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Synthesis, structures and photophysical properties of phosphorus-containing silver 3,5-bis(trifluoromethyl)pyrazolates

Aleksei A. Titov, Alexander F. Smol'yakov, Kristina F. Baranova, Oleg A. Filippov and Elena S. Shubina

Materials and methods.

^{1}H, ^{19}F, and ^{31}P NMR experiments were carried out on a Bruker Avance 400 spectrometer. Infrared (IR) spectra were recorded on a Shimadzu IRPresige 21 FT-IR spectrometer using KBr pellets. Steady-state luminescence and excitation spectra were recorded on a Fluorolog FL 3-22 Horiba-Jobin-Yvon photon counting emission spectrometer equipped with a 450 W xenon lamp and double monochromators for excitation and emission. The luminescence spectra were corrected for the nonlinear response of the instrument using predetermined factors. The crystals for these measurements were packed in quartz capillaries.

Characteristics of the obtained complexes.

2. ^{1}H NMR (CD_2Cl_2), δ: 1.17−2.15 (m, CH, 66 H), 6.80 (s, 2H^{Pz}). ^{19}F NMR (CD_2Cl_2), δ: -59.74. ^{31}P{^{1}H } NMR (CD_2Cl_2), δ: 42.17 (dd, $J^{P\text{-}Ag}$ = 694.85 Hz, $J^{P\text{-}Ag}$ = 600.53 Hz). IR (KBr), ν/cm^{-1}: 3158 (CH^{Pz}), 2933, 2854 (CH^{Cy}), 1635 (CN^{Pz}), 1538, 1520, 1450, 1257, 1150, 1128 Found (%): C, 46.71; H, 5.80; N, 4.74; F, 19.28; P, 5.24. Calculated (%): C, 46.82; H, 5.73; N, 4.68; F, 19.23; P, 5.19.

3. ^{1}H NMR (CD_2Cl_2), δ: 1.11−2.09 (m, CH, 66 H), 6.92 (s, 2H^{Pz}). ^{19}F NMR (CD_2Cl_2), δ: –60.49. ^{31}P NMR {^{1}H} (CD_2Cl_2), δ: 41.09 (br s), 44.64 (br s). IR (KBr), ν/cm^{-1}: 3150 (CH^{Pz}), 2935, 2855 (CH^{Cy}), 1626 (CN^{Pz}), 1540, 1502, 1451, 1262, 1128. Found (%): C, 40.75; H, 4.87; N, 7.31; F, 14.88; P, 4.04. Calculated (%): C, 40.82; H, 5.80; N, 4.25; F, 14.96; P, 3.95.

X-ray diffraction study.

Single-crystal X-ray diffraction experiments were carried on a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software[1] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction. All calculations (space group and structure determination, refinements, graphics, and structure reporting) were made using the SHELXL2014[2] and OLEX2[3] program packages. Experimental details and crystal parameters are listed in Table S1. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation.

References

[1] *APEX II software package*, Bruker AXS Inc., 2005.

[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

Table S1 Crystal data, data collection and structure refinement parameters for **2** and **3**.

Compound	**2**	**3**
Molecular formula	$C_{46}H_{70}Ag_2F_{12}N_4P_2$	$C_{56}H_{70}Ag_4F_{24}N_8P_2$
Formula weight	1182.30	1804.59
Dimension, mm	0.33×0.27×0.19	0.35×0.29×0.07
Temperature, K	120(2)	120(2)
Crystal system	monoclinic	Triclinic
Space group	*C*2/c	$P\ \bar{1}$
a, Å	20.7067(11)	11.269(2)
b, Å	14.8154(8)	12.710(3)
c, Å	20.6394(12)	13.624(3)
α, deg.	90	63.96(3)
β, deg.	114.5200(10)	78.31(3)
γ, deg.	90	77.24(3)
V, Å^3	5760.7(6)	1697.5(8)
Z	8	1
ρ_{calc}, g cm^{-3}	1.463	1.765
Linear absorption (μ), cm^{-1}	8.11	12.92
T_{min}/T_{max}	0.675/0.746	0.643/0.746
$2\theta_{max}$, deg.	60	60
No. unique refl. (R_{int})	61760 (0.0279)	22507(0.0174)
No. observed refl. ($I > 2\sigma(I)$)	7702	9190
No. parameters	326	424
R_1 (on *F* for observed refl.)[a]	0.0361	0.0246
wR_2 (on F^2 for all refl.)[b]	0.0694	0.0588
GOOF	1.075	1.021

