



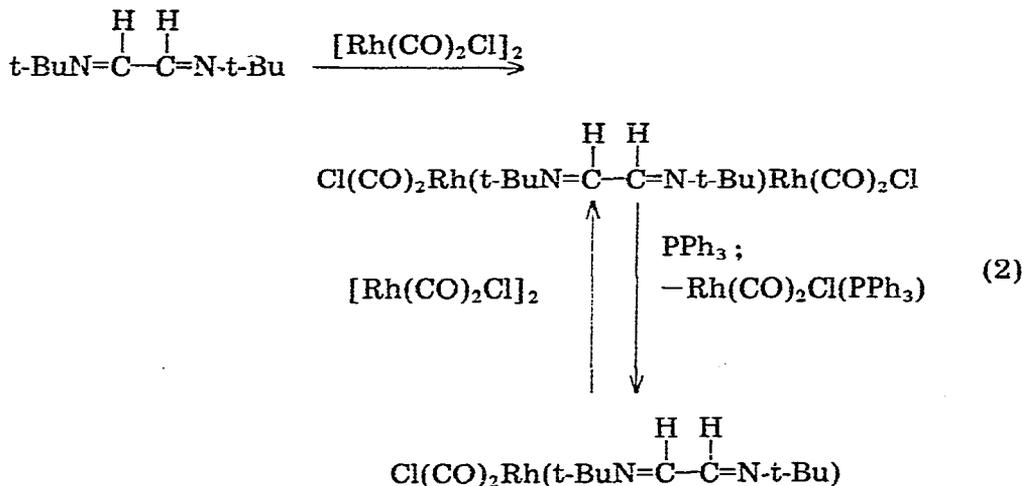
toluene- $d_8$ ) of the two  $-\text{C}(\text{H})=\text{N}-t\text{-Bu}$  groups in I was inferred from the observation of an AX-pattern for the imine protons ( $\delta_A$  7.59,  $\delta_X$  9.81 ppm;  $J_{AX}$  7.8 Hz) and two singlets for the  $t\text{-Bu}$  protons (1.43 and 1.81 ppm). The  $^{13}\text{C}$  NMR spectrum (in  $\text{CDCl}_3$ ) 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);  $\text{CH}_3$  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 ( $\delta$  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  $1630\text{ cm}^{-1}$  (free ligand I,  $1640\text{ cm}^{-1}$ ) and a shoulder at  $1574\text{ w cm}^{-1}$  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  $\text{CH}_2\text{Cl}_2$  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 ( $^1\text{H}$  NMR:  $\text{CH}=\text{N}$  8.77;  $t\text{-Bu}$  1.49 ppm) which is, however, compatible with both bridging (coordination polymer) and chelating ( $\sigma,\sigma$ ) 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  $(t\text{-BuNCHCHN}-t\text{-Bu})\text{Fe}(\text{CO})_3$  is  $\sigma,\pi$  bonded to the iron. The marked high field shifts for the  $^{13}\text{C}$  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  $\text{CHCl}_3$  found (calcd.) for  $\text{L}[\text{Rh}(\text{CO})_2\text{Cl}]_2$ : 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  $^1\text{H}$  (vide supra) and in the  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  ( $\text{HC}=\text{N}$ , 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  $\nu(\text{C}\equiv\text{O})$  region (2080, 2064, 2010, 1984  $\text{cm}^{-1}$ ) arising from  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{PPh}_3$  to a solution of V in  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_3$   $^{13}\text{C}$  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.

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### References

- 1 H. tom Dieck and I.W. Renk, *Chem. Ber.*, 104 (1971) 92 and references cited therein.
- 2 H. tom Dieck and I.W. Renk, *Chem. Ber.*, 104 (1971) 110.
- 3 H. tom Dieck and H. Bruder, *J. Chem. Soc., Chem. Commun.*, (1977) 24 and references cited therein.
- 4 D. Leibfritz and H. tom Dieck, *J. Organometal. Chem.*, 105 (1976) 255.
- 5 P. Krumholz, O.A. Serra and M.A. De Paoli, *Inorg. Chim. Acta*, 15 (1975) 25.
- 6 H. Li Chum and T. Rabockai, *Inorg. Chim. Acta*, 19 (1976) 145 and references cited therein.
- 7 D. Walther, *Z. Chem.*, 15 (1975) 72.
- 8 L.H. Staal, D.J. Stufkens and A. Oskam, to be published.
- 9 C. Tänzer, R. Price, E. Breitmaier, G. Jung and W. Voelter, *Angew. Chem.*, 82 (1970) 23, 957.
- 10 G.K.N. Reddy and B.R. Ramesh, *J. Organometal. Chem.*, 87 (1975) 347.
- 11 D. Brodzki and G. Pannetier, *J. Organometal. Chem.*, 104 (1976) 241.
- 12 D.N. Lawson and G. Wilkinson, *J. Chem. Soc.*, (1965) 1900.
- 13 G. Winkhaus and H. Singer, *Chem. Ber.*, 99 (1966) 3593.
- 14 W. Hieber und V. Frey, *Chem. Ber.*, 99 (1966) 2607.
- 15 A.L. Balch, *J. Amer. Chem. Soc.*, 98 (1976) 8049 and references cited therein.