An unprecedented cyclometallated platinum(II) complex incorporating a phosphinine co-ligand: synthesis and photoluminescence behaviour

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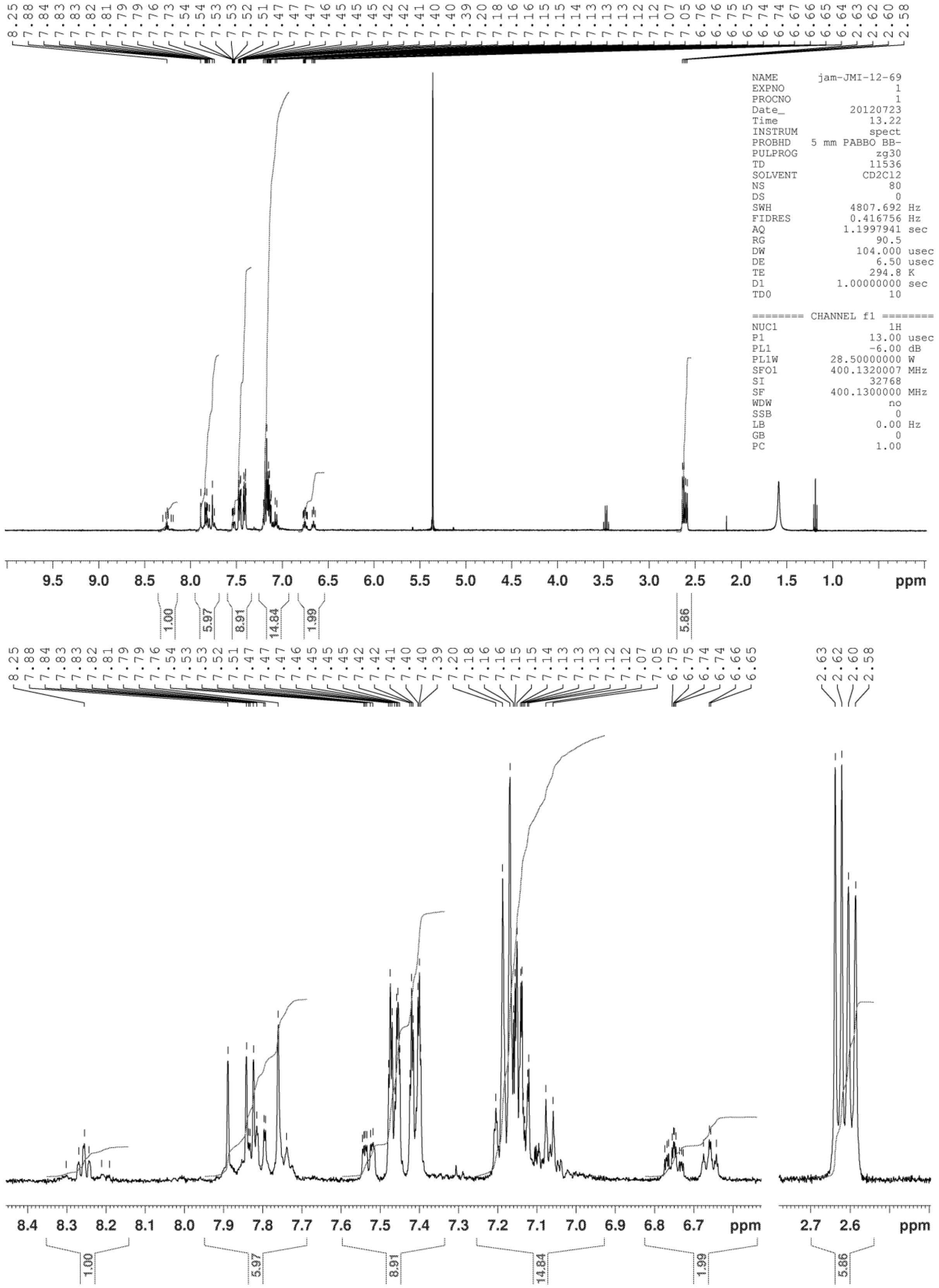
Supplementary Information

