Electronic Supplementary Information for Dalton Transactions

Supplementary Material (ESI) for

Syntheses and Structures of Thermally Stable Diketiminato Complexes of Gold and Copper

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Experimental

General considerations

All manipulations were conducted under dry nitrogen using standard inert atmosphere Schlenk techniques. All reagents were used as purchased without further purification unless otherwise stated. Solvents were dried over Na/benzophenone (tetrahydrofuran, diethyl ether), sodium (toluene, light petroleum), or CaH_2 (dichloromethane) before use. Deuterated NMR solvents (acetone, acetonitrile, benzene-d_6, toluene-d_8, CD_2Cl_2 and $CDCl_3$) were degassed by several freeze-thaw cycles and dried over activated 4 Å molecular sieves. NMR spectra were recorded on a Bruker DPX-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent peak; ^{19}F (282.4 MHz) NMR spectra were referenced externally to $CFCl_3$.

Crystals of compounds **2** and **3** were examined at 140 K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Data were processed using the CrysAlisPro-CCD and –RED[14] programs, The structures were determined by the direct methods routines in the SHELXS program[15] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[15] In general, the non-hydrogen atoms were refined with anisotropic thermal parameters, Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Refinement results are included in Table 2. Scattering factors for neutral atoms were taken from reference 16. Computer programs used in this analysis have been noted above, and were run through WinGX[17] on a Dell Precision 370 PC at the University of East Anglia.

The ligand precursor **1**-H was prepared following the method by Sadighi et al.[6] by heating 2 equiv of 3,5-bis(trifluoromethyl)phenylimino-triphenylphosphorane with 1,1,1,5,5,5-

hexafluoro-2,4-pentanedione (1.4 mL, 8.4 mmol) in toluene (80 mL) at 90 °C for 15 h. Concentrating the mixture *in vacuo* created a dark-yellow solution. Cooling yielded a crystalline product containing triphenylphosphine oxide, which was washed with light petroleum. Filtration and recrystallisation afforded **1**-H as a yellow solid. Column chromatography on silica gel (petroleum / ethyl acetate 19:1) gave purified **1**-H as light-yellow crystals. ^{1}H-NMR (C_6D_6, 300.13MHz) δ 11.7 (s, 1H), 7.7 (2H), 7.6 (4H), 6.08 (s,1H). ^{19}F NMR (C_6D_6, 282.404MHz): δ -62.80 (s, 6F), -63.03 (s, 12F). The crystals were suitable for X-ray diffraction.

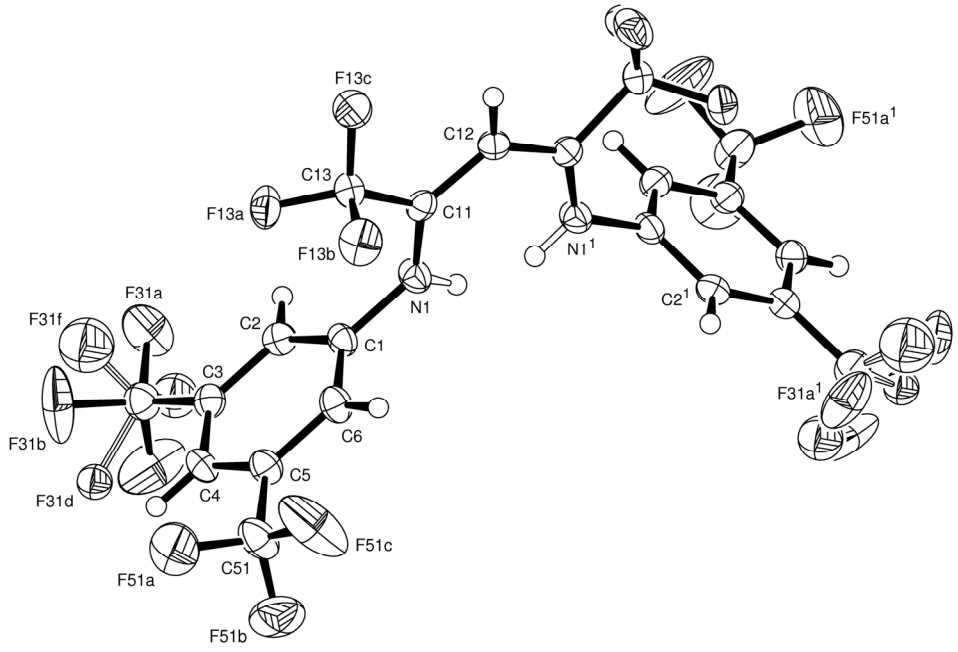

Fig. S1. Molecular structure of Ar-NC(CF_3)CHC(CF_3)NH-Ar [Ar = 3,5-$(CF_3)_2C_6H_3$] (**1**-H), indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were identified in difference maps, and were included in idealised sites to ride on the parent carbon or nitrogen atom; the hydrogen on N(1) is assumed to have, overall, half-occupancy.

