Puebla, Pue., Mexico

[c]Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 México D.F., Mexico

SUPPORTING INFORMATION

1- Experimental

All experiments were carried out under dry oxygen-free dinitrogen atmospheres using Schlenk techniques. Solvents were dried and degassed using standard techniques.[1] Thin layer chromatography (TLC) (Merck, 5×7.5 cm^2 Kiesegel 60 F_{254}) was used to monitor the progress of the reactions under study.

^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Varian Unity 300 spectrometer operating at 299.79 MHz ^1H, 282.15 MHz ^{19}F and 121.35 ^{31}P MHz respectively. Chemical shifts are relative to TMS $\delta = 0$ (^1H), external $CFCl_3$ $\delta = 0$ (^{19}F) and external phosphoric acid $\delta = 0$ (^{31}P). A standard variable-temperature unit was used to control the probe and it was checked periodically by thermocouple to ensure temperature readings were within ±1°C. Complexes were studied in C_3D_6O and $C_6D_5CD_3$.

FAB^+ spectra were recorded on a JEOL JMS SX102-A mass spectrometer operated at an accelerating voltage of 10 KV. Samples were desorbed from 3-nitrobenzyl alcohol

matrix using 3 KeV xenon atoms. Mass measurements in FAB are performed at 3000 resolution using magnetic field scans and the matrix ions as the reference material, or electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions.

Simulations were carried out with gNMR.[2] *Trans*-[$PtCl_2(P(C_6H_5)_2(C_6F_5))_2$] and $Pb(SC_6HF_4\text{-}4)_2$ were prepared according to the literature methods.[3, 4]

***trans*-[$PtCl_2(P(C_6H_5)_2(C_6F_5))_2$] + $Pb(SC_6HF_4\text{-}4)_2$.** *trans*-[$PtCl_2(P(C_6H_5)_2(C_6F_5))_2$] (390 mg, 0.4 mmol) dissolved in 25 ml of acetone and $Pb(SC_6HF_4\text{-}4)_2$ (228 mg, 0.4 mmol) dissolved in 25 ml of acetone were mixed and kept at room temperature with magnetic stirring for 1 hr. After this period, the white solid of $PbCl_2$ formed is filtered off and the yellow solution chromatographed through a column using silica gel as the stationary phase and diluted with a mixture of acetone-chloroform (30:70) to obtain four fractions: 1) yellow fraction with compounds **1** and **2** (145 mg, 29% yield); 2) yellow fraction containing compounds **3** and **4** (85 mg, 12% yield); 3) yellow fraction containing compound **5** (99 mg, 23% yield); 4) colourless fraction with the free phosphine $P(C_6H_5)_2(C_6F_5)$ (72 mg). Fractional crystallisation of each portion by slow evaporation of the solvent under a current of dry N_2 renders crystals of compounds **1** to **5**. Formulas for complexes **1**-**5** are depicted in the scheme of the *Acta C* article.

***trans*-[$Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2$] 1**. ^{1}H NMR, acetone-D_6, 300 K, ppm: δ = 7.80, m, C_6H_5; δ = 7.6, m, C_6H_5; δ = 7.24, m, $H_{SR\text{-}p}$. $^{19}F\{^1H\}$ NMR, acetone-D_6, 300 K, ppm: δ = -135.03, m, $F_{SR\text{-}o}$; δ = -142.14, m, $F_{SR\text{-}m}$; δ = -123.05, m, $F_{phos\text{-}o}$; δ = -161.80, m, $F_{phos\text{-}m}$; δ = -151.20, m, $F_{phos\text{-}p}$. ^{31}P NMR, acetone-D_6, 300 K, ppm: δ = 7.65, s + d, $^1J_{Pt\text{-}P}$ = 3000 Hz. Mass spectra (FAB^+-MS): *m/z* = 1261, $[Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]^+$. Anal. Calcd. for $C_{48}H_{22}F_{18}P_2PtS_2$: C 45.69%, H 1.76%, S 5.08%. Found: C 45.6%, H 1.7%, S 5.1%.