General experimental methods: All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Diethyl ether was distilled from sodium–benzophenone, CH_2Cl_2 was distilled from CaH_2 and acetone was distilled from K_2CO_3. ^{1}H NMR spectra were recorded at 400.13 MHz, ^{13}C NMR spectra were recorded at 100.61 MHz, ^{31}P NMR spectra were recorded at 121.49 MHz in CD_2Cl_2. Ligand *2,6-diphenyl-4-methylphos-phorin* (***L$_p$***) was prepared according to a slightly modified procedure described in the literature.[1] Other reagents were obtained from commercial suppliers and used as received. Infra-red spectra were measured using Tensor 27 (ATR diamond) Bruker spectrometer.

Synthesis of complex [Pt(ppy)(*Lp*)$_2$](OTf) (1): To a stirred suspension of $[Pt(ppy)Cl]_2$ (36 mg; 0.05 mmol) in acetone (15 mL) was added an acetone solution (10 mL) of AgOTf (26 mg; 0,10 mmol) the resulting mixture was stirred at room temperature with the exclusion of light for 30 min during which AgCl precipitated out of solution. Then the heterogeneous mixture was filtered through a pad of celite directly into a Schlenk tube containing an acetone solution (5 mL) of the phosphinine ligand ***Lp*** (58 mg; 0.21 mmol). The latter mixture was allowed to react for 2 hours at room temperature in the dark and the solvent volume was reduced to approximately 3-4 mL under vacuum, subsequent addition of diethyl ether (30 mL) caused precipitation of beige microcrystalline solid which was separate through cannula filtration and washed with two more portions of diethyl ether (15 mL each). The microcrystalline solid was then recrystallized from a dichloromethane/diethylether mixture (93 mg; 0.084 mmol). Yield: 84 %. Anal. Calcd. (%) for $C_{48}H_{38}F_3NO_3P_2PtS\cdot CH_2Cl_2$ (1107.9 g.mol^{-1}): C 53.12, H 3.64; N 1.26; found: C 53.06, H 3.75; N 1.41. ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 8.25 (m, 1 H, *py*), 7.89-7.74 (m, 6 H, *H$_\beta$-phosphabenzene* + *ppy*), 7.53 (m, 1 H, *ppy*), 7.46 (m, 4 H, *phenyl*), 7.41 (m, 4 H, *phenyl*), 7.21-7.06 (m, 14 H, *phenyl* + *ppy*), 6.75 (m, 1 H, *ppy*), 6.66 (m, 1 H, *ppy*), 2.62 (d, 3 H, $^5J_{H\text{-}P}$ = 6.8 Hz, *CH$_3$*), 2.59 (d, 3 H, $^5J_{H\text{-}P}$ = 7.2 Hz, *CH$_3$*) ppm.

^{31}P{^{1}H} NMR (121.47 MHz, CD_2Cl_2): δ = 133.3 (1P, $^1J_{P\text{-}Pt}$ = 4470 Hz, $^2J_{P\text{-}P}$ = 46 Hz, *P trans to N*); 157.7 (1P, $^1J_{P\text{-}Pt}$ = 1760 Hz, $^2J_{P\text{-}P}$ = 46 Hz, *P trans to C*) ppm. IR (ATR): ν = 3055, 1641, 1607, 1576, 1438, 1446, 1273, 1217, 1069, 1028, 1167, 822, 752, 694, 635, 515, 325, 270, 222, 206 cm^{-1}.

Figure S1 ^{1}H NMR spectrum of complex **1** in CD_2Cl_2.



