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Supporting Informations for:

Silver(I)-organophosphane complexes of electron withdrawing CF₃- or NO₂-substituted scorpionate ligands

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Material and methods

Elemental analyses (C,H,N,S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin-Elmer System 2000 FT-IR instrument. IR annotations used: m = medium, mbr = medium broad, s = strong, sbr = strong broad, sh = shoulder, w = weak. ¹H-, ¹³C-, ¹⁹F- and ³¹P-NMR spectra were recorded on a Oxford-400 Varian spectrometer (400.4 MHz for ¹H, 100.1 MHz for ¹³C, 376.8 MHz for ¹⁹F, and 162.1 MHz for ³¹P). Chemical shifts for ¹H NMR spectra are relative to internal Me₄Si. ¹³C NMR spectra were run with ¹H decoupling, and the chemical shifts are reported in ppm vs Me₄Si. ¹⁹F NMR and ³¹P NMR chemical shifts were referenced to an external CFCl₃ and an 85% H₃PO₄ standard, respectively. The ³¹P NMR spectroscopic data were accumulated with ¹H decoupling. NMR annotations used: d = doublet, dd = double doublet, dbr = broad doublet, m = multiplet, mbr = broad multiplet, s = singlet, sbr = broad singlet, t = triplet. Electrospray mass spectra (ESIMS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone mobile phase. The compounds were added to the reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 µl) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 µl min⁻¹, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in

this ESIMS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the IsoPro 3.0 computer program.¹

Syntheses

K[H₂B(3-(NO₂)pz)₂] (1). IR (Nujol, cm⁻¹): 3143w, 3122w (CH), 2423m, 2381m, 2266m, 2201w (BH), 1667m (C=C + C=N), 1530s (ν_{asym} NO₂), 1301s (ν_{sym} NO₂), 616m (NO₂), 442m. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

K[H₂B(3-(CF₃)pz)₂] (2). IR (nujol, cm⁻¹): 3183m (CH), 2407s, 2277m (BH), 1508m (C=C + C=N), 667s, 652sh, 626m, 552m, 517w, 458br, 382s, 338w, 280w. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 283 (100) [H₂B(3-(CF₃)pz)₂]⁻, 605 (20) [2 H₂B(3-(CF₃)pz)₂ + K]⁻.

{[H₂B(3-(NO₂)pz)₂]Ag[P(C₆H₅)₃]₂} (3). IR (nujol, cm⁻¹): 3164w (CH), 2417m, 2380w (BH), 1535s (C=C + C=N), 1503m (ν_{asym} NO₂), 1303s (ν_{sym} NO₂), 617m (NO₂), 542m, 512s, 500sbr, 487sbr (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 632 (100) {Ag[P(C₆H₅)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

{[H₂B(3-(NO₂)pz)₂]Ag[P(*o*-C₆H₄CH₃)₃]} (4). IR (nujol, cm⁻¹): 3149w, 3125w, 3044w (CH), 2441m, 2364m (BH), 1588m, 1531s (C=C + C=N), 1489s (ν_{asym} NO₂), 1306s (ν_{sym} NO₂), 615m (NO₂), 565m, 558sh, 522m, 515m, 464s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*o*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

{[H₂B(3-(NO₂)pz)₂]Ag[P(*m*-C₆H₄CH₃)₃]} (5). IR (nujol, cm⁻¹): 3142w, 3119w, 3041w (CH), 2453m, 2389m (BH), 1588m, 1530s (C=C + C=N), 1489s (ν_{asym} NO₂), 1307s (ν_{sym} NO₂), 614w (NO₂), 548s, 538sh, 471m, 454s, 451s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*m*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

{[H₂B(3-(NO₂)pz)₂]Ag[P(*p*-C₆H₄CH₃)₃]} (6). IR (nujol, cm⁻¹): 3142w (CH), 2458m, 2386m (BH), 1597m, 1537s (C=C + C=N), 1495s (ν_{asym} NO₂), 1309s (ν_{sym} NO₂), 614m (NO₂), 520s, 505s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*p*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

{[H₂B(3-(NO₂)pz)₂]Ag[PCH₃(C₆H₅)₂]} (7). IR (nujol, cm⁻¹): 3151w, 3147w, 3051w (CH), 2426m, 2412m (BH), 1585w, 1523m (C=C + C=N), 1483s (ν_{asym} NO₂), 1298s (ν_{sym} NO₂), 617m (NO₂), 498s, 479s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 508 (100) {Ag[P(CH₃)(C₆H₅)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 237 (100) [H₂B(3-(NO₂)pz)₂]⁻.