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

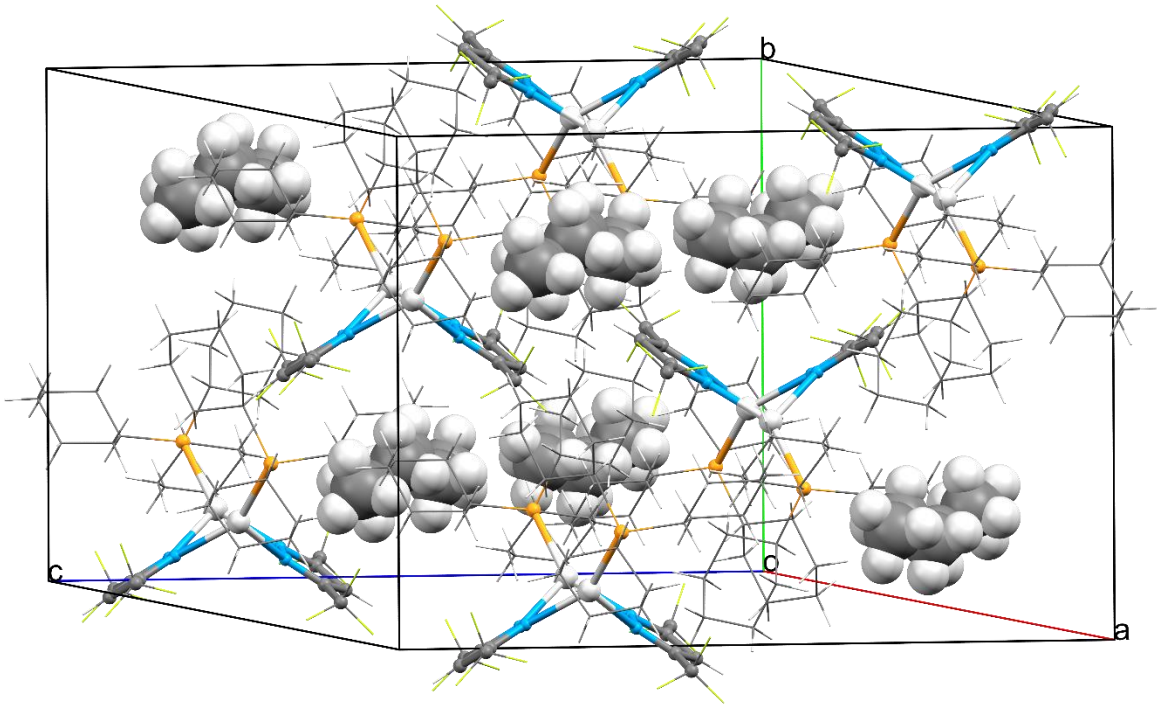

Figure S1 Unit cell of **2** in the solid state.