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TD                    11536
SOLVENT              CD2Cl2
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AQ                1.1997941 sec
RG                     90.5
DW                  104.000 usec
DE                     6.50 usec
TE                    294.8 K
D1               1.00000000 sec
TD0                      10

======== CHANNEL f1 ========
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PL1                   -6.00 dB
PL1W            28.50000000 W
SFO1            400.1320007 MHz
SI                    32768
SF              400.1300000 MHz
WDW                      no
SSB                       0
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Figure S2 $^{31}P\{^1H\}$ NMR spectrum of complex **1** in CD_2Cl_2.

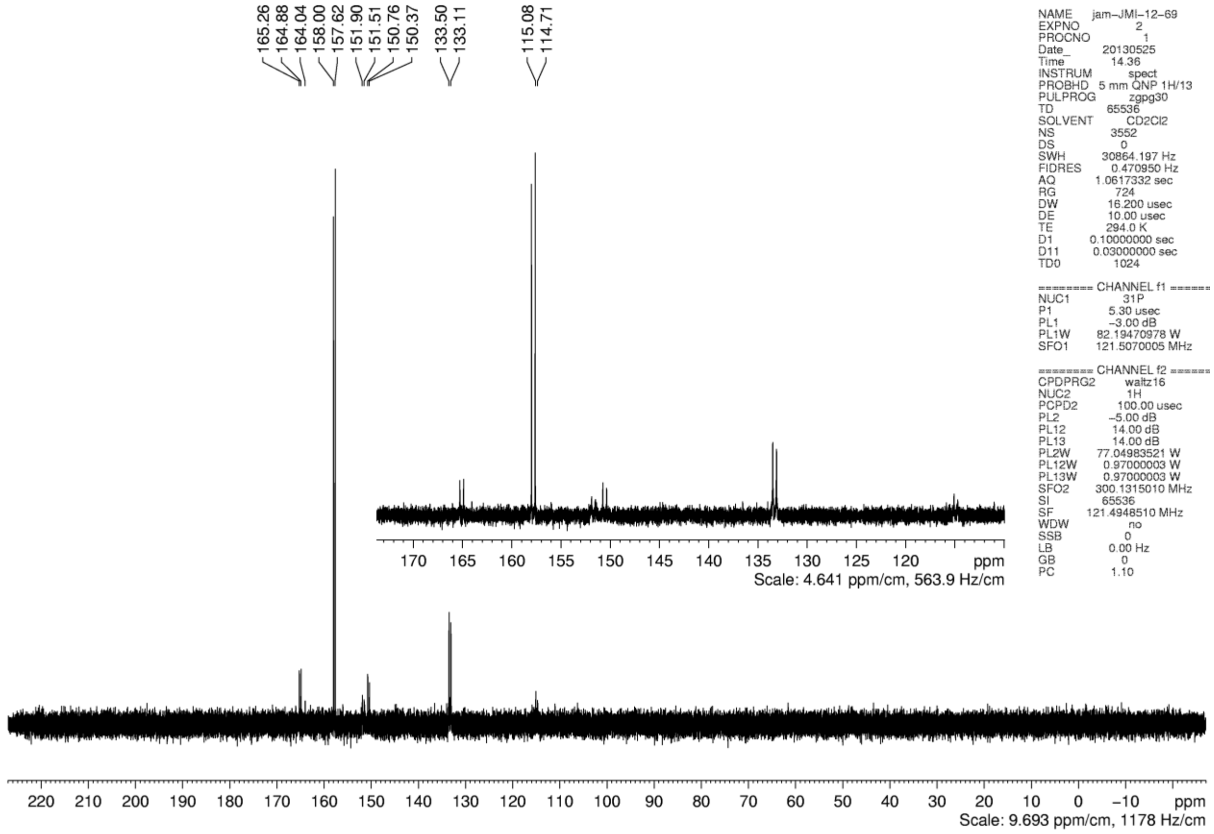


Figure S3 $^{13}C\{^1H\}$ NMR spectrum of complex **1** in CD_2Cl_2.

