adducts of metal acetyls are close analogues of Fischer-type carbenes.

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Registry No. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)\cdot BF_3$, 73104-94-6; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)\cdot BCl_3$, 73104-95-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)\cdot BBr_3$, 73104-96-8; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)\cdot AlMe_3$, 73104-97-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)\cdot AlBr_3$, 73104-98-0; $(CH_3)_2CO\cdot BF_3$, 661-27-8; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\cdot BCl_3$, 43198-12-5; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\cdot BBr_3$, 41666-89-1; $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$, 12203-87-1; $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4\cdot BF_3$, 39466-88-1; $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4\cdot BCl_3$, 39334-00-4; $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4\cdot BBr_3$, 39333-98-7; $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4\cdot AlBr_3$, 39466-84-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(=O)CH_3)$, 12108-22-4; $(CH_3)_2CO$, 67-64-1.

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Novel Bonding Modes of α-Diimines. Synthesis and Characterization of $[MCl_2L(\alpha\text{-diimine})]$ and $[MCl_2(\alpha\text{-diimine})_n]$ (M = Pd, Pt; L = Phosphine, Arsine; $n = 1$, 2) Containing σ,σ-N,N′, σ-N, or $\sigma\text{-N} \leftrightarrow \sigma\text{-N}'$ Bonded α-Diimines

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Compounds of the type $[PdX_2(RN{=}CHCH{=}NR)_n]$ (n = 1, 2; X = Cl, Br, I) and $[M^{II}Cl_2L(RN{=}CHCH{=}NR)]$ (L = monodentate phosphine or arsine; M = Pd, Pt; R = alkyl) have been synthesized starting from the α-diimine (R-dim) and $[PdCl_2(PhCN)_2]$ or $[(M^{II}Cl_2L)_2]$, respectively. Three types of metal–α-diimine interactions have been established: (i) σ,σ-N,N′ chelate bonded R-dim in $[PdX_2(\text{R-dim})]$; (ii) σ-N monodentate bonded R-dim in monomeric *trans*-$[PdX_2(\text{R-dim})_2]$ (^1H and ^{13}C NMR spectroscopy reveals that the R-dim ligand has the anti conformation with the C–C and Pd–N bonds of the coordinated part of the ligand in the cis configuration. This brings the β-imine proton (δ(CH) 9.70) in the proximity of the palladium atom.); (iii) $\sigma\text{-N} \leftrightarrow \sigma\text{-N}'$ bonded R-dim in the monomeric complexes, *trans*-$[M^{II}Cl_2L(\text{R-dim})]$, which contain monodentate (σ-N) bonded R-dim in the slow-exchange limit (−55 °C). At 120 °C (fast-exchange limit) the complexes are fluxional by an intramolecular process which involves a pentacoordinate intermediate containing σ,σ-N,N′ bonded R-dim. These novel bonding modes for the R-dim ligand in these palladium and platinum complexes are a clear indication of the versatile coordination properties of the R-dim ligand compared with ligands such as bpy and phen, which also contain the N=CC=N skeleton.

A large number of metal–α-diimine complexes have been reported in which the α-diimine (R-dim) ligand acts as a σ,σ-chelating ligand.[1-4] To date only a limited number of complexes of R-dim ligands with Pt, Pd, or Rh have been described. Maresca, Natile, and Cattalini[5] reported the isolation of $[PtCl_2(C_2H_4)(\text{R-dim})]$ (R-dim = *N,N′*-di(cyclopropyl- or *p*-tolyl)biacetyl diimine) while Brodie and Otsuka[6] recently described the synthesis of palladium complexes with *N,N′*-(1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-diylidene)dianiline ligands. In these complexes the R-dim ligand is also σ,σ-chelating.

These observations seem to be consistent with the σ,σ-bonding mode found for the related bipyridine (bpy) and phenanthroline (phen) ligands which like the R-dim ligand have two N lone pairs suitably positioned for symmetric coordination. Recently, Dixon[7] showed that the solid-state structure of $[PtCl(PEt_3)_2(\text{phen})]BF_4$ contained two different Pt–N distances, pointing to a monodentate coordinated phen ligand. However, in solution no evidence for such monodentate behavior of the phen or bpy ligand in related $[PtCl(PEt_3)_2(\text{bpy})]BF_4$ was found. This was explained by a fluxional process involving a simple oscillatory motion of the bpy and phen ligands via a trigonal-bipyramidal transition state. It is important to note that this is a low-energy process due to the favorable orientation of the N lone pairs. In the phen ligand this lone-pair orientation is locked because of the rigid phen ring system. Apparently the bpy ligand also contains extra rigidity leading to high preference for the σ,σ-chelating bonding mode.[8-10] It can be anticipated that the monodentate bonding mode would be stabilized when conformations of the coordinating ligand having the coordinated and noncoordinated N atoms in trans positions would become more favorable. Comparison of the molecular skeleton of the R-dim and bpy ligands reveals that rotation around the NC–CN bond is less hindered in the R-dim ligand, both in the free molecule and in the monodentate bonded form.

In this paper we report the isolation and characterization of the first examples of stable metal–R-dim complexes in which the R-dim molecule is monodentate bonded.[11] Moreover, complexes will be described in which at low temperatures the R-dim molecule is bonded to the metal atom via one N atom while at higher temperatures the R-dim molecule rapidly exchanges its point of attachment to the metal from one N to the other. It will be shown that in particular the degree of flexibility of the R-dim skeleton plays an important role in the bonding mode of the R-dim ligand in these complexes.