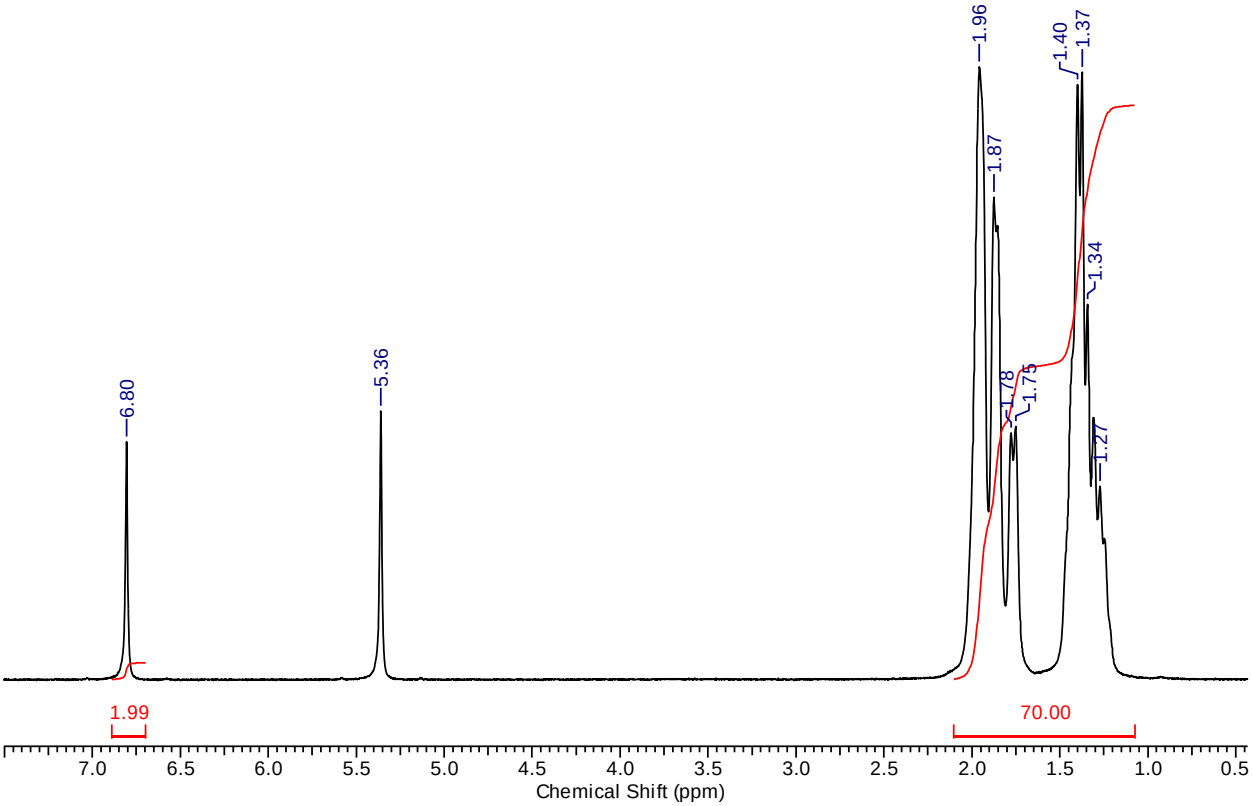

Figure S2 ^{1}H NMR spectrum of **2** in CD_2Cl_2.

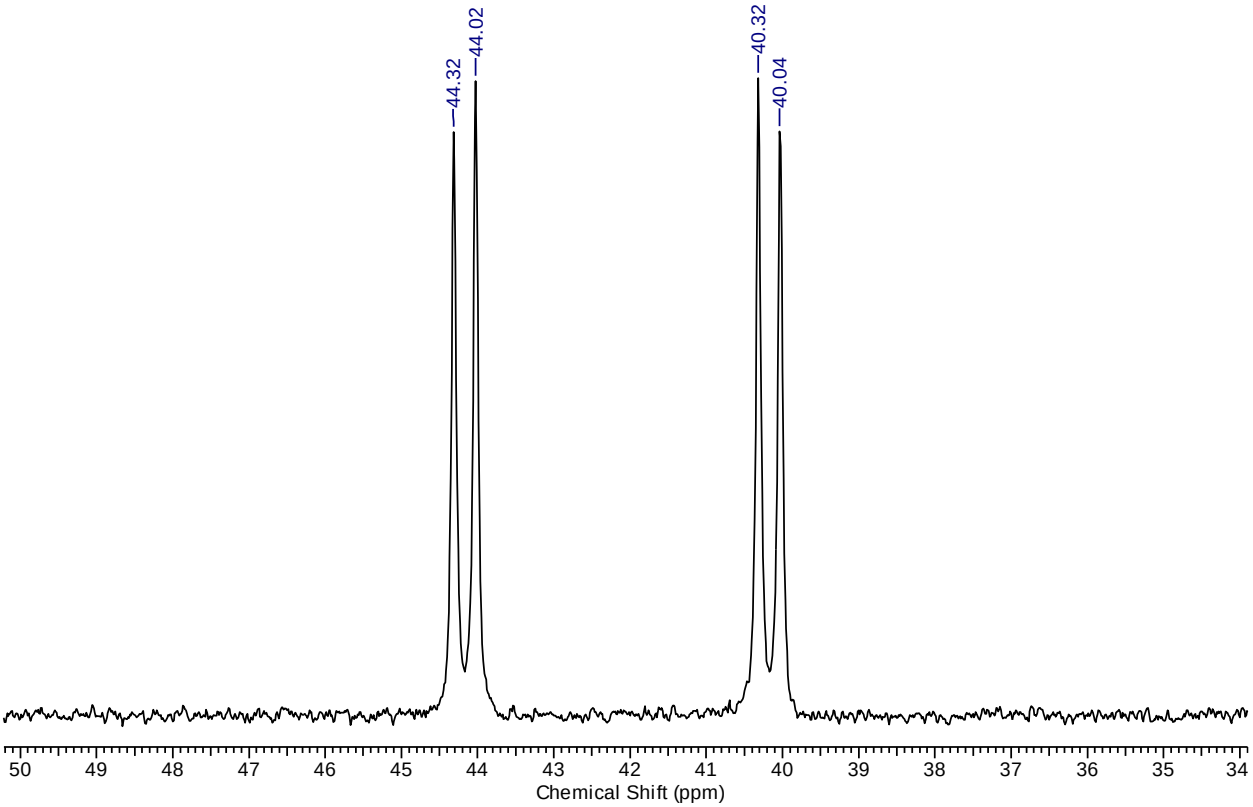

Figure S3 ^{31}P $\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2.