Carbonyl complexes of copper(i) stabilized by bridging fluorinated pyrazolates and halide ions

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Syntheses of neutral and anionic, di- and tetra-nuclear copper carbon monoxide complexes using binary copper(i) pyrazolate precursors are reported. The reaction of {[3,5-(CF3)2Pz]Cu}3 (2), {[4-Cl-3,5-(CF3)2Pz]Cu}3 (3) or {[3,4,5-(CF3)3Pz]Cu}3 (4) with CO in CH2Cl2 led to copper carbonyl complexes. They however, lose CO quite easily if not kept under a CO atmosphere. Compounds {[3,5-(CF3)2Pz]Cu(CO)}2 (5) and {[3,4,5-(CF3)3Pz]Cu(CO)}2 (7) were characterized by X-ray crystallography. They are dinuclear species with a Cu2N4 core. The reaction of {[3,5-(CF3)2Pz]Cu}3 with CO in the presence of [NEt4]Br or [NEt4][3,5-(CF3)2Pz] affords relatively more stable [NEt4][{[3,5-(CF3)2Pz]Cu(CO)}4(?4-Br)] (8) and [NEt4]{[3,5-(CF3)2Pz]3Cu2(CO)2} (9). The related [NEt4][{[4-Cl-3,5-(CF3)2Pz]Cu(CO)}4(?4-Br)] (10) and [NEt4][{[4-Cl-3,5-(CF3)2Pz]Cu(CO)}4(?4-Cl)] (11) can be synthesized using {[4-Cl-3,5-(CF3)2Pz]Cu}3, CO and [NEt4]Br or [NEt4]Cl. The X-ray structures show that 8, 10 and 11 are tetranuclear species with terminal Cu-CO groups and quadruply bridging Cl- and Br- ions. Compound 9 features an anionic cage of nearly D3h symmetry formed by three bridging [3,5-(CF3)2Pz]- ions and two terminal Cu-CO moieties. Theoretical calculations show that bonding in these 16- and 18-electron copper complexes follows Dewar-Chatt-Duncanson (DCD) model, where the CO stretching frequencies correlate well to the orbital interaction energy ?Eorb. The major Cu-CO interaction however is electrostatic in nature. Further theoretical exploration of the role of the substituent at pyrazolyl ring 4-position between -H, -Cl, and -CF3, shows a slight decrease in covalent character of the Cu-CO interaction and

diminished ?-back bonding as pyrazolate groups become more weakly donating with added electron withdrawing substituents.