1-K: A suspension of KH (0.034 g, 0.85 mmol) in diethyl ether (15 mL) was added to a solution of **1**-H (0.486 g, 0.77 mmol) in diethyl ether (10 mL). The solution turned immediately from yellow to orange. The mixture was stirred for 5 h at room temperature and filtered. The solvent was removed under vacuum to leave an orange solid, yield 0.49 g (95 %). ^{1}H NMR (300.13 MHz, $(CD_3)_2CO$): δ 7.11 (s, 2H, *p*-Ar^{F}), 6.20 (s, 4H, *o*-Ar^{F}), 6.08 (s,

1H, C*H*), ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ -63.68 (s, 12F), -69.53 (s, 6F). Anal. Found: C, 37.79; H, 1.11; N, 4.28. Calcd for $C_{21}H_7F_{18}KN_2$: C, 37.74; H, 1.06; N, 4.19 %.

2: An orange-red solution of **1**-K (0.31 g, 0.466 mmol) in dry THF (15 mL) was added by syringe to a colourless solution of $AuCl(PPh_3)$ (0.23 g, 0.466 mmol) in dry THF (20 mL) cooled on an ice bath. After 1 h at 0 ºC and 1h at room temperature the THF was removed to leave an orange-red solid, which was recrystallized from light petroleum at -28 °C. Orange crystals were obtained, accompanied by a very small amount of yellow crystals, yield 0.486 g (92%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.51 (m, 21 H, 15H (P*Ph*$_3$), 6H (Ar^F), 5.86 (s, 1H, C*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.7 (br. s), 148.6 (br. s) 133.8 (d, *J* = 13.6 Hz), 132.2 (s), 132.0 (q, *J* = 30.2 Hz), 129.4 (d, *J* = 12.1 Hz), 128.1 (d, *J* = 62.6 Hz), 125.0 (br. s), 121.2 (br. s), 120.4 (br. s), 118.7 (br. s), 114.1 (br. s), 93.6 (br. s). ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): δ -63.01 (br, 6F, 5-aryl), -63.30 (br, 6F, 1-aryl), -66.18 (br, 3F, 4-CF_3), -71.95 (br, 3F, 2-CF_3). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ 30.35 (s). Anal. Found: C, 42.92; H, 2.13; N, 2.48. Calcd for $C_{39}H_{22}AuFN_2P$: C, 43.03; H, 2.04; N, 2.57 %.

3: To a solution of **1**-K (0.285 g, 0.43 mmol) in dry diethyl ether (40 mL) was added an addition of $(Ph_3P)_3CuBr$ (0.440 g, 0.47 mmol) was made. The mixture was stirred for 2 h at room temperature and filtered by cannula. The solvent was removed under vacuum to leave a deep orange solid, yield 0.49 g (93 %). **3** was crystallised from light petroleum at -5 °C and the product washed with cold Et_2O to yield as a red crystals for x-ray crystallography. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (m, 2H, *p*-Ar^F), 7.58 (m, 4H, *o*-Ar^F), 7.34 (m, 3H, P*Ph*$_3$), 7.26 (m, 6H, P*Ph*$_3$), 7.06 (m, 6H, P*Ph*$_3$), 5.90 (s, 1H, C*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.2 (s), 133.8 (d, *J* = 16.5 Hz), 133.1(d, *J* = 17.0 Hz), 131.5 (q, *J* = 33.6 Hz) 129.6 (s), 128.7 (d, *J* = 8.8 Hz), 124.7 (s), 123.4 (br. s), 122.1 (s), 121.1 (s), 85.8 (m). ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): δ -62.91 (s, 12F), -57.93 (s, 6F), ^{31}P NMR (121.49 MHz, $CDCl_3$): δ 29.3 (s, PPh_3). Anal. Found: C, 56.36; H, 3.17; N, 2.22. Calcd for $C_{39}H_{22}AuFN_2P$: C, 56.24; H, 3.06; N, 2.30 %.