***cis*-[$Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2$] 2**. ^{1}H NMR, acetone-D_6, 300 K, ppm: δ = 7.9, m, C_6H_5; δ = 7.65, m, C_6H_5; δ = 7.12, m, $H_{SR\text{-}p}$. $^{19}F\{^1H\}$ NMR, acetone-D_6, 300 K, ppm: δ = -134.9, m, $F_{SR\text{-}o}$; δ = -144.7, m, $F_{SR\text{-}m}$; δ = -128.12, m, $F_{phos\text{-}o}$; δ = -159.83, m, $F_{phos\text{-}m}$; δ = -150.21, m,

$F_{phos\text{-}p}$. ^{31}P NMR, acetone-D_6, 300 K, ppm: δ = 8.48, s + d, $^1J_{Pt\text{-}P}$ = 2896 Hz. Mass spectra (FAB^+-MS): *m/z* = 1261, $[Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]^+$. Anal. Calcd. for $C_{48}H_{22}F_{18}P_2PtS_2$: C 45.69%, H 1.76%, S 5.08%. Found: C 45.5%, H 1.6%, S 5.0%.

***cis*-[Pt$_2$(μ-SC$_6$HF$_4$-4)$_2$(SC$_6$HF$_4$-4)$_2$(PPh$_2$(C$_6$F$_5$))$_2$] 3**. ^1H NMR, acetone-D_6, 300 K, ppm: δ = 7.97, m, C_6H_5; δ = 7.61, m, C_6H_5; δ = 7.10, m, $H_{SR\text{-}p}$; δ = 7.12, br m, $H_{\mu\text{-}SR\text{-}p}$. $^{19}F\{-^1H\}$ NMR, acetone-D_6, 300 K, ppm: δ = -130.37, m, $F_{SR\text{-}o}$; δ = -137.20, m, $F_{SR\text{-}m}$; δ = -126.79, m, $F_{\mu\text{-}SR\text{-}o}$ *trans* to P; δ = -135.41, m, $F_{\mu\text{-}SR\text{-}m}$ *trans* to P; δ = -118.20, m, $F_{\mu\text{-}SR\text{-}o}$ *trans* to S; δ = -133.43, m, $F_{\mu\text{-}SR\text{-}m}$ *trans* to S; δ = -120.90, m, $F_{phos\text{-}o}$; δ = -156.23, m, $F_{phos\text{-}m}$; δ = -142.35, m, $F_{phos\text{-}p}$. ^{31}P NMR, acetone-D_6, 300 K, ppm: δ = 6.5, s + d, $^1J_{Pt\text{-}P}$ = 3687 Hz. Mass spectra (FAB^+-MS): *m/z* = 1819, $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]^+$. Anal. Calcd. for $C_{60}H_{24}F_{26}P_2Pt_2S_4$: C 39.62%, H 1.33%, S 7.05%. Found: C 39.5%, H 1.2%, S 7.1%.

***trans*-[Pt$_2$(μ-SC$_6$HF$_4$-4)$_2$(SC$_6$HF$_4$-4)$_2$(PPh$_2$(C$_6$F$_5$))$_2$] 4**. ^1H NMR, acetone-D_6, 300 K, ppm: δ = 7.87, m, C_6H_5; δ = 7.63, m, C_6H_5; δ = 7.22, m, $H_{SR\text{-}p}$; δ = 7.17, br m, $H_{\mu\text{-}SR\text{-}p}$. $^{19}F\{-^1H\}$ NMR, acetone-D_6, 300 K, ppm: δ = -131.45, m, $F_{SR\text{-}o}$; δ = -138.14, m, $F_{SR\text{-}m}$; δ = -127.01, m, $F_{\mu\text{-}SR\text{-}o}$ *trans* to P; δ = -133.7, m, $F_{\mu\text{-}SR\text{-}m}$ *trans* to P; δ = -120.19, m, $F_{\mu\text{-}SR\text{-}o}$ *trans* to S; δ = -131.60, m, $F_{\mu\text{-}SR\text{-}m}$ *trans* to S; δ = -122.20, m, $F_{phos\text{-}o}$; δ = -157.39, m, $F_{phos\text{-}m}$; δ = -143.01, m, $F_{phos\text{-}p}$. ^{31}P NMR, acetone-D_6, 300 K, ppm: δ = 7.8, s + d, $^1J_{Pt\text{-}P}$ = 3244 Hz. Mass spectra (FAB^+-MS): *m/z* = 1819, $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]^+$. Anal. Calcd. for $C_{60}H_{24}F_{26}P_2Pt_2S_4$: C 39.62%, H 1.33%, S 7.05%. Found: C 39.3%, H 1.1 %, S 6.9%.

