

Supplementary Information for:**Novel pincer complexes of Ag(I), coordination of toluene and their comparison with indium analogues.**

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Experimental Details

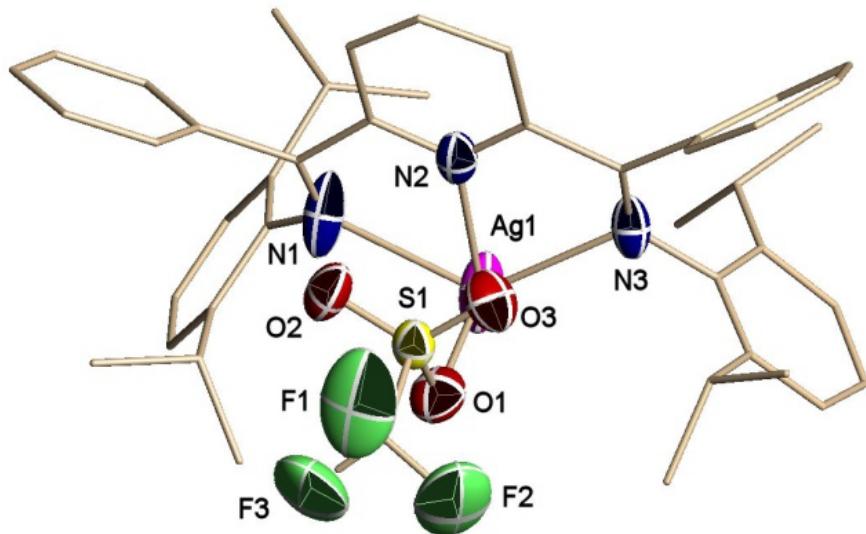
General Methods. Reactions were performed in a glovebox with a nitrogen atmosphere, with the exception of ligand synthesis, which was performed using standard Schlenk technique under a flow of N₂. All solvents were sparged with nitrogen and then dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated chloroform was dried using activated molecular sieves. Metal halides were purchased from Strem Chemicals and used as received. All other chemicals were purchased from Aldrich and used without further purification. Compounds **1** and **2** were synthesized according to literature procedure.¹ NMR spectra were run on a Bruker Avance 300 MHz spectrometer with CDCl₃ as solvents and internal standards. Elemental analyses for **3** and **4** were performed by Midwest Microlab LLC, Indianapolis IN.

[Ag-2,6-Bis{1-[(2,5-ditertbutylphenyl)imino]-benzyl}pyridine]/[OSO₂CF₃] (3): AgOSO₂CF₃ powder (38 mg, 0.150 mmol) was added to a clear yellow solution of **1** (100 mg, 0.151 mmol) in 8 mL of toluene. The reaction mixture was sealed, wrapped in aluminum foil due to light sensitivity of AgOSO₂CF₃ and allowed to stir for 14 hours, gradually becoming opaque yellow. The solution was then held at -20°C overnight, over which time a bright yellow precipitate formed. The solution was filtered and the precipitate was washed with 5 x 2 mL hexanes, and allowed to dry under vacuum. A bright yellow powder was isolated in 69% yield. Large yellow cubic crystals suitable for X-ray analysis were grown by diffusion of hexanes into a saturated CDCl₃ solution and storing at -20°C for several days. ¹H NMR (CDCl₃, 300 MHz): δ 7.89(br t, 1 H, py, *p*-CH), 7.60(br d, 2 H, py, *m*-CH), 7.40-7.10(br m, 12 H, aromatic), 6.96(br d, 1 H, aromatic), 6.93(br d, 1 H, aromatic), 6.53(br d, 2 H, aromatic), 1.49(br s, 18H, *t*Bu), 0.96(br s, 18H, *t*Bu). ¹³C NMR (CDCl₃, 75 MHz). δ 165.6(C=N imine), 152.7(py, *o*-C=N), 149.9(Ar-CH), 148.3(Ar-CH), 138.9(Ar, *i*-C), 138.1(Ar-CH), 134.3(Ar, *i*-C), 129.8(Ar-CH), 129.3(Ar-CH), 128.3(Ar-CH), 126.1(Ar-CH), 125.0 (Ar-CH), 121.9(Ar-*t*Bu, C-*t*Bu), 120.7(Ar-*t*Bu, C-*t*Bu), 35.5(Ar-*t*Bu, C-(CH₃)₃), 34.2(Ar-*t*Bu, C-(CH₃)₃), 31.2(Ar-*t*Bu, CH₃), 30.9(Ar-*t*Bu, CH₃). Sample for elemental analysis was obtained by recrystallization in toluene, resulting in a 1:1 toluene adduct of **3** calculated (%) for [C₄₈H₅₅AgF₃N₃O₃S][C₇H₈]: C 65.34, H 6.28, N 4.16, found C 64.92, H 5.97, N 3.90.