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Experimental Section

Preparation of Compounds. α-Diimines (R-dim = RNCHCHNR) were prepared by the method of tom Dieck et al.,[13] except for bis(1,1-dimethylpropyl)diimine of which the preparation will be outlined below. The starting complexes *trans*-$[PdX_2(PhC{\equiv}N)_2]$ (X = Cl, Br), *cis*-$[PtCl_2(PhC{\equiv}N)_2]$, $[PtCl_2(1,5\text{-octadiene})]$, $[\{PdCl_2(C_2H_4)\}_2]$, $[\{PdCl_2(PR_3)\}_2]$ (R = Ph, Et), $[\{PdCl_2(AsEt_3)\}_2]$, and $[\{PtCl_2(PR_3)\}_2]$ (R = Ph, Bu) were prepared by methods described elsewhere.[14] The preparation of the new metal complexes, which were carried out in a N_2 atmosphere, are outlined below. Solvents were distilled before use.

Bis(1,1-dimethylpropyl)diimine. A solution of (1,1-dimethylpropyl)amine (10 mmol) in diethyl ether (25 mL) was added to a stirred 30% aqueous glyoxal solution (5 mmol). The reaction mixture was stirred for 15 min, and the ether and water layers were separated. A further amount of the amine (2 mmol) was added to the ether layer, which contained a mixture of the iminooxo compound ((1,1-dimethylpropyl)imino)acetaldehyde and the corresponding R-dim.[15] This reaction mixture was stirred for 30 min and washed with water (5 × 50 mL). The etheral solution was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Distillation of the oily residue afforded pure colorless bis(1,1-dimethylpropyl)diimine (bp 60 °C (10 mm); 60% yield).

***cis*-$[PdX_2(R\text{-}dim)]$ (X = Cl, Br).** R-dim (1 mmol) was added to a stirred solution of *trans*-$[PdX_2(PhC{\equiv}N)_2]$ (1 mmol) in dichloromethane (25 mL). The reaction mixture was stirred for 15 min and concentrated to 5 mL. Addition of diethyl ether (25 mL) resulted in complete precipitation of the complex as a yellow or yellow-orange solid which was filtered off. The complex was washed with dichloromethane (3 × 25 mL), methanol (3 × 25 mL), and diethyl ether (3 × 25 mL) and then dried in vacuo at room temperature; yield 60–80%. Anal. Calcd for $[PdCl_2(R\text{-}dim)]$ (R = *i*-Pr): C, 30.24; H, 5.04; N, 8.82. Found (R = *i*-Pr): C, 30.32; H, 4.93; N, 8.96. Calcd (R = *t*-Bu): C, 34.74; H, 5.79; N, 8.11. Found (R = *t*-Bu): C, 35.04; H, 5.45; N, 7.98.

***cis*-$[PdI_2(i\text{-}Pr\text{-}dim)]$.** A solution of NaI (2.2 mmol) in acetone (10 mL) was added to a stirred suspension of *cis*-$[PdCl_2(i\text{-}Pr\text{-}dim)]$ (1 mmol) in acetone (10 mmol). This mixture was stirred for 10 min, evaporated until dryness, washed with water (5 × 10 mL), and then dried over P_2O_5; yield 90% of brownish red [*cis*-$PdI_2(i\text{-}Pr\text{-}dim)$].

***trans*-$[PdX_2(R\text{-}dim)_2]$ (X = Cl, Br; R = *t*-Bu, $EtMe_2C$) Starting from *trans*-$[PdX_2(PhC{\equiv}N)_2]$.** R-dim (3 mmol) was added to a stirred solution of *trans*-$[PdX_2(PhC{\equiv}N)_2]$ (1 mmol) in dichloromethane (25 mL). After being stirred for 1 h the solution was filtered through a short layer of aluminum oxide. The filtrate was concentrated to 5 mL, and the complex precipitated as a yellow solid by addition of hexane (50 mL). The precipitate was filtered off and washed with hexane (5 × 25 mL) and then dried in vacuo at room temperature; yield 75%. Purification was achieved by recrystallization from a dichloromethane/hexane mixture. Anal. Calcd for $[PdCl_2(R\text{-}dim)_2]$ (R = *t*-Bu): C, 46.74; H, 7.85; mol wt 514. Found (R = *t*-Bu): C, 46.24; H, 7.83; mol wt 525 ($CHCl_3$). Calcd (R = $EtMe_2C$): C, 50.57; H, 8.23; N, 9.83; Cl, 12.44; mol wt 578. Found (R = $EtMe_2C$): C, 49.98; H, 8.38; N, 9.57; Cl, 12.46; mol wt 586 ($CHCl_3$). Calcd for $[PdBr_2(t\text{-}Bu\text{-}dim)_2]$: C, 39.85; H, 6.69; N, 9.29. Found: C, 39.68; H, 6.82; N, 9.16.

***trans*-$[PdCl_2(R\text{-}dim)_2]$ (R = *t*-Bu, $EtMe_2C$) Starting from $[\{PdCl_2(C_2H_4)\}_2]$.** R-dim (3 mmol) was added to a stirred suspension of $[\{PdCl_2(C_2H_4)\}_2]$ (0.5 mmol) in dichloromethane (25 mL). After being stirred for 1 h the complex was worked up as described above starting from *trans*-$[PdX_2(PhC{\equiv}N)_2]$.

***trans*-$[PdI_2(t\text{-}Bu\text{-}dim)_2]$.** A solution of NaI (2.2 mmol) in acetone (10 mL) was added to a stirred solution of *trans*-$[PdCl_2(t\text{-}Bu\text{-}dim)_2]$ (1 mmol) in acetone (10 mL). The reaction mixture which was stirred for 10 min was evaporated to dryness, washed with water (5 × 10 mL), and then dried over P_2O_5; yield 90% of brownish red *trans*-$[PdI_2(t\text{-}Bu\text{-}dim)_2]$.

