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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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Summary

Complexes of di(t-butyl)diimine with $PdCl_2(PhCN)_2$ and with $(CO)_2RhCl$ dimer have been synthesized and characterized. The diimine ligand is monodentate bonded in $PdCl_2$(t-butyldiimine)$_2$, while in (t-butyldiimine)-$[Rh(CO)_2Cl]_2$ it bridges two $Cl(CO)_2Rh$ 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 t-BuN=CHCH=N-t-Bu (I) to a solution of $[PdCl_2(PhCN)_2]$ (II) in CH_2Cl_2 afforded a yellow solid (III) (yield 75%) which according to elemental analysis had the stoichiometry $PdCl_2$(t-BuN=CHCH=N-t-Bu)$_2$ and which existed in $CHCl_3$ as a monomer (osmometry) (eq. 1). ^{1}H NMR spectroscopy (in $CDCl_3$) revealed the presence in III of two

$$\underset{\text{(I)}}{2\ \text{t-BuN=C(H)—C(H)=N-t-Bu}} \xrightarrow[-2L]{PdCl_2L_2} \underset{\text{(III)}}{Cl_2Pd(\text{t-BuN=C(H)—C(H)=N-t-Bu})_2} \qquad (1)$$

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 [Mo(CO)$_5$(PhNCHCHNPh)] of monodentate bonded diimine was recently established [8].

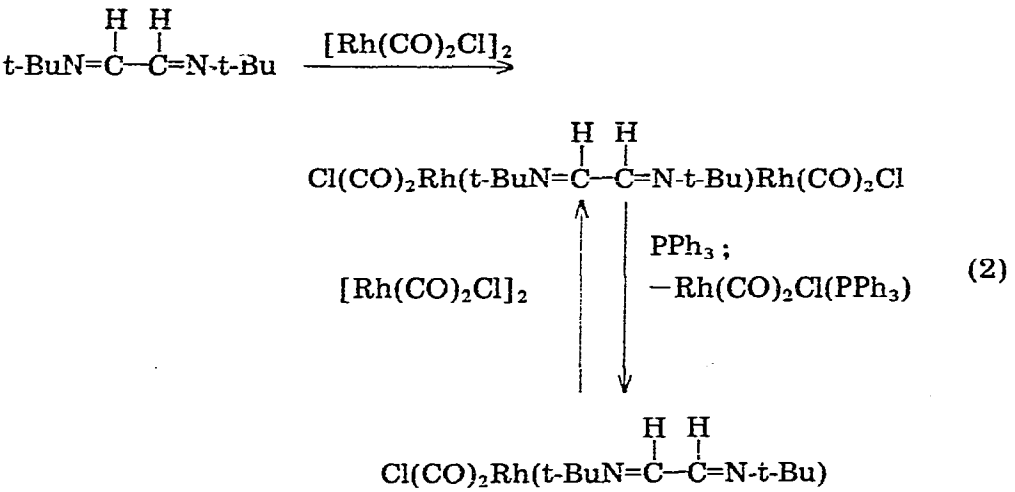
toluene-d_8) of the two —C(H)=N-t-Bu groups in I was inferred from the observation of an AX-pattern for the imine protons (δ_A 7.59, δ_X 9.81 ppm; J_{AX} 7.8 Hz) and two singlets for the t-Bu protons (1.43 and 1.81 ppm). The ^{13}C NMR spectrum (in $CDCl_3$) showed two sets of resonances due to two distinct sites in the diimine molecule [—(H)C=N—C$(CH_3)_3$ coord. (free): —C(H)=,168.31 (154.82); =N—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 —(H)C=N-t-Bu site is coordinated to palladium via a σ-N—Pd bond.

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

Reaction of I in CH_2Cl_2 with $PdCl_2(PhCN)_2$ in a 1/1 ratio gave an immediate yellow precipitate of $PdCl_2$(t-BuN=CHCH=N-t-Bu) (IV) which was insoluble in common organic solvents: in DMSO-d_6 the two —C=N-t-Bu groups of I in IV are isochroneous (^1H NMR: CH=N 8.77; t-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 $[Rh(CO)_2Cl]_2$ (eq. 2). NMR spec-



(2)

troscopy revealed that at a 1/2 diimine/Rh ratio the imine protons appear at 9.28 ppm and the t-Bu protons at 1.67 ppm, which points to equivalent t-BuN=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 (N=CH 8.58 and N—t-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-BuNCHCHN-t-Bu)$Fe(CO)_3$ is σ,π bonded to the iron. The marked high field shifts for the ^{13}C resonances are $\Delta\delta$(HC=N-t-Bu) 14.9 ppm; $\Delta\delta$(HC=N-t-Bu) 51.3 ppm [4,9].

The 1/2 complex $[Rh(CO)_2Cl]_2$(t-BuN=CHCH=N-t-Bu) (V) was isolated as a stable orange coloured solid [60% yield: monomeric in $CHCl_3$ found (calcd.) for L$[Rh(CO)_2Cl]_2$: 512 (556.8)] from the 1/2 reaction of I with $[Rh(CO)_2Cl]_2$ in hexane. The chemical shift equivalence of the —C=N-t-Bu groups of the diimine ligand both in the ^1H (vide supra) and in the ^{13}C NMR spectrum in $CDCl_3$ (HC=N, 163.78; N—C 66.48 and —CH_3, 30.70 ppm) confirms that the diimine ligand bridges the two Rh centres via nitrogen (upfield shift for CH=N 9.54 ppm vide supra).

The IR spectrum of V shows four strong bands in the ν(C≡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 $[Rh(CO)_2Cl]_2$ (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 $Rh(CO)_2(PPh_3)Cl$.

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 $Rh(CO)_2Cl$ complex V, because diimines containing secondary N-substituents react with $[PdCl_2(PhCN)_2]$ to give only the corresponding 1/1 complexes and with $[Rh(CO)_2Cl]_2$ only the bridged form. This is supported by the observation that the CH_3 ^{13}C resonance of the coordinated —(H)C=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.

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