The objective of this work is to employ spin-polarized density functional theory (sDFT) calculations for the exploration of ultrathin magnetic films with large magnetic moments and a strong perpendicular anisotropy. Monolayer films of Fe1−xCox (with x=0, 0.25, 0.5, 0.75, and 1) on Rh(001) were addressed to study their magnetic properties using the all-electron full-potential linearized augmented plane wave (FLAPW) method in film geometry. We studied the magnetic order of these films including structural relaxations of the topmost layers. Fe1−xCox monolayer films were found to be ferromagnetic (FM) in a broad range of Co content x with a maximum magnetic moment of 2.8 μB and of an out-of-plane magneto-crystalline anisotropy of 0.25 meV per magnetic atom at x=0.5. The sDFT results were mapped onto a classical Heisenberg model, demonstrating FM Fe-Co and Co-Co couplings, while the Fe-Fe interaction is antiferromagnetic on Rh(001). The ordering temperature of the FeCo film was estimated to be well above room temperature (482 K)