$[MCl_2(XPh_3)(t\text{-}Bu\text{-}dim)]$ (M = Pd, Pt; X = P, As). *t*-Bu-dim (3 mmol) was added to a stirred suspension of $[\{MCl_2(XPh_3)\}_2]$ (1 mmol) in 25 mL of dichloromethane. The reaction mixture was stirred for 1 h and then filtered. The filtrate was concentrated, and the resulting solid washed with hexane (6 × 25 mL) and dried in vacuo at room temperature. Yields amounted to 85% for both the Pd compounds (orange) and the Pt compounds (yellow). It appeared to be difficult to obtain these compounds analytically pure which is due to the formation of $[\{MCl_2(XPh_3)\}_2(R\text{-}dim)]$ during the recrystallization procedure. Anal. Calcd for $[PtCl_2(PPh_3)(t\text{-}Bu\text{-}dim)]$: C, 48.28; H, 5.06; N, 4.02; Cl, 10.18; P, 4.45; mol wt 697. Found: C, 47.68; H, 5.02; N, 3.59; Cl, 10.94; P, 4.18; mol wt 680 ($CHCl_3$). Calcd. for $[PdCl_2(PPh_3)(R\text{-}dim)]$ (R = *t*-Bu): C, 55.32; H, 5.80; N, 4.60; Cl, 11.66. Found (R = *t*-Bu): C, 54.27; H, 5.76; N, 4.30; Cl, 12.66. Calcd (R = $EtMe_2C$): C, 55.66; H, 6.18; N, 4.40; P, 4.87. Found (R = $EtMe_2C$): C, 55.31; H, 6.00; N, 3.84; P, 4.88.

$[PdCl_2(XEt_3)(t\text{-}Bu\text{-}dim)]$ (X = P, As) and $[PtCl_2(PBu_3)(t\text{-}Bu\text{-}dim)]$. *t*-Bu-dim (1 mmol) was added to a stirred suspension of $[\{MCl_2XR_3\}_2]$ (0.33 mmol) in 2 mol of acetone-d_6 or chloroform-d_1. The reaction mixture was stirred for 10 min and filtered through a short layer of aluminum oxide. The resulting clear solutions were then used for the NMR experiments described below in the text.

Physical Measurements. Microanalyses were performed by W. J. Buis of the Institute for Organic Chemistry T.N.O. (Utrecht, The Netherlands). Molecular weights were measured in chloroform by using a 302 B Hewlett-Packard vapor pressure osmometer. ^1H NMR spectra were recorded on a Varian A-60, T-60, or HA-100 spectrometer with tetramethylsilane (Me_4Si) as internal standard; ^{13}C NMR spectra were obtained on a Varian CFT-20 using either chloroform-d_1 or Me_4Si as internal standard; ^{31}P NMR spectra were obtained on a Varian XL-100 using H_3PO_4 as external standard, and the ^{195}Pt NMR spectra were obtained on a Bruker WH 90 with $[\delta\text{-}[\{PtCl_2(PBu_3)\}_2]$ as internal standard $[\delta\text{-}[\{PtCl_2(PBu_3)\}_2] = 1121$ ppm].[16] Infrared spectra were measured on a Beckman 4250 spectrophotometer as Nujol mulls between CsI plates or as dichloromethane solutions in a polystyrene cell (ν(M—Cl)) or NaCl cell (ν(C=N)).

Results

The reaction of *trans*-$[PdX_2(PhC{\equiv}N)_2]$ (X = Cl, Br) with R-dim (*R* = *i*-Pr, *t*-Bu, $EtMe_2C$–, PhMeCH–, c-C_6H_{11}, 4-tolyl, 2,6-$Me_2C_6H_3$, and 2,4,6-$Me_3C_6H_2$) in a 1/1 molar ratio in dichloromethane afforded stable yellow or yellow-orange solids. According to elemental analyses these solids have $[PdX_2(R\text{-}dim)]$ stoichiometry. The use of an excess of R-dim up to a molar ratio of 1/3 still afforded the 1/1 complexes except for R-dim (R = *t*-Bu or $EtMe_2C$–) which afforded the 1/2 complexes *trans*-$[PdX_2(R\text{-}dim)_2]$.[17] The corresponding iodide complexes were synthesized via the 1/2 reaction of the chloride complexes with NaI in acetone.

Attempts to synthesize the corresponding 1/1 or 1/2 platinum–R-dim complexes starting from *cis*-$[PtCl_2(PhC{\equiv}N)_2]$ or $[PtCl_2(1,5\text{-cyclooctadiene})]$ using equimolar amounts or excess of diimine failed. However, heating the novel five-coordinate platinum compound $[(PtCl_2(olefin)(R\text{-}dim)]$ (R = *i*-Pr, *t*-Bu, and $EtMe_2C$) between 90 and 120 °C resulted in quantitative formation of the 1/1 complex *cis*-$[PtCl_2(R\text{-}dim)]$.[18]

The use of platinum or palladium complexes $[\{MCl_2L\}_2]$ in which one of the coordination sites is blocked by a phosphine or arsine ligand resulted in the synthesis of novel types of 1/1 and 2/1 metal–α-diimine complexes. It appeared that the nature of the coligand had a large influence on the type of products formed as well as on the ease of isolation of the complexes. When triarylphosphines or arsines are used, both the 2/1 and 1/1 platinum–*t*-Bu-dim complexes could be isolated as stable yellow solids in nearly quantitative yields. In the case of M = Pd only the 1/1 complexes could be isolated.