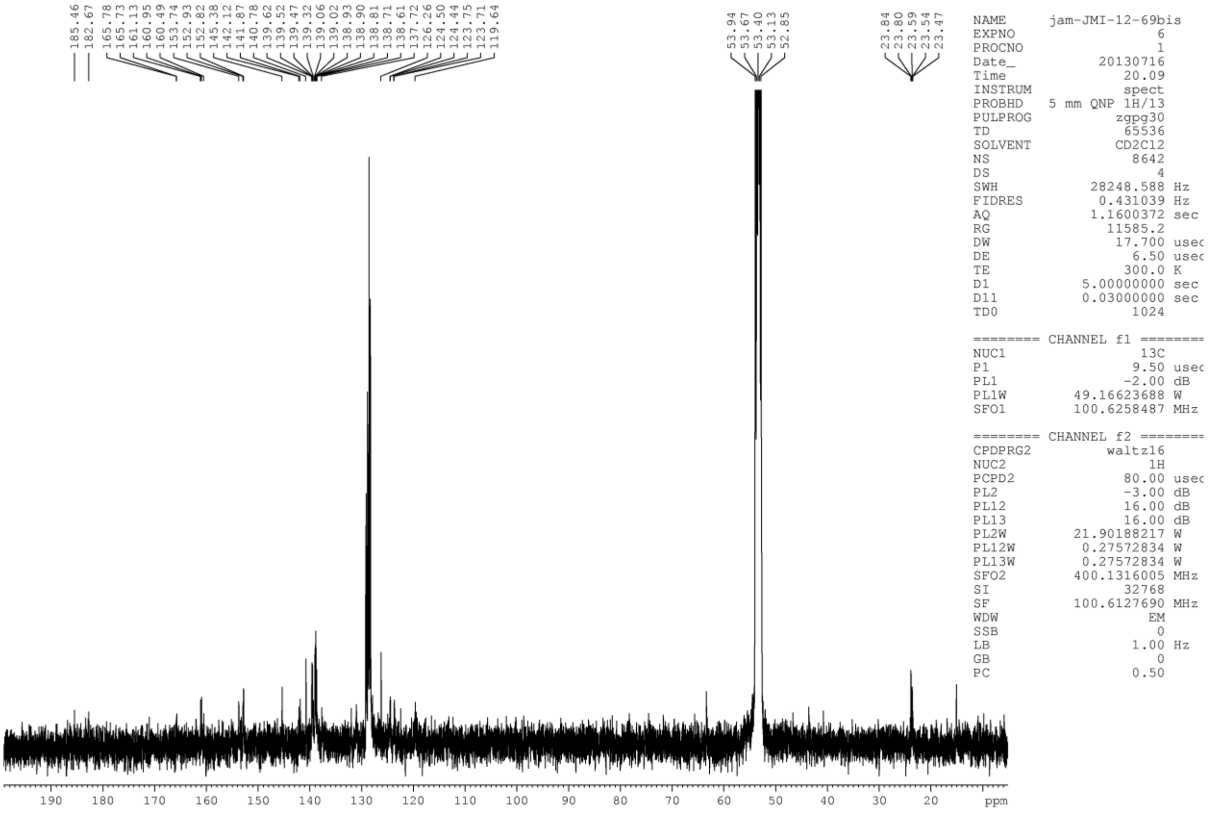
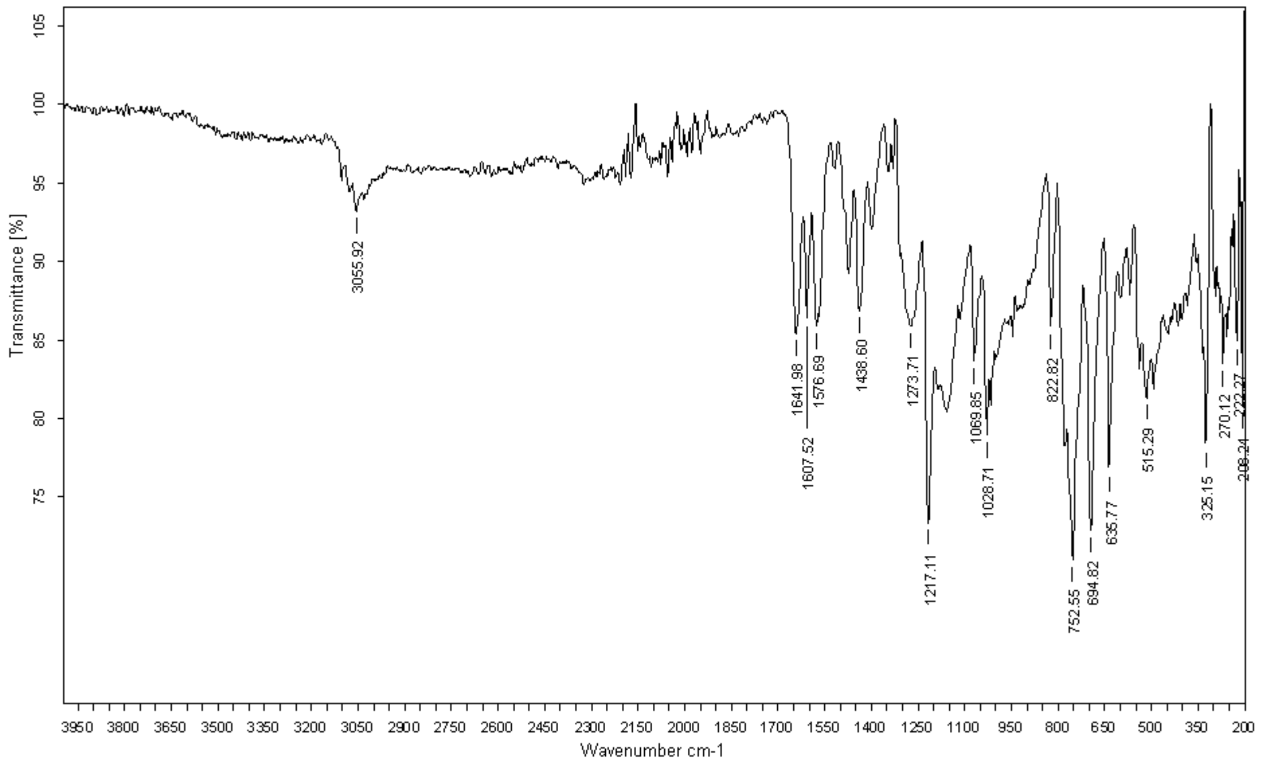