{[H₂B(3-(CF₃)pz)₂]Ag[P(C₆H₅)₃]₂} (8). IR (nujol, cm⁻¹): 3173w (CH), 2396m (BH), 1581m (C=C + C=N), 540s, 509s, 495s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 632 (100) {Ag[P(C₆H₅)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 283 (100) [H₂B(3-(CF₃)pz)₂]⁻.

{[H₂B(3-(CF₃)pz)₂]Ag[P(*o*-C₆H₄CH₃)₃]} (9). IR (nujol, cm⁻¹): 3146w (CH), 2436m, 2352m (BH), 1589s (C=C + C=N), 565s, 557s, 515m, 462s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*o*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 283 (100) [H₂B(3-(CF₃)pz)₂]⁻.

{[H₂B(3-(CF₃)pz)₂]Ag[P(*m*-C₆H₄CH₃)₃]} (10). IR (nujol, cm⁻¹): 3161w (CH), 2407m, 2372m (BH), 1590s (C=C + C=N), 544s, 519sh, 445s (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*m*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 283 (100) [H₂B(3-(CF₃)pz)₂]⁻.

{[H₂B(3-(CF₃)pz)₂]Ag[P(*p*-C₆H₄CH₃)₃]} (11). IR (nujol, cm⁻¹): 3108w (CH), 2403mbr, 2386m (BH), 1597s (C=C + C=N), 552w, 515sbr (R₃P). ESIMS (major positive-ions, CH₃OH), *m/z* (%): 717 (100) {Ag[P(*p*-C₆H₄CH₃)₃]₂}⁺. ESIMS (major negative-ions, CH₃OH), *m/z* (%): 283 (100) [H₂B(3-(CF₃)pz)₂]⁻, 674 (20) [2H₂B(3-(CF₃)pz)₂ + Ag]⁻.

X-ray crystallography

A suitable crystal of each sample covered with a layer of hydrocarbon oil was selected and mounted with paratone-N oil on a cryo-loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data of K[H₂B(3-(NO₂)pz)₂], [H₂B(3-(NO₂)pz)₂]Ag[P(C₆H₅)₃]₂, [H₂B(3-(NO₂)pz)₂]Ag[P(*p*-C₆H₄CH₃)₃], and [H₂B(3-(CF₃)pz)₂]Ag[P(C₆H₅)₃] were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å). The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated

with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using a multi-scan technique (SADABS).² The X-ray intensity data of $K[H_2B(3-(CF_3)pz)_2]$ were measured at 193(2) K on a Siemens P4 diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package.² $K[H_2B(3-(NO_2)pz)_2]$ crystallizes in the monoclinic $P2_1/c$ space group. The β -angle ($90.073(1)^\circ$) was uncomfortably closer to 90° indicating possible orthorhombic cell choice. However, data merging was relatively poor and the structure solution was difficult when the orthorhombic cell was used as compared to the monoclinic option. $K[H_2B(3-(NO_2)pz)_2]$ was solved in $P2_1/c$ using direct methods. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms on the pyrazolyl rings and on boron were located from the difference map and included, and refined isotropically. Final check using PLATON did not identify a higher symmetry alternative.³ $K[H_2B(3-(CF_3)pz)_2]$ structure was solved using direct methods. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms on the boron were located from the difference map and included, and refined isotropically. Pyrazolyl ring hydrogen atoms were placed at calculated positions and refined using a riding model. The silver adducts $[H_2B(3-(NO_2)pz)_2]Ag[P(C_6H_5)_3]_2$ and $[H_2B(3-(NO_2)pz)_2]Ag[P(p-C_6H_4CH_3)_3]$ crystallize in the monoclinic crystal system as well. $[H_2B(3-(CF_3)pz)_2]Ag[P(C_6H_5)_3]$ crystallizes in $P-1$ space group, and there are two chemically similar molecules in the asymmetric unit. Their structures were solved using direct methods. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on boron were located from the difference map and included. Further details are in the cif files.

References

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