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Table I. Infrared Spectra of $[MCl_2(R\text{-dim})]$, $[MCl_2(R\text{-dim})_2]$, and $[MCl_2L(R\text{-dim})]$ Complexes

compd	solvent	ν(C=N), cm^{-1}	ν(M–Cl), cm^{-1}
	Ligand		
i-Pr-dim	Nujol	1633	
t-Bu-dim	Nujol	1632	
$EtMe_2C$-dim	Nujol	1636	
	Chelating		
cis-$[PdCl_2(i\text{-Pr-dim})]$	Nujol	1598 br	330 s, 365 s
cis-$[PdBr_2(i\text{-Pr-dim})]$	Nujol		210 w, 250 w
cis-$[PdCl_2(t\text{-Bu-dim})]$	Nujol	1604 br	318 s, 350 s
cis-$[PdCl_2(EtMe_2C\text{-dim})]$	Nujol	1601 br	318 s, 337 s
cis-$[PdBr_2(EtMe_2C\text{-dim})]$	Nujol	1590 m	–, 251 m
	Monodentate		
trans-$[PdCl_2(t\text{-Bu-dim})_2]$	Nujol (CH_2Cl_2)	1624 s	342 s (345 s)
trans-$[PdBr_2(t\text{-Bu-dim})_2]$	Nujol (CH_2Cl_2)	1620 s	255 m (252 s)
trans-$[PdCl_2(EtMe_2C\text{-dim})_2]$	Nujol	1618 s	343 s
trans-$[PdBr_2(EtMe_2C\text{-dim})_2]$	Nujol (CH_2Cl_2)	1615 m (1619 m)	249 m (251 s)
	Fluxional		
trans-$[PdCl_2(PPh_3)(t\text{-Bu-dim})]$	Nujol	1623 m	348 m
trans-$[PdCl_2(PPh_3)(EtMe_2C\text{-dim})]$	Nujol	1620 m	345 s
trans-$[PtCl_2(PPh_3)(t\text{-Bu-dim})]$	Nujol (CH_2Cl_2)	1620 m (1620 m)	342 m (339 s)
trans-$[PtCl_2(AsPh_3)(t\text{-Bu-dim})]$	Nujol	1621 m	343 m
trans-$[PdCl_2(PEt_3)(t\text{-Bu-dim})]$	CH_2Cl_2	1624 m	345 s
trans-$[PdCl_2(AsEt_3)(t\text{-Bu-dim})]$	CH_2Cl_2	1623 m	344 s
trans-$[PtCl_2(PBu_3)(t\text{-Bu-dim})]$	CH_2Cl_2	1619 m	340 s

In contrast, the use of trialkylphosphines or arsines as coligands yielded the 2/1 platinum or palladium complexes as stable solids. The 1/1 complexes were formed in solution. However, attempts to isolate the 1/1 complexes from these solutions (acetone, dichloromethane, or methanol) either by precipitation with hexane or by concentration of the solutions resulted in crystallization of the 2/1 complex while the equivalent of *t*-Bu-dim formed remained in solution. Addition of a second equivalent of *t*-Bu-dim to a suspension of the 2/1 palladium–*t*-Bu-dim complex in acetone yielded quantitatively a solution of the 1/1 complex.

Discussion

σ,σ-N,N′ Chelating R-dim: 1/1 Complexes *cis*-$[PdCl_2(R\text{-dim})]$. The structural characterization of the 1/1 complexes was difficult because of the insolubility of the complexes in noncoordinating solvents. Accordingly, determination of the aggregation state in solution was impossible. The two IR absorptions in Nujol at 330 and 365 cm^{-1} of almost equal intensity in the spectra of the *cis*-$[PdCl_2(R\text{-dim})]$ complexes could be assigned to the ν_{sym}- and ν_{asym}(Pd–Cl) of two cis-positioned Cl atoms (see Table I). This assignment was confirmed by the absence of these bands in the corresponding $[PdI_2(R\text{-dim})]$ and $[PdBr_2(R\text{-dim})]$ complexes. In the Br compounds the Pd–Br stretching modes were found at 210 and 250 cm^{-1}.

^1H and ^{13}C NMR spectra of solutions of the 1/1 complexes R = *i*-Pr, *t*-Bu, and $EtMe_2C$– in $Me_2SO\text{-}d_6$ (see Tables II and III) showed that the respective ^1H and ^{13}C resonances of the ligand were shifted to lower field upon coordination. Only a single resonance pattern was observed for the R group, the N=CH protons, and the imine-carbon atoms which indicates that in solution both R-N=CH halves of the R-dim ligand are equal. These results are compatible with a structure consisting of monomeric, square-planar $[PdX_2(R\text{-dim})]$ units, containing a σ,σ-coordinated chelating R-dim ligand, possibly stacked[19] in the solid analogous to the recently proposed structures of $[PtCl_2(bpy)]$ and $[Rh(CO)_2(bpy)]Cl$.[20,21] Interestingly, tom Dieck and Svoboda reported the isolation of the corresponding $NiBr_2$ complexes which, however, are monomers with a tetrahedral coordination geometry.[22]

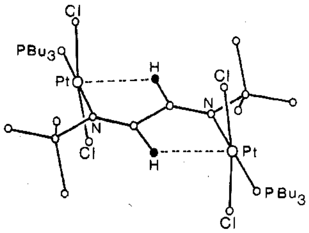

Figure 1. Molecular geometry of $[PtCl_2(PBu_3)_2(t\text{-Bu-dim})]$ (calculated Pt···H_β distance amounts to 2.6 Å [23]).