References:

14 Programs CrysAlisPro, Oxford Diffraction Ltd., Abingdon, UK (2010).

15 G. M. Sheldrick, SHELX-97 – Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Cryst.* 2008, **A64**, 112.

16 *'International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht 1992. Vol. C, pp. 500, 219 and 193.

17 L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837.

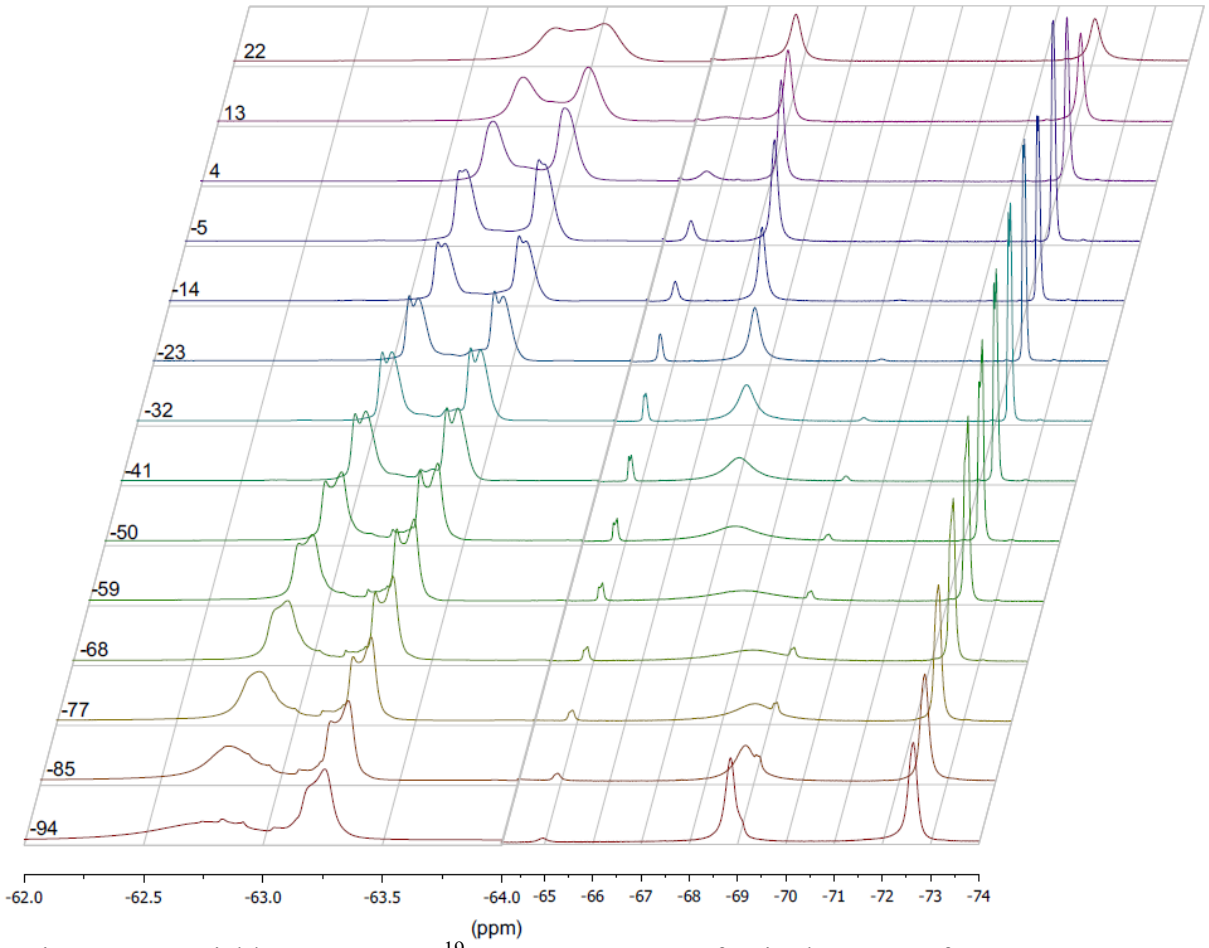

Figure S2. Variable temperature ^{19}F NMR spectrum of **2** in the range of 22 to -94 °C (CD_2Cl_2). The aryl-CF_3 region of δ -62.5 to -63.5 on cooling shows first hindered rotation of the two inequivalent aryl groups, and below -70 °C the hindered CF_3 rotation of one of the rings. The shift of the ketiminate 4-CF_3 signal at -65.5 to -69 is thought to be a reflection of E/Z isomerisation of the non-coordinated N atom, whereas the gold-bonded N atom undergoes no fluxional process.