

Substitution of CO by picolines and amines in $\text{RhCl}(\text{CO})(\text{PR}_3)_2$. Synthesis and crystal structure of *cis*- $\text{RhCl}(3\text{-pic})\{\text{P}(\text{OPh})_3\}_2$.

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The title complex, *cis*- $\text{RhCl}(3\text{-pic})\{\text{P}(\text{OPh})_3\}_2$ (3-pic = 3 picoline), has been prepared with two other isostructural rhodium complexes, respectively with 4-picoline and $\text{CH}_2=\text{CH}=\text{CH}_2\text{NH}_2$. The $\text{RhCl}(3\text{-pic})\{\text{P}(\text{OPh})_3\}_2$ compound crystallizes in space group *P* with $a = 10.531(6)$, $b = 12.025(9)$, $c = 15.943(8)$ Å, $\alpha = 83.01(5)$, $\beta = 79.46(4)$, $\gamma = 86.33(5)^\circ$, $Z = 2$. The $\text{RhCl}(\text{amine})\{\text{P}(\text{OPh})_3\}_2$ complexes were obtained in the reactions of $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$, $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ (cod = cycloocta-1,5-diene) or $\text{RhCl}(\text{CO})\{\text{P}(\text{OPh})_3\}_2$ with amines. CO substitution by amines $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ complexes [$\text{PR}_3 = \text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, $\text{P}(\text{O-}o\text{-MeC}_6\text{H}_4)_3$, $\text{P}(\text{O-}m\text{-MeC}_6\text{H}_4)_3$, PEt_2Ph , PEtPh_2 , PMe_2Ph , PMePh_2 or PPh_3] is limited by steric properties of amine and PR_3 ligands. 3-Picoline substitutes CO only in complexes with PR_3 ligands with cone angle $\gamma \leq 140^\circ$ [16]. The rate of CO substitution by 2-picoline is less than half that by 3-picoline.

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