σ-N-Monodentate R-dim: 1/2 Complexes *trans*-$[PdX_2(R\text{-dim})_2]$. Detailed structural information could be obtained for the 1/2 complexes *trans*-$[PdX_2(R\text{-dim})_2]$ (X = Cl, Br, I; R = *t*-Bu, $EtMe_2C$) which are monomers in chloroform. The IR spectra of *trans*-$[PdCl_2(R\text{-dim})_2]$ compounds showed a strong absorption at 342 cm^{-1}, which was assigned to the ν_{asym} (Pd–Cl) of trans-positioned Cl atoms; this band was found at 255 cm^{-1} for the ν_{asym}(Pd–Br) in spectra of the corresponding Br derivatives (see Table I).

Conclusive evidence for the monodentate behavior of the R-dim ligand in these complexes was obtained by ^1H and ^{13}C NMR spectroscopy which will be illustrated for the *t*-Bu-dim complexes. The data for the respective complexes have been compiled in Tables II and III. ^1H and ^{13}C NMR spectra of *trans*-$[PdX_2(t\text{-Bu-dim})_2]$ in $CDCl_3$ revealed that the resonances arising from the two *t*-BuN=CH halves of the ligand are anisochronous over the temperature range studied (−60 to +60 °C) which excludes the occurrence of intramolecular exchange processes. Moreover, intermolecular exchange could be excluded because excess ligand did not affect the resonance pattern. The HC=N protons (δ 7.47 d and 9.70 d ppm)

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(19) A study concerning the conductivity properties of this type of compound is in progress.

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Table II. ^{1}H NMR Spectra of [MX_2(R-dim)], [MX_2(R-dim)$_2$], and [MCl_2(R-dim)] Complexes

compd	solvent (temp, °C)^a	δ^b			
		CH$_3$	CH$_2$	CH	HC=N
		Ligand			
i-Pr-dim	$CDCl_3$	1.24 d		3.43 m	7.93 s
t-Bu-dim	$CDCl_3$	1.30 s			7.93 s
$EtMe_2C$-dim	$CDCl_3$	0.85 t, 1.23 s	1.63 q		7.88 s
		Chelating			
[$PdCl_2$(*i*-Pr-dim)]	Me_2SO-d_6	1.41 d		4.55 m	8.05 s
[$PdBr_2$(*i*-Pr-dim)]	Me_2SO-d_6	1.42 d		4.87 m	8.30 s
[PdI_2(*i*-Pr-dim)]	Me_2SO-d_6	1.42 d		5.05 m	8.39 s
[$PdCl_2$(*t*-Bu-dim)]	Me_2SO-d_6	1.49 s			8.77 s
[$PdBr_2$(*t*-Bu-dim)]	Me_2SO-d_6	1.53 s			8.57 s
[$PdCl_2$($EtMe_2C$-dim)]	Me_2SO-d_6	0.91 t, 1.53 s	1.83 q		8.57 s
		Monodentate			
[$PdCl_2$(*t*-Bu-dim)$_2$]	$CDCl_3$	1.43 s, 1.81 s			7.60 d, 9.91 d^c
[$PdBr_2$(*t*-Bu-dim)$_2$]	$CDCl_3$	1.43 s, 1.80 s			7.47 d, 9.70 d^c
[PdI_2(*t*-Bu-dim)$_2$]	$CDCl_3$	1.40 s, 1.80 s			7.35 d, 9.40 d^c
[$PdCl_2$($EtMe_2C$-dim)$_2$]	$CDCl_3$	0.92 t, 1.38 s, 1.82 s	1.70 m		7.52 d, 9.92 d^c
[$PdBr_2$($EtMe_2C$-dim)$_2$]	$CDCl_3$	0.96 t, 1.39 s, 1.81 s	1.75 m		7.43 d, 9.77 d^c
		Fluxional			
[$PdCl_2$(PEt_3)(*i*-Pr-dim)]	$CDCl_3$	1.40 d		4.51 m	8.69 d^d
[$PdCl_2$($AsEt_3$)(*t*-Bu-dim)]	$CDCl_3$	1.52 s			8.80 s
[$PdCl_2$(PEt_3)(*t*-Bu-dim)]	$CDCl_3$	1.48 s			8.71 d^d
	(−50)	1.48 s			8.7 br
[$PdCl_2$(PPh_3)(*t*-Bu-dim)]	$CDCl_3$	1.53 s			8.70 d^e
[$PdCl_2$(PPh_3)($EtMe_2C$-dim)]	$CDCl_3$	0.9 m, 1.53 s	1.70 m		8.61 d^e
[$PtCl_2$(PBu_3)(*t*-Bu-dim)]	$C_2H_2Cl_4$ (120)	1.55 s			9.01 m^f
	$CDCl_3$	1.48 s			9.0 br
	(−55)^g	1.38 s, 1.69 s			8.42 d of d, 9.69 d^h
[$PtCl_2$(PPh_3)(*t*-Bu-dim)]	$C_2H_2Cl_4$ (110)	1.6 s			9.05 m^i
	$CDCl_3$ (55)	1.52 s			9.0 br
	(−55)^g	1.41 s, 1.79 s			8.43 d of d, 9.69 d^j
[$PtCl_2$($AsPh_3$)(*t*-Bu-dim)]	$C_2H_2Cl_4$	1.58 s			9.47^k
	$CDCl_3$	1.59 s			8.74 d, 10.21 d^l
	(−55)^g	1.31 s, 1.69 s			