[Ag-2,6-Bis{1-[(2,6-diisopropylphenyl)imino]-benzyl}pyridine]/[OSO₂CF₃] (4): AgOSO₂CF₃ powder (42 mg, 0.164 mmol) was added to a clear yellow solution of **2** (100 mg, 0.165 mmol) in 8 mL of 5:1 hexanes to toluene solution. The reaction mixture was sealed, wrapped in aluminum foil due to light sensitivity of AgOSO₂CF₃ and allowed to stir for 14 hours, gradually becoming opaque yellow. The solution was then held at -20°C overnight, over which time a bright yellow precipitate formed. The precipitate was removed by filtration and washed with 5 x 2 mL hexanes, and allowed to dry under vacuum. A bright yellow powder was isolated in 84% yield. Large yellow cubic crystals suitable for X-ray analysis were grown in a saturated solution of 1:1 toluene/hexanes, and storing at -20°C for several days. ¹H NMR (CDCl₃, 300 MHz): ¹H NMR (CDCl₃, 23°C): δ 7.98(t, 1H, py, *p*-CH), 7.79(d, 2H, py, *m*-CH), 7.42-6.95(br m, 16H, aromatic), 2.92(br m, 4H, *t*Pr-CH), 1.21(br d, 12H, CH₃), 0.91(br d, 12H, CH₃). ¹³C NMR

(CDCl₃). δ 165.6(C=N imine), 152.3(py, *o*-C=N), 144.5(py, *m*-CH), 139.3(py, *p*-CH), 136.7(Ph, *m*-CH), 133.2(Ph, *o*-CH), 130.7(Ar-*iPr*, C-*iPr*), 129.4(Ar-*iPr*, CH), 129.3(Ph, *i*-C), 128.4(Ph, *p*-CH), 125.8(Ar-*iPr*, C-*iPr*), 123.6(Ar-*iPr*, CH), 28.7(Ar-*iPr*,CH₃), 24.6(Ar-*iPr*, CH-(CH₃)₂), 22.6(Ar-*iPr*,CH₃). Sample for elemental analysis was obtained by recrystallization in toluene, resulting in a 1:1 toluene adduct of **4** calculated (%) for [C₄₄H₄₇AgF₃N₃O₃S][C₇H₈]: C 64.15, H 5.81, N 4.40, found C 64.83, H 5.78, N 4.19.

Figure S1: Structure of compound 4, with hydrogen atoms and solvent of crystallization (toluene) omitted for clarity. Selected bond distances (\AA): Ag(1)-N(1), 2.526(6); Ag(1)-N(2), 2.347(6); Ag(1)-N(3), 2.492(6); Ag(1)-O(1), 2.638(6).