[Pt(SC$_6$HF$_4$-4)$_2$(1,2-C$_6$F$_4$(SC$_6$HF$_4$)(PPh$_2$))] 5. ^1H NMR, acetone-D_6, 300 K, ppm: δ = 7.78, m, C_6H_5; δ = 7.54, m, C_6H_5; δ = 7.11, m, $H_{SR\text{-}p}$; δ = 7.06, br m, $H_{SR\text{-}p}$, $H_{R\text{-}SR\text{-}p}$. $^{19}F\{-^1H\}$ NMR, acetone-D_6, 300 K, ppm: δ = -113.31, m, $F_{SR\text{-}o}$ *trans* to P; δ = -121.70, m, $F_{SR\text{-}m}$ *trans* to P; δ = -111.41, m, $F_{SR\text{-}o}$ *trans* to S; δ = -121.28, m, $F_{SR\text{-}m}$ *trans* to S; δ = -111.09, m, $F_{R\text{-}SR\text{-}o}$; δ = -116.30, m, $F_{R\text{-}SR\text{-}m}$; δ = -101.01, m, $F_{S\text{-}P\text{-}3}$; δ = -107.68, m, $F_{S\text{-}P\text{-}4}$; δ = -124.23, m, $F_{S\text{-}P\text{-}5}$; δ = -125.72, m, $F_{S\text{-}P\text{-}6}$. ^{31}P NMR, acetone-D_6, 300 K, ppm: δ = 11.41, s + d, $^1J_{Pt\text{-}P}$ = 3014 Hz. Mass spectra (FAB^+-MS): *m/z* = 1071, $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh_2))]^+$. Anal.

Calcd. for $C_{36}H_{13}F_{16}PPtS_3$: C 40.35%, H 1.22%, S 8.97%. Found: C 40.0%, H 1.2%, S 8.7%.

2- Crystallography

Complexes **1** and **2**: this work. Complex **5**: the X-ray structure was previously published.[5] See compound **5** in this communication. Structure deposition: CCDC 239572; CSD Refcode BIGXOF.

3- Computational details

Geometry optimization of the isolated isomers was performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).[6, 7] The calculations of the systems are described by the standard 6-31+G(d) basis set function on C, F, H, S, and P atoms.[8] A relativistic effective core potential (ECP) on Pt atom was used to replace the inner core electrons keeping the outer core (18 explicit electrons for neutral Pt).[9] Vibrational analysis was performed at each stationary point, confirming its identity as an energy minimum. Based on the optimization geometry, TD-DFT [10] was used to calculate the HOMO and LUMO molecular orbital and their energies, as well as the energy gap for both isomers. The population analysis has also been performed by the NBO method [11] at B3LYP/6-31+G(d) level of theory, using NBO program.[12] All calculations were carried out with the Gaussian 09 package.[13]

The energies, the energy gaps, and the optimized structures are given in **Table S1** and **Figure S1**, while HOMO and LUMO molecular orbital are illustrated in **Figure S2**. As can be seen from Table S1, the *trans* isomer is more stable than the *cis* isomer by 2.7644 kcal/mol, while the energy gap is to be highest in the former isomer; this means that UV absorptions are expected at 375.56 and 376.40 nm for *trans* and *cis* isomers, respectively.

Table S1. *Calculated values of the electronic properties for two isomers in gas phase*.

Isomer	Energy (kcal/mol)	HOMO (eV)	LUMO (eV)	ΔE_{GAP} (cm^{-1})
Trans	0.00[a]	-5.7060	-2.4047	26626.6598
Cis	2.7644	-5.7623	-2.4684	26567.4017

