

Preliminary communication

α -DIIMINES AS MONODENTATE OR BRIDGING LIGANDS; SYNTHESIS AND CHARACTERIZATION OF PALLADIUM(II) AND RHODIUM(I) DI(*t*-BUTYL)DIIMINE COMPLEXES

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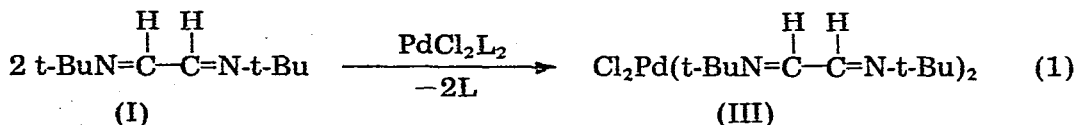
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Summary

Complexes of di(*t*-butyl)diimine with $\text{PdCl}_2(\text{PhCN})_2$ and with $(\text{CO})_2\text{RhCl}$ dimer have been synthesized and characterized. The diimine ligand is monodentate bonded in $\text{PdCl}_2(\text{t-butyl}diimine)_2$, while in $(\text{t-butyl}diimine)-[\text{Rh}(\text{CO})_2\text{Cl}]_2$ it bridges two $\text{Cl}(\text{CO})_2\text{Rh}$ units.

A large number of metaldiimine complexes have been reported in the literature in which the diimine ligand acts as a σ, σ or σ, π chelating ligand [1–7]. We now report the isolation and characterization of the first examples of novel types of metal–diimine complexes in which the diimine molecule behaves as a monodentate* or as a bridging ligand. Our interest in these complexes originated in a study of the course of the palladium, rhodium or zinc catalyzed hydrogenation of diimines.

Addition of an excess of $\text{t-BuN}=\text{CHCH}=\text{N-t-Bu}$ (I) to a solution of $[\text{PdCl}_2(\text{PhCN})_2]$ (II) in CH_2Cl_2 afforded a yellow solid (III) (yield 75%) which according to elemental analysis had the stoichiometry $\text{PdCl}_2(\text{t-BuN}=\text{CHCH}=\text{N-t-Bu})_2$ and which existed in CHCl_3 as a monomer (osmometry) (eq. 1). ^1H NMR spectroscopy (in CDCl_3) revealed the presence in III of two



equivalent diimine ligands each coordinated to palladium via only one site. The intramolecular non-equivalence (on the NMR time scale up to 100°C in

* The presence in $[\text{Mo}(\text{CO})_5(\text{PhNCHCHNPh})]$ of monodentate bonded diimine was recently established [8].

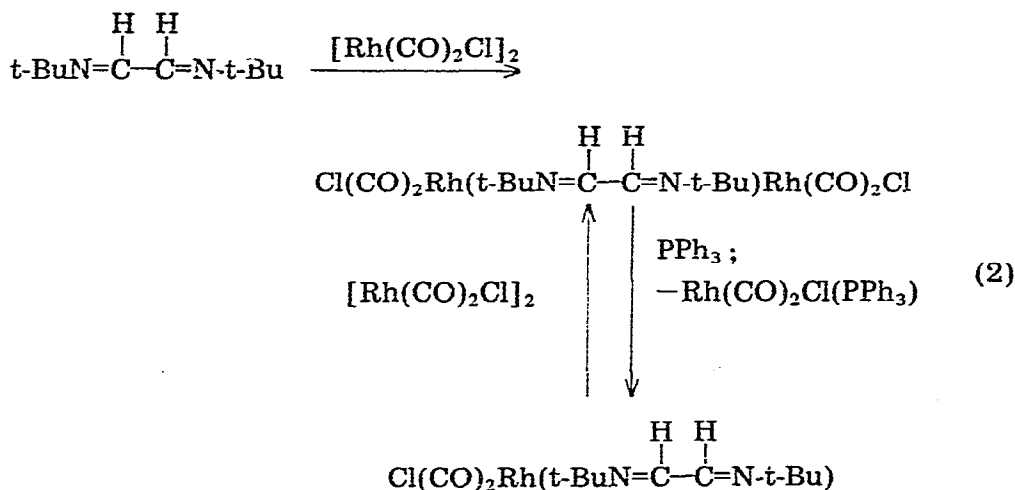
toluene- d_8) of the two $-\text{C}(\text{H})=\text{N}-t\text{-Bu}$ groups in I was inferred from the observation of an AX-pattern for the imine protons (δ_A 7.59, δ_X 9.81 ppm; J_{AX} 7.8 Hz) and two singlets for the $t\text{-Bu}$ protons (1.43 and 1.81 ppm). The ^{13}C NMR spectrum (in CDCl_3) showed two sets of resonances due to two distinct sites in the diimine molecule [$-(\text{H})\text{C}=\text{N}-\text{C}(\text{CH}_3)_3$ coord. (free): $-\text{C}(\text{H})=$, 168.31 (154.82); $=\text{N}-\text{C}$ 65.50 (59.93); CH_3 31.71 (29.03) ppm].

