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^{31}P-NMR and X-ray studies of new rhodium(I) β-ketoiminato complexes $Rh(R_1C(O)CHC(NH)R_2)(CO)(PZ_3)$ where PZ_3=PPh_3, PCy_3, $P(OPh)_3$ or $P(NC_4H_4)_3$.

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Artykuł

The substitution of the CO ligand in rhodium(I) β-ketoiminato complexes $Rh(R_1\{O,N\}R_2)(CO)_2$ ($\{O,N\}=R_1C(O)CHC(NH)R_2$; R_1, $R_2=CF_3$, Me, CMe_3 in several combinations) by phosphorus ligands PZ_3 ($PZ_3=PCy_3$, PPh_3, $P(OPh)_3$, $P(NC_4H_4)_3$) leads to $Rh(R_1\{O,N\}R_2)(CO)(PZ_3)$ complexes characterised by $^{31}P\{^1H\}$-NMR and X-ray methods. The stronger σ-donor PZ_3 ligands ($PZ_3=PCy_3$, PPh_3) substitute almost exclusively the CO group *trans* to N, forming P-*trans*-to-N isomers. The complexes $Rh(CF_3\{O,N\}Me)(CO)(PCy_3)$ (**II**), $Rh(CF_3\{O,N\}CMe_3)(CO)(PCy_3)$ (**III**), $Rh(CF_3\{O,N\}Me)(CO)(PPh_3)$ (**IV**) and $Rh(CF_3\{O,N\}CMe)(CO)(PPh_3)$ (**V**) are of a square-planar geometry with a slight tetrahedral distortion around the rhodium atom in **II**, **III** and **V**. The Rh–$P(PCy_3)$ bonds are slightly longer than the Rh–$P(PPh_3)$ bonds. The reaction of stoichiometric amounts of the less basic $P(OPh)_3$ or $P(NC_4H_4)_3$ ligands leads to the formation of both isomers of the $Rh(R_1\{O,N\}R_2)(CO)(P(OPh)_3)$ or $Rh(R_1\{O,N\}R_2)(CO)(P(NC_4H_4)_3)$ complex in comparable yields. The Rh–$P(P(OPh)_3)$ distance (2.195(2) Å) in the isomer of $Rh(CF_3\{O,N\}CMe_3)(CO)(P(OPh)_3)$ with $P(OPh)_3$ coordinated *trans* to N (**VI**) is ca. 0.04 Å longer than in the isomer of that complex with $P(OPh)_3$ coordinated *trans* to O (**VII**). The CO substitution in $Rh(R_1\{O,N\}R_2)(CO)_2$ by PZ_3 ligands (PPh_3, PCy_3, $P(OPh)_3$) causes the shortening of the Rh–C(CO) bond by ca. 0.04 Å compared to $Rh(CF_3\{O,N\}Me)(CO)_2$ (**I**), making difficult the coordination of another PZ_3 ligand, especially one with stronger σ-donor properties. The more π-acceptor $P(OPh)_3$ ligands form bis-phosphito complexes and $Rh(CF_3\{O,N\}CMe_3)\{P(OPh)_3\}_2$ (**VIII**) exhibits inequivalence of the two $P(OPh)_3$ 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 $Rh(R_1C(O)CHC(NH)R_2)(CO)_2$ (R_1, $R_2=CF_3$, Me, CMe_3) by phosphorus ligands PZ_3 ($PZ_3=PPh_3$, PCy_3, $P(OPh)_3$, $P(NC_4H_4)_3$) leads to $Rh(R_1C(O)CHC(NH)R_2)(CO)(PZ_3)$ complexes of square-planar geometry. The formation of P-*trans*-to-N isomers is observed for stronger σ-donor, PZ_3 ligands ($PZ_3=PPh_3$, 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 ($PZ_3=P(OPh)_3$, $P(NC_4H_4)_3$). The structures of the $Rh(R_1C(O)CHC(NH)R_2)(CO)(PZ_3)$ 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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