Figure S4 Infrared spectrum of complex **1** (ATR technique).



Echantillon : **JMI-11-8**

mesuré le 01/10/2011 sur TENSOR 27
résolution : 4 cm-1 (16 scans)

Spectre : JMI-11-8.0 (dans C:\SPECTRES\ARC\jamal)
Technique : ATR
Opérateur : jamal

Figure S5 Luminescence decay of L_p in EPA at 77 K (experimental data in blue, monoexponential fit in red).

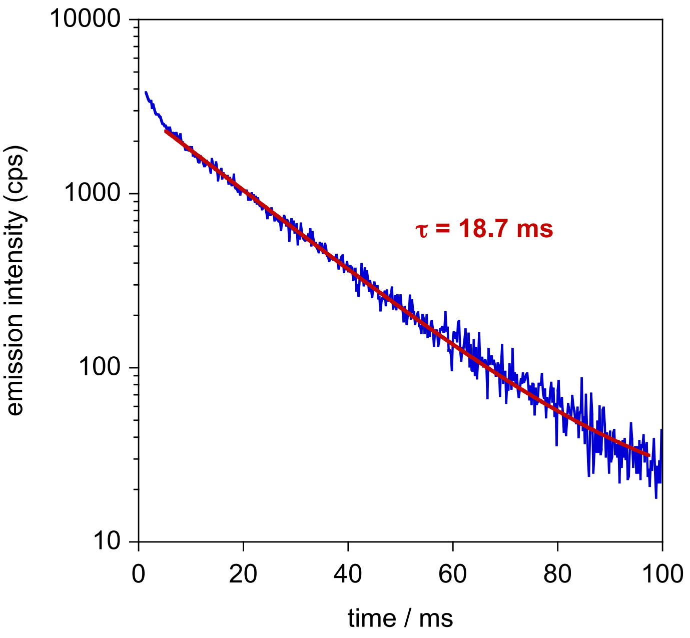