[a] Recorded at ambient temperature unless indicated otherwise. [b] Me_4Si internal standard. Key: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and d of d = doublet of doublets. [c] ^3J(H–H) = 8 Hz. [d] $^4J(^{31}P–H)$ = 8 Hz. [e] $^4J(^{31}P–H)$ = 9 Hz. [f] $^4J(^{31}P–H)$ = 7 Hz. $^3J(^{195}Pt–H)$ = 25 Hz. [g] Slow-exchange limit; monodentate. [h] ^3J(H–H) = 8 Hz; $^4J(^{31}P–H)$ = 12 Hz. [i] $^4J(^{31}P–H)$ = 7.5 Hz; $^3J(^{195}Pt–H)$ = 29 Hz. [j] ^3J(H–H) = 8 Hz; $^4J(^{31}P–H)$ = 13 Hz. [k] $^3J(^{195}Pt–H)$ = 37 Hz. [l] ^3J(H–H) = 9 Hz.

Table III. ^{13}C NMR Spectra of [MCl_2(R-dim)], [MX_2(R-dim)$_2$], and [MCl_2L(R-dim)] Complexes

compd	solvent (temp, °C)^a	δ^b			
		CH$_3$	CH$_2$	C–N	C=N
		Ligand			
i-Pr-dim	$CDCl_3$	23.47		60.87	156.46
t-Bu-dim	$CDCl_3$	28.42		56.94	156.59
$EtMe_2C$-dim	$CDCl_3$	8.02, 25.97	35.08	60.16	157.85
		Chelating			
[$PdCl_2$(*t*-Bu-dim)]	Me_2SO-d_6	29.93		61.96	161.59
[$PdCl_2$($EtMe_2C$-dim)]	Me_2SO-d_6	6.77, 25.72	33.20	63.22	159.88
		Monodentate			
[$PdCl_2$(*t*-Bu-dim)$_2$]	$CDCl_3$	29.03, 31.71		59.93, 65.90	154.82, 168.31
[$PdBr_2$(*t*-Bu-dim)$_2$]	$CDCl_3$	29.25, 32.17		60.20, 65.87	155.34, 169.28
[PdI_2(*t*-Bu-dim)$_2$]	$CDCl_3$	29.27, 31.97		60.21, 65.96	155.84, 170.04
[$PdCl_2$($EtMe_2C$-dim)$_2$]	$CDCl_3$	8.40, 8.86, 26.32, 29.25	35.39, 35.87	62.69, 68.56	155.81, 168.46
[$PdBr_2$($EtMe_2C$-dim)$_2$]	$CDCl_3$	8.44, 9.02, 26.38, 29.35	35.35, 36.17	62.74, 69.13	156.09, 169.11
		Fluxional			
[$PdCl_2$(PEt_3)(*i*-Pr-dim)]	$CDCl_3$	23.39		61.35	160.09
[$PdCl_2$($AsEt_3$)(*t*-Bu-dim)]	$CDCl_3$	30.10		61.60	160.34
	acetone-d_6 (−81)			58.47, 61.84 (br)	155.36, 154.87 (br)
[$PdCl_2$(PEt_3)(*t*-Bu-dim)]	$CDCl_3$	29.95		61.17	159.98
	acetone-d_6 (−86)			58.47, 61.54 (br)	155.36, 165.18 (br)
[$PdCl_2$(PPh_3)(*t*-Bu-dim)]	$CDCl_3$	30.38		61.69	160.61
[$PdCl_2$(PPh_3)($EtMe_2C$-dim)]	$CDCl_3$	8.54, 27.52	35.38	64.49	160.83
[$PtCl_2$(PBu_3)(*t*-Bu-dim)]	$CDCl_3$ (+60)	30.11		62.19	160.35
	$CDCl_3$ (−55)	28.71, 31.06		59.33, 65.14	154.75, 164.66
[$PtCl_2$(PPh_3)(*t*-Bu-dim)]	$CDCl_3$	30.39		62.68	160.24
	$CDCl_3$ (−55)	28.69, 31.44		59.91, 65.73	154.58, 165.17

[a] Recorded at ambient temperature unless indicated otherwise. [b] $CDCl_3$ or Me_4Si as internal standard.

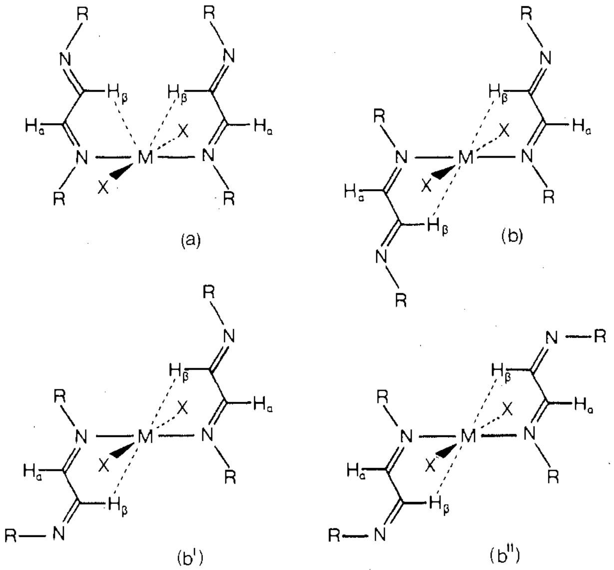

Figure 2. Stereoisomers for $[MX_2(R\text{-dim})_2]$ complexes as a result of rotation around the M–N axis (a vs. b, b′, and b″) and by inversion at the noncoordinated N site (b, b′, and b″).