[a] Total Energy = -5237.79145318 hartree

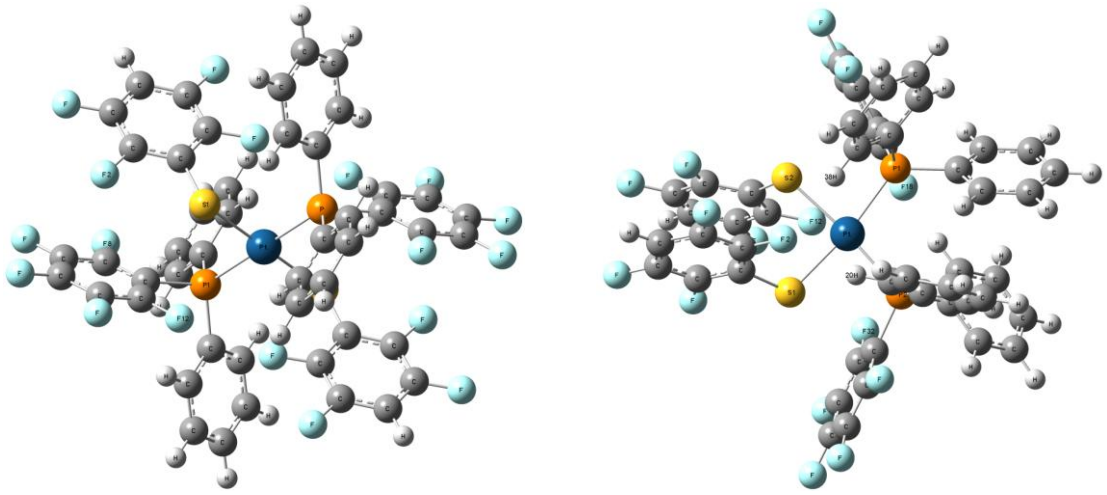

Figure S1. Representation of optimized molecular structures in gas phase for the *trans* (left) and *cis* (right) isomers.

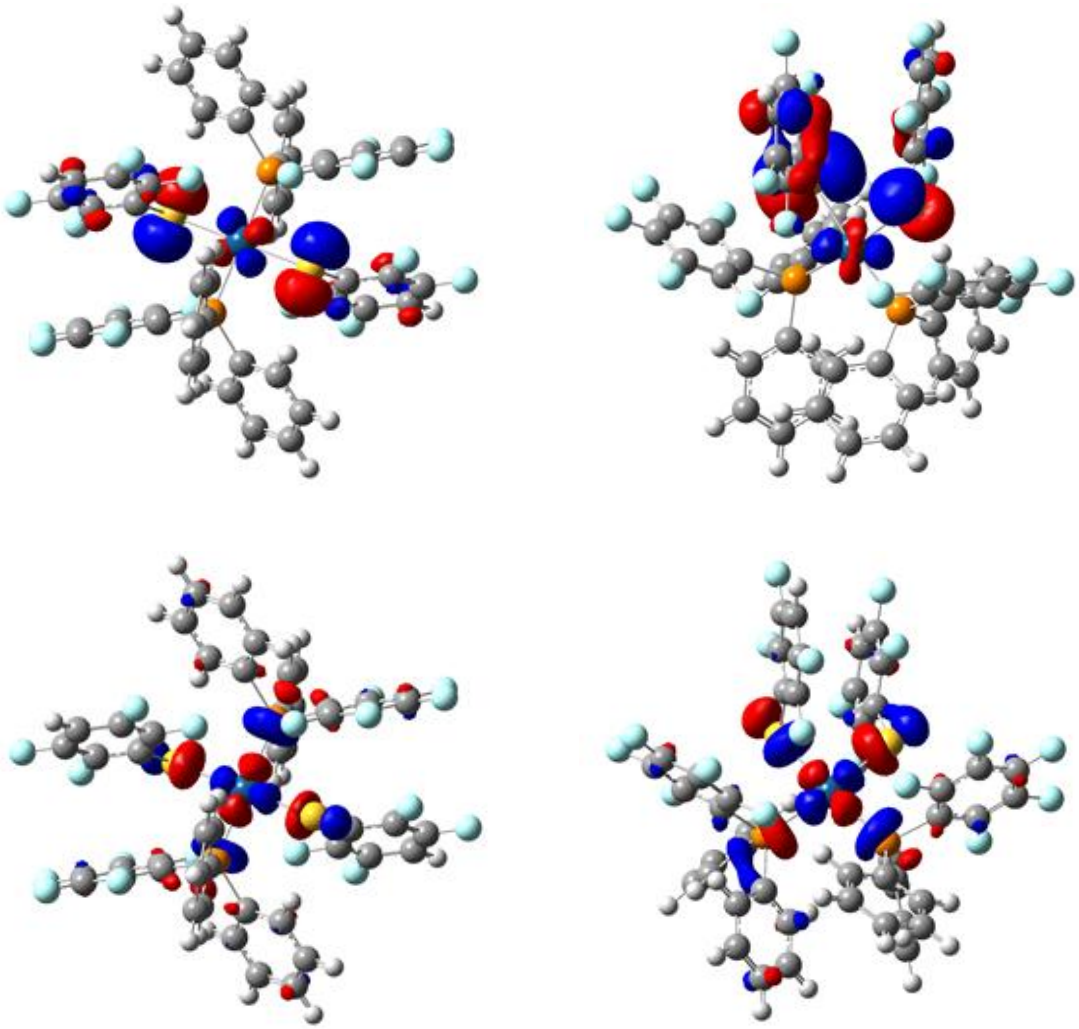

Figure S2. TD-DFT HOMO-LUMO molecular orbital, where the electron density of both isomers is shown.

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