1,3,5-Triphospha-1,4-pentadiene-2,4-diamine reacts with  $[M(CO)_4L]$  (M = Mo, L = nbd (norbornadiene); M = W, L = 2 CH<sub>3</sub>CN) to give the chelate complexes  $[M(CO)_4(PMes\{C(NHCy)PMes\}_{2^-} \kappa P^1, P^3)]$ . In contrast, an unusual intramolecular rearrangement occurred with  $[Cu(CH_3CN)_4]PF_6$  leading to the dimeric copper(I) complex  $[Cu(CNCy)\{PHMesPMesC(NHCy)PMes-\kappa P^1, P^3\}]_2(PF_6)_2$ . The mechanism of the rearrangement was supported by quantum mechanical calculations. The transition metal complexes were characterized by multinuclear NMR spectroscopy, mass spectrometry, infrared spectroscopy and X-ray crystallography.