Figure S6 Luminescence decay of complex **1** in CH_2Cl_2 at 77 K (experimental data in blue, monoexponential fit in red).

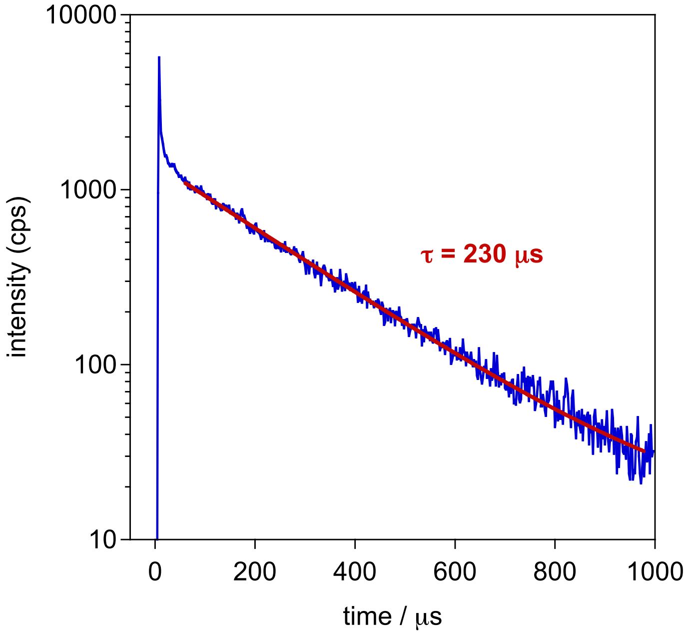


Figure S7 Cyclic voltammogram of complex **1** in CH_2Cl_2 at 298 K, using Bu_4NPF_6 as the supporting electrolyte, scan rate 300 mV s^{-1}.

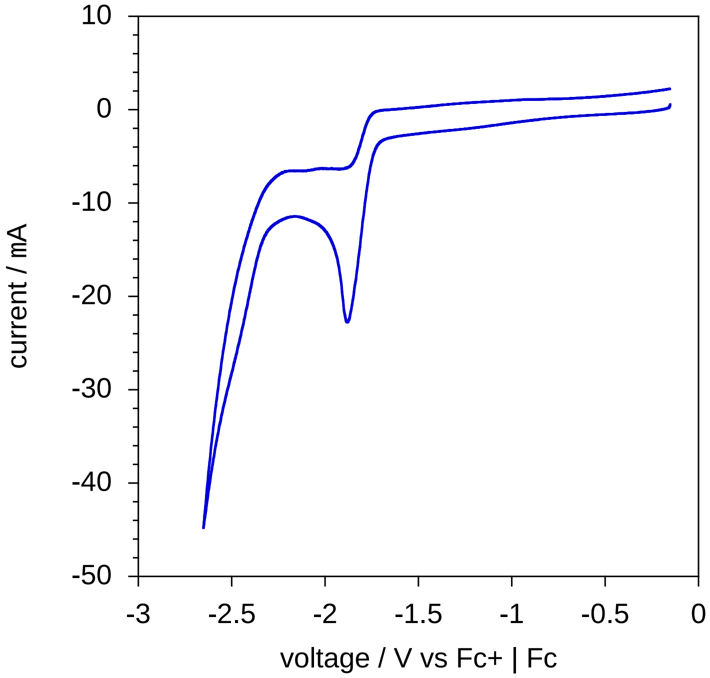
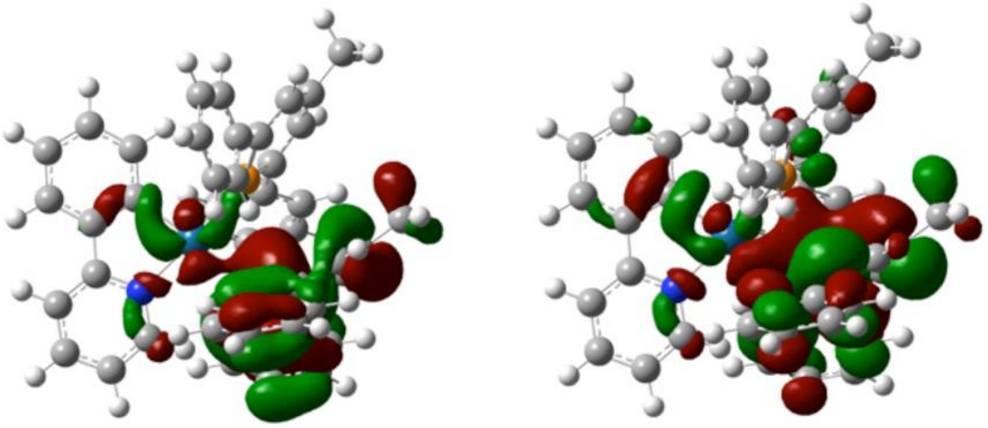