The observation of only a small upfield shift* for the imine-C atom ($\Delta\delta$ 8.56 ppm) in III with respect to the free ligand (δ 56.94 ppm) indicates that the $-(\text{H})\text{C}=\text{N}-t\text{-Bu}$ site is coordinated to palladium via a $\sigma\text{-N}-\text{Pd}$ bond.

The strong $\nu(\text{C}=\text{N})$ band at 1630 cm^{-1} (free ligand I, 1640 cm^{-1}) and a shoulder at 1574 cm^{-1} due to the coordinated $-(\text{H})\text{C}=\text{N}-$ in the IR spectrum of III provides further support for the proposed bonding scheme.

Reaction of I in CH_2Cl_2 with $\text{PdCl}_2(\text{PhCN})_2$ in a 1/1 ratio gave an immediate yellow precipitate of $\text{PdCl}_2(t\text{-BuN}=\text{CHCH}=\text{N}-t\text{-Bu})$ (IV) which was insoluble in common organic solvents: in $\text{DMSO}-d_6$ the two $-\text{C}=\text{N}-t\text{-Bu}$ groups of I in IV are isochroneous (^1H NMR: $\text{CH}=\text{N}$ 8.77; $t\text{-Bu}$ 1.49 ppm) which is, however, compatible with both bridging (coordination polymer) and chelating (σ,σ) diimine.

Unambiguous evidence for a bridging di(t -butyl)diimine ligand emerged from a study of the reaction of I with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (eq. 2). NMR spec-



troscopy revealed that at a 1/2 diimine/Rh ratio the imine protons appear at 9.28 ppm and the $t\text{-Bu}$ protons at 1.67 ppm, which points to equivalent $t\text{-BuN}=\text{CH}-$ groups for the diimine ligand in a 2/1 complex V. A second distinct resonance pattern (VI) was observed at a 1/1 ratio ($\text{N}=\text{CH}$ 8.58 and $\text{N}-t\text{-Bu}$ 1.50 ppm). Further increase of the diimine/Rh ratio gave, in addition to the pattern of VI, the pattern of the free ligand. This 1/1 complex VI is not stable.

*The imine ligand in $(t\text{-BuNCHCHN}-t\text{-Bu})\text{Fe}(\text{CO})_5$ is σ,π bonded to the iron. The marked high field shifts for the ^{13}C resonances are $\Delta\delta(\text{HC}=\text{N}-t\text{-Bu})$ 14.9 ppm; $\Delta\delta(\text{HC}-\text{N}-t\text{-Bu})$ 51.3 ppm [4.9].

The 1/2 complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2(\text{t-BuN}=\text{CHCH}=\text{N-t-Bu})$ (V) was isolated as a stable orange coloured solid [60% yield: monomeric in CHCl_3 found (calcd.) for $[\text{Rh}(\text{CO})_2\text{Cl}]_2$: 512 (556.8)] from the 1/2 reaction of I with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in hexane. The chemical shift equivalence of the $-\text{C}=\text{N-t-Bu}$ groups of the diimine ligand both in the ^1H (vide supra) and in the ^{13}C NMR spectrum in CDCl_3 ($\text{HC}=\text{N}$, 163.78; $\text{N}-\text{C}$ 66.48 and $-\text{CH}_3$, 30.70 ppm) confirms that the diimine ligand bridges the two Rh centres via nitrogen (upfield shift for $\text{CH}=\text{N}$ 9.54 ppm vide supra).

The IR spectrum of V shows four strong bands in the $\nu(\text{C}=\text{O})$ region (2080, 2064, 2010, 1984 cm^{-1}) arising from ν_{sym} and ν_{asym} of two sets of two *cis*-positioned CO ligands. Other examples of bidentate bridging ligands in rhodium chemistry are bipyridine, 2-(aminomethyl)pyridine, etc. [10–15].

The limited thermal stability of the 1/1 complex VI prevented its isolation in the pure state. However, the reaction of VI prepared in situ in CH_2Cl_2 with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (VI/Rh ratio 1/1) afforded the 1/2 complex V. On the other hand, addition of one equivalent of PPh_3 to a solution of V in CH_2Cl_2 gave the 1/1 complex VI together with $\text{Rh}(\text{CO})_2(\text{PPh}_3)\text{Cl}$.

Steric effects may play an important role in the formation of both the monodentate bonded di(*t*-BuNCHCHN-*t*-Bu)palladium complex III and the diimine bridged $\text{Rh}(\text{CO})_2\text{Cl}$ complex V, because diimines containing secondary N-substituents react with $[\text{PdCl}_2(\text{PhCN})_2]$ to give only the corresponding 1/1 complexes and with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ only the bridged form. This is supported by the observation that the CH_3 ^{13}C resonance of the coordinated $-(\text{H})\text{C}=\text{N-t-Bu}$ group both in III and V are multiplets, indicating hindered rotation of the *t*-Bu groups as a result of steric crowding about the respective metal atoms.

Acknowledgement

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