Synthese und Struktur der Nitridokomplexe $(Ph_3Sb)_2Cl_3Os{\equiv}N\text{-}RhCl(COD)$, $(Me_2PhP)_2(PhCN)Cl_2Re{\equiv}N\text{-}RhCl_2(C_5Me_5)$, $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}OsCl_2(CO)_3][OsCl_3(CO)_3]$ und $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}ReCl_4\text{-}N{\equiv}ReCl(NCPh)(PMe_2Ph)_3][OsCl_4(CO)_2]$

Synthesis and Structure of the Nitrido Complexes $(Ph_3Sb)_2Cl_3Os{\equiv}N\text{-}RhCl(COD)$, $(Me_2PhP)_2(PhCN)Cl_2Re{\equiv}N\text{-}RhCl_2(C_5Me_5)$, $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}OsCl_2(CO)_3][OsCl_3(CO)_3]$, and $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}ReCl_4\text{-}N{\equiv}ReCl(NCPh)(PMe_2Ph)_3][OsCl_4(CO)_2]$

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The reaction of $(Ph_3Sb)_2Cl_3OsN$ with $[Rh(\mu\text{-}Cl)(COD)]_2$ in benzonitrile yields the heteronuclear nitrido complex $(Ph_3\underline{Sb})_2Cl_3Os{\equiv}N\text{-}RhCl(COD)$ (**1**). It crystallizes as dark brown blocks in the triclinic space group $P1$ with $a = 1080.09(5)$, $b = 1173.15(5)$, $c = 1702.28(9)$ pm, $\alpha = 101.214(4)$, $\beta = 92.923(8)$, $\gamma = 92.836(5)^\circ$, and $Z = 2$. The complex fragment RhCl(COD) is coordinated to the osmium nitrido complex *via* a linear nitrido bridge Os≡N-Rh, with a bond angle Os-N-Rh = 175.3(5)° and distances Os-N = 168.6(6) and Rh-N = 184.6(6) pm. The heteronuclear complexes $(Me_2PhP)_2(PhCN)Cl_2Re{\equiv}N\text{-}RhCl_2(C_5Me_5)$ (**2**) and $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}OsCl_2(CO)_3][OsCl_3(CO)_3]$ (**3**) are obtained by the reaction of $(Me_2PhP)_3Cl_2ReN$ with $[RhCl(\mu\text{-}Cl)(C_5Me_5)]_2$ and $[OsCl(\mu\text{-}Cl)(CO)_3]_2$, respectively, in benzonitrile. **2** forms orange red crystals with the composition $\mathbf{2}\cdot C_6H_5CN$ in the monoclinic space group $P2_1/c$ and $a = 910.23(7)$, $b = 1255.4(1)$, $c = 3761.5(3)$ pm, $\beta = 95.617(9)^\circ$ and $Z = 4$. The nitrido bridge Re≡N-Rh to the complex fragment $[RhCl_2(C_5Me_5)]$ has a bond angle Re-N-Rh of 171.9(3)° and distances Re-N = 169.4(5) and Rh-N = 201.9(5) pm. **3** forms yellow orange plates with the monoclinic space group $P2_1/c$ and $a = 1113.74(5)$, $b = 2038.5(2)$, $c = 2130.1(1)$ pm, $\beta = 90.298(6)^\circ$ and $Z = 4$. The nitrido bridge within the complex cation $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}OsCl_2(CO)_3]^+$ is characterized by a bond angle Re-N-Os of 167.7(4)° and distances Re-N = 169.5(8) and Os-N = 206.1(8) pm. The ligands of the octahedral anion $[OsCl_3(CO)_3]^-$ are in a facial arrangement. The synthesis of **3** yields $[\{(Me_2PhP)_3(PhCN)ClRe{\equiv}N\}_2ReCl_4][OsCl_4(CO)_2]$ (**4**) as a byproduct. It crystallizes as red brown blocks with the composition $\mathbf{4}\cdot CH_2Cl_2$ in the space group $P1$ and $a = 1444.2(1)$, $b = 1536.3(1)$, $c = 2150.5(2)$ pm, $\alpha = 87.41(1)$, $\beta = 88.54(1)$, $\gamma = 62.453(8)^\circ$ and $Z = 2$. In the two symmetry independent, centrosymmetric cations $[(Me_2PhP)_3(PhCN)ClRe{\equiv}N\text{-}ReCl_4\text{-}N{\equiv}ReCl(NCPh)(PMe_2Ph)_3]^{2+}$ of **4** two nitrido complexes $[(Me_2PhP)_3(PhCN)ClReN]^+$ coordinate with their terminal nitrido ligands a central, square planar $ReCl_4$ unit. The resulting nitrido bridges with bond angles Re(1)-N(1)-Re(2) = 167.0(4)° and Re(3)-N(2)-Re(4) = 168.9(4)°, respectively, exhibit distances Re(1)-N(1) = 172.4(7) and Re(2)-N(1) = 197.1(7) or Re(3)-N(2) = 171.4(6) and Re(4)-N(2) = 197.1(6) pm. The two carbonyl ligands of the anion $[OsCl_4(CO)_2]^{2-}$ are in *cis* position.

Key words: Rhenium, Osmium, Rhodium, Nitrido Complexes, Crystal Structure