appeared as an AX spectrum (^3J(HH) = 8 Hz) which was established by a double-resonance experiment (irradiation at 9.7 ppm resulted in a singlet resonance at 7.4 ppm). The low-field doublet at 9.70 ppm was assigned to the respective β-H–C protons. This assignment has been based on the large downfield shifts observed for such protons in *trans*-$[Cl_2(PR_3)Pt(R'NCHCHNR')Pt(PR_3)Cl_2]$-*trans* for which the configuration of the *t*-Bu-dim ligand was studied by an X-ray structure determination (see Figure 1 and discussion section). For *trans*-$[PdX_2(t\text{-Bu-dim})_2]$ a similar configuration for the *t*-Bu-dim ligand has been proposed. This leads to structures of the type a or b shown in Figure 2 of which on steric grounds the b set do seem more likely. Depending on the configuration at the noncoordinated part of the R-dim ligand the existence of a further three isomers (b,b′,b″ in Figure 2), which in principle have different NMR patterns, can be anticipated. The observation of only one pattern for the *trans*-$[PdBr_2(t\text{-Bu-dim})_2]$ suggests the presence of only one isomer in solution. Furthermore, the occurrence of a process involving inversion at the noncoordinated N atom thus rendering the isomers equivalent seems unlikely because even at −60 °C sharp resonances were still observed.

σ-N↔σ-N′ Fluxional R-dim: 1/1 Complexes $[MCl_2(XR_3)(R'\text{-dim})]$ (M = Pt, Pd; X = P, As). The monomeric aggregation state of the 1/1 palladium(platinum)-*R*-dim complexes could be established for $[MCl_2(PPh_3)(t\text{-Bu-dim})]$ (M = Pd, Pt). The IR spectrum of the compounds (Nujol and KBr or in dichloromethane solution) revealed a medium strong absorption at 1620 cm^{-1}, which was assigned to the stretching mode of the imine group; see Table I. The presence of trans-positioned M–Cl bonds was deduced from the observation of a strong band at 342 cm^{-1} [ν_{asym} (M–Cl)].

On the basis of the combined NMR (^{1}H, ^{13}C, ^{31}P, and ^{195}Pt) spectroscopic data of the 1/1 complexes, a full understanding of the nature of metal-R-dim interaction could be obtained. The NMR spectra of the palladium and platinum complexes appeared to be similar with respect to temperature dependence of the resonance patterns and will be discussed in detail for $[PtCl_2(PBu_3)(t\text{-Bu-dim})]$.

Table IV. ^{31}P NMR Spectra of $[\{MCl_2PR_3\}_n(R\text{-dim})_m]$ ($n = 2, m = 0; n = 2, m = 1; n = 1, m = 1$) Complexes

compd	δ(^{31}P)^a	δ(^{195}Pt)^b
$[\{PdCl_2(PEt_3)\}_2]$	48.19	
$[\{PdCl_2(PEt_3)\}_2(t\text{-Bu-dim})]$	34.68	
$[PdCl_2(PEt_3)(t\text{-Bu-dim})]$	33.01	
$[\{PdCl_2(PEt_3)\}_2(i\text{-Pr-dim})]$	33.05	
$[PdCl_2(PEt_3)(i\text{-Pr-dim})]$	33.40	
$[PdCl_2(PPh_3)(t\text{-Bu-dim})]$	27.10	
$[PdCl_2(PPh_3)(EtMe_2C\text{-dim})]$	26.28	
$[\{PtCl_2(PBu_3)\}_2]$	2.28 (3830)	1121
$[\{PtCl_2(PBu_3)\}_2(t\text{-Bu-dim})]$	−8.43 (3448)	1051.36
$[PtCl_2(PBu_3)(t\text{-Bu-dim})]$	−9.48 (3425)	1067.47
$[\{PtCl_2(PPh_3)\}_2]$	14.57 (3675)	
$[\{PtCl_2(PPh_3)\}_2(t\text{-Bu-dim})]$	1.92 (3679)	
$[PtCl_2(PPh_3)(t\text{-Bu-dim})]$	1.48 (3660)	

^{a} H_3PO_4 as external standard. ^{b} $[\{PtCl_2(PBu_3)\}_2]$ as internal standard. Values of $^1J(^{195}Pt\text{–}^{31}P)$ in Hz between parentheses.

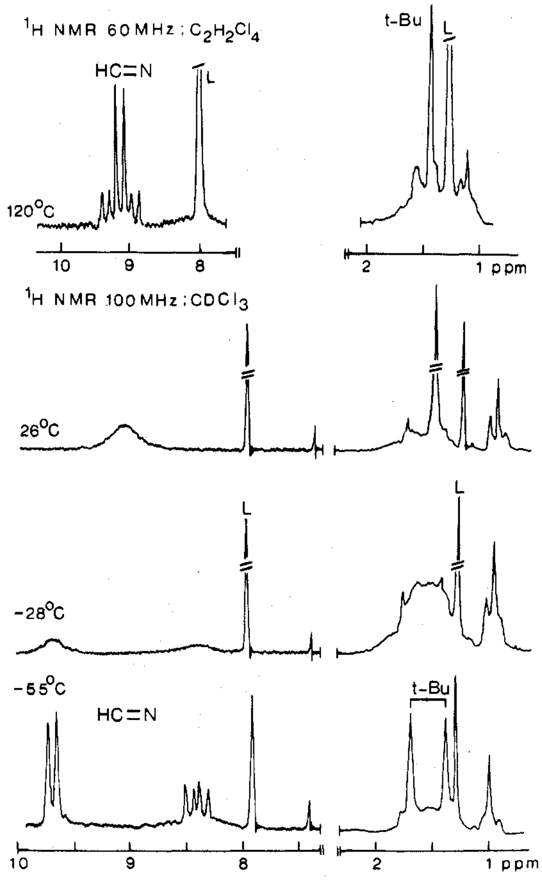

Figure 3. ^{1}H NMR spectra (60 and 100 MHz) of $[PtCl_2(PBu_3)(t\text{-Bu-dim})]$ in the presence of excess of *t*-Bu-dim (L).