Computational Details

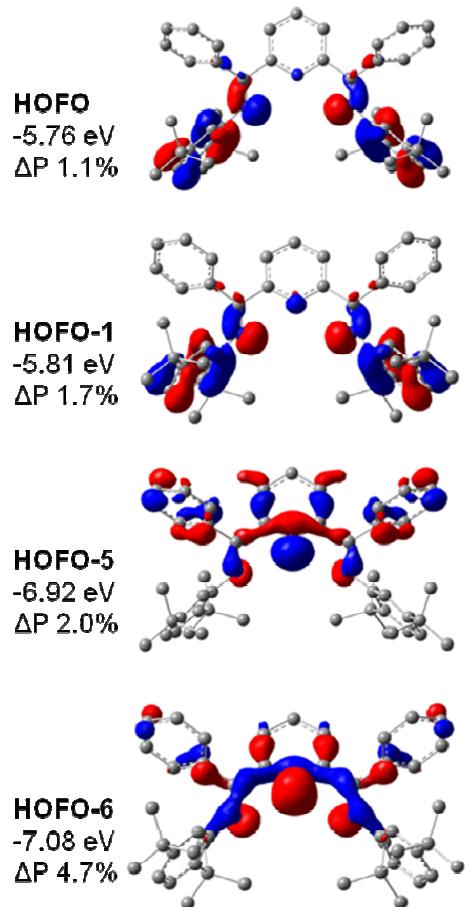
Density Functional Theory (DFT) calculations have been performed using the Gaussian 03 package.¹ Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation (XC) functional with the mixed basis set (DZVP on Ag and TZVP on all other atoms). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force gradients were used to determine the nature of the stationary points.

The analysis of the molecular orbital (MO) compositions in terms of occupied and unoccupied orbitals of the fragment species (HOFOs and LUFOs, respectively), the construction of MO diagram (Figure 5) and Mayer bond orders were calculated using the AOMix program.^{2,3} Atomic charges and Wiberg bond orders in the natural atomic orbital basis were evaluated by using the natural population analysis (NPA).⁴

Table S1. Comparison of selected bond lengths (Å) and angles (deg) between the experimental (X-ray) and DFT optimized geometries of $[\{\text{ArN}=\text{CPh}\}_2(\text{NPh})]\text{Ag}^+(\text{OTf})^-$ ($\text{Ar} = 2,5\text{-tBu}_2\text{C}_6\text{H}_3$ **3**; $2,6\text{-iPr}_2\text{C}_6\text{H}_3$ **4**).

Compound 3			Compound 4		
	calcd	exptl		calcd	exptl
$\text{Ag-N}_{\text{imine}}$					
Ag(1)-N(2)	2.6074	2.523(7)	Ag(1)-N(1)	2.5836	2.526(6)
			Ag(1)-N(3)	2.5631	2.492(6)
$\text{Ag-N}_{\text{pyridine}}$					
Ag(1)-N(1)	2.3873	2.270(9)	Ag(1)-N(2)	2.377	2.347(6)
Ag(1)-O(1)	2.3745	2.331(8)	Ag(1)-O(1)	2.404	2.638(6)
N(2)-C(4)	1.2892	1.291(9)	N(1)-C(1)	1.2873	1.263(11)
			N(3)-C(7)	1.2880	1.284(9)
O(1)-S(1)	1.5016	1.421(10)	S(1)-O(3)	1.4768	1.411(5)
O(2)-S(1)	1.4777	1.410(8)	S(1)-O(2)	1.468	1.425(5)
			S(1)-O(1)	1.500	1.449(6)
N(1)-Ag(1)-O(1)	104.978	105.7(3)	N(2)-Ag(1)-O(1)	96.107	86.37(16)
N(2)#1-Ag(1)-N(2)	129.379	133.1(3)	N(3)-Ag(1)-O(1)	103.46	95.52(18)
			N(1)-Ag(1)-O(1)	104.43	99.10(18)
			N(3)-Ag(1)-N(1)	126.130	131.1(3)

Figure S2. The four most significant donor orbitals of the pincer ligand in **3**. The energy of each orbital is provided with the label. The change in the orbital population (%) upon the interaction with Ag(I) is provided by the value of ΔP and indicates the relative charge transfer from this orbital.



References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A. ; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: 2003.
2. Gorelsky, S. I.; version 6.36 ed.; University of Ottawa: Ottawa, Canada, 2007.
3. Gorelsky, S. I.; Lever, A. B. P. *Journal of Organometallic Chemistry* **2001**, *635*, 187-196.
4. Reed, A. E.; Weinstock, R. B.; Weinhold, F. J. *Chem. Phys.* **1985**, *83*, 735-746.

ⁱ Jurca, T., Dawson, K., Mallov, I., Burchell, T., Yap, G.P.A., Richeson, D.S., *Dalton Trans*, **2010**, 39, 1266-1272