Treatment of the aromatic nitrile complexes \( \text{trans-}[\text{PtCl}_2(\text{RC}_6\text{H}_4\text{CN})_2] \) with the aryl amidoximes \( p-\text{R'C}_6\text{H}_4\text{C}=(\text{NH}_2)=\text{NOH} \), followed by addition of 1 equiv of AgOTf and then 5 equiv of \( \text{Et}_3\text{N} \) leads to the chelates \( \text{PtCl} \{\text{H}N=\text{C}(\text{RC}_6\text{H}_4)\text{ON}=\text{C}(\text{C}_6\text{H}_4\text{R}'-p)\text{NC}(\text{RC}_6\text{H}_4)=\text{NH}\} \) (15 examples; yields 71–88% after column chromatography) derived from the platinum(II)-mediated coupling between metal-activated nitriles and amidoximes. The combined experimental and theoretical results indicate that the coupling with the nitrile ligands involves both the \( \text{HON} \) and monodeprotonated \( \text{NH}_2 \) groups of the amidoximes.