



^{31}P -NMR and X-ray studies of new rhodium(I) β -ketoiminato complexes
 $\text{Rh}(\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2)(\text{CO})(\text{PZ}_3)$ where $\text{PZ}_3 = \text{PPh}_3$, PCy_3 , P(OPh)_3 or $\text{P}(\text{NC}_4\text{H}_4)_3$.

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Streszczenie

The substitution of the CO ligand in rhodium(I) β -ketoiminato complexes $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ ($\{\text{O},\text{N}\}=\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2$; $\text{R}_1, \text{R}_2=\text{CF}_3, \text{Me}, \text{CMe}_3$ in several combinations) by phosphorus ligands PZ_3 ($\text{PZ}_3=\text{PCy}_3, \text{PPh}_3, \text{P}(\text{OPh})_3, \text{P}(\text{NC}_4\text{H}_4)_3$) leads to $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes characterised by $^{31}\text{P}\{^1\text{H}\}$ -NMR and X-ray methods. The stronger σ -donor PZ_3 ligands ($\text{PZ}_3=\text{PCy}_3, \text{PPh}_3$) substitute almost exclusively the CO group *trans* to N, forming *P-trans*-to-N isomers. The complexes $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PCy}_3)$ (**II**), $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ (**III**), $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PPh}_3)$ (**IV**) and $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ (**V**) are of a square-planar geometry with a slight tetrahedral distortion around the rhodium atom in **II**, **III** and **V**. The $\text{Rh}\cdots\text{P}(\text{PCy}_3)$ bonds are slightly longer than the $\text{Rh}\cdots\text{P}(\text{PPh}_3)$ bonds. The reaction of stoichiometric amounts of the less basic $\text{P}(\text{OPh})_3$ or $\text{P}(\text{NC}_4\text{H}_4)_3$ ligands leads to the formation of both isomers of the $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{P}(\text{OPh})_3)$ or $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{P}(\text{NC}_4\text{H}_4)_3)$ complex in comparable yields. The $\text{Rh}\cdots\text{P}(\text{P}(\text{OPh})_3)$ distance (2.195(2) Å) in the isomer of $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ with $\text{P}(\text{OPh})_3$ coordinated *trans* to N (**VI**) is ca. 0.04 Å longer than in the isomer of that complex with $\text{P}(\text{OPh})_3$ coordinated *trans* to O (**VII**). The CO substitution in $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ by PZ_3 ligands ($\text{PPh}_3, \text{PCy}_3, \text{P}(\text{OPh})_3$) causes the shortening of the $\text{Rh}\cdots\text{C}(\text{CO})$ bond by ca. 0.04 Å compared to $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})_2$ (**I**), making difficult the coordination of another PZ_3 ligand, especially one with stronger σ -donor properties. The more π -acceptor $\text{P}(\text{OPh})_3$ ligands form bis-phosphito complexes and $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)\{\text{P}(\text{OPh})_3\}_2$ (**VIII**) exhibits inequivalence of the two $\text{P}(\text{OPh})_3$ ligands in solution (^{31}P -NMR) as well as in solid form (X-ray). The substitution of the CO ligand in rhodium(I) β -ketoiminato complexes $\text{Rh}(\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2)(\text{CO})_2$ ($\text{R}_1, \text{R}_2=\text{CF}_3, \text{Me}, \text{CMe}_3$) by phosphorus ligands PZ_3 ($\text{PZ}_3=\text{PPh}_3, \text{PCy}_3, \text{P}(\text{OPh})_3, \text{P}(\text{NC}_4\text{H}_4)_3$) leads to $\text{Rh}(\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes of square-planar geometry. The formation of *P-trans*-to-N isomers is observed for stronger σ -donor, PZ_3 ligands ($\text{PZ}_3=\text{PPh}_3, \text{PCy}_3$) and comparable yields of *P-trans*-to-N and *P-trans*-to-O isomers are observed when less basic PZ_3 ligands are used ($\text{PZ}_3=\text{P}(\text{OPh})_3, \text{P}(\text{NC}_4\text{H}_4)_3$). The structures of the $\text{Rh}(\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes were confirmed in solution (^{31}P -NMR) and in solid form (X-ray).

Słowa kluczowe

Rhodium(I) complexes, β -Ketoiminato complexes, X-ray,
Substitution reaction

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