Figure S8 HOMO and LUMO for the T_1 state of complex **1** calculated at the optimised T_1 geometry.



HOMO LUMO

Instrumentation for photophysical measurements

Absorption spectra were recorded for solutions in dichloromethane containined within 1 cm pathlength quartz cuvettes using a Biotek Instruments XS spectrometer. Luminescence spectra were recorded using a FluoroMax-2 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube. Samples were contained within 4 mm o.d. tubes held within a quartz Dewar. Spectra were corrected for the wavelength dependence of the detector and emission grating. The luminescence lifetimes were measured by multichannel scaling, following excitation with a microsecond pulsed xenon flashlamp. The emitted light was detected at 90° using a Peltier-cooled R928 photomultiplier tube after passage through a monochromator.

Instrumentation for electrochemical measurements

Cyclic voltammetry was carried out using a μAutolab Type III potentiostat with computer control and date storage via GPES Manager software. Solutions of concentration 1 mM in CH_2Cl_2 at 298 ± 3 K were used, containing NBu_4PF_6 as the supporting electrolyte. A three-electrode assembly was employed, consisting of a glassy carbon working electrode, and platinum wire counter and reference electrodes. Solutions were purged for at least 5 minutes with solvent-saturated nitrogen gas with stirring, prior to measurements being taken under a nitrogen atmosphere without stirring. The voltammograms were referenced to the ferrocence-ferrocenium couple measured under the same conditions.

Details of TD DFT calculations

Calculations were performed using the Gaussian 09[2] suite of programmes with the PBE0 functional.[3] The LANL2DZ basis set was used for Pt(II), with the inner core electrons replaced by a relativistic core potential, and the all-electron cc-PVDZ basis set was used for the ligands. A polarised continuum model (PCM) was used for the solvent dichloromethane. Geometries were fully optimised without symmetry constraints, and the triplet state geometries were calculated directly by minimisation of the SCF triplet state. Harmonic vibrational wavenumber calculations were performed to confirm that the structures obtained correspond to minima of the potential energy surface. Time-dependent calculations were carried out on the optimised structures to determine the relevant transitions.

References

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1. G. Märkl, *Angew. Chem. Int. Ed. Engl.*, 1966, **5**, 846.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

Honda, O. Kitao, H. Nakai, T. Vreven, Montgomery, Jr., J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, 2009, Gaussian 09.

3. J. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.