The NMR spectra of solutions with $PtCl_2PBu_3/t$-Bu-dim molar ratios ranging from 3/2 to 1/4 revealed that no intermolecular exchange between the free ligand, the $[\{PtCl_2(PBu_3)\}_2]$, and the 1/1 and 2/1 complexes occurred on the ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR time scale (see Table IV). Each of these spectra shows sharp resonances belonging to the respective compounds. The δ(^{31}P) of the PBu_3 ligand shifts by about 10 ppm upon coordination of the *t*-Bu-dim ligand. Moreover, the $^1J(^{195}Pt\text{–}^{31}P)$ moves from 3830 Hz in $[\{PtCl_2(PBu_3)\}_2]$ to 3425 Hz for $n = 1$ and to 3448 Hz for $n = 2$ in the $[(PtCl_2PBu_3)_n(t\text{-Bu-dim})]$ complexes. Also in the ^{195}Pt NMR spectra of a 2/3 $PtCl_2PBu_3/t$-Bu-dim solution, two Pt resonances were observed which on the basis of the $^1J(^{195}Pt\text{–}^{31}P)$ values could be assigned to the bridged and the monodentate bonded *t*-Bu-dim complexes. The spectrum of solutions containing excess of *t*-Bu-dim showed only one resonance with $^1J(^{195}Pt\text{–}^{31}P)$ of 3425 Hz of the monodentate *t*-Bu-dim complex.

The fluxional behavior of the *t*-Bu-dim ligand is demonstrated by the ^{1}H and ^{13}C NMR spectra of the 1/1 complex. In Figures 3 and 4 relevant ^{1}H and ^{13}C NMR spectra at

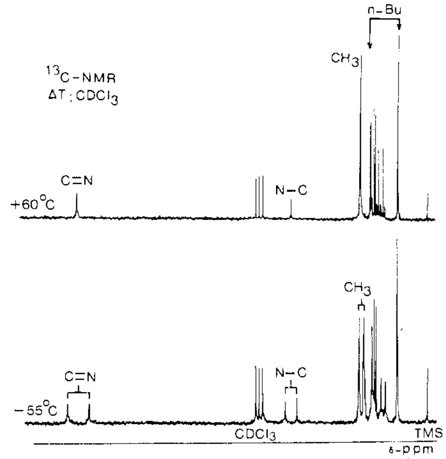

Figure 4. ^{13}C NMR spectra (20 MHz) of [PtCl$_2$(PBu$_3$)(*t*-Bu-dim)] in the fast (60 °C) and slow (−55 °C) exchange limit.

different temperatures are shown. The ^{1}H NMR spectrum at −55 °C clearly shows that the *t*-Bu-dim ligand is monodentate bonded as is shown in Figure 7. The imine protons appear in the spectrum as an AX pattern. The fact that only the highfield doublet is observed as a doublet of doublets resulting from $^4J(^{31}P-^1H)$ of 8 Hz enables the assignment of this resonance pattern to the α-CH proton. The downfield shift of the doublet arising from the β-CH proton ($\Delta\delta$ 1.76 ppm) indicates that the configuration of the monodentate ligand in the 1/1 complex and the *trans*-[PdCl$_2$(R-dim)$_2$] must be similar (see Figure 2b). This is confirmed by the ^{13}C NMR spectra at −55 °C in which separate resonance patterns are observed for the coordinated and free –C=N-*t*-Bu part of the *t*-Bu-dim ligand. On raising of the temperature the two patterns coalesce to give at 120 °C a ^{1}H NMR spectrum containing one singlet for the *t*-Bu protons and one multiplet pattern for the imine protons. The latter pattern results from $^4J(^{31}P-^1H)$ and $^3J(^{195}Pt-^1H)$ couplings with isochronous imine protons. The coalesced proton signal appears at the averaged chemical shift position of the multiplets in the slow-exchange limit. Moreover the $^4J(^{31}P-^1H)$ value at 120 °C appears to be about half of the value observed in the slow-exchange spectrum at −55 °C (see Table II). These data point to a process proceeding via a symmetric intermediate with a five-coordinate platinum center and σ,σ-N,N′-bonded *t*-Bu-dim ligand[24] (see Figure 7).

Structural Features of the α-Diimine–M Bonding Modes. The structural features found in the compounds presented in this paper are a clear demonstration of the versatile bonding properties of the α-diimine ligand. In particular the monodentate R-dim–M interaction is, at first sight, surprising because of the analogy of the N=C—C=N skeleton in the R-dim and the bpy ligands. For the latter ligand monodentate coordination behavior in ground-state molecules is virtually unknown. In Figure 5 the σ,σ-chelating and monodentate bonding modes for both ligands are presented. Comparison of the two rotational isomers of the bpy–metal interaction reveals that in the monodentate bonding situation the $H_{\alpha'}$ atom represents steric bulkiness in the absence of an M–H interaction. Of course, this steric bulkiness can be diminished at the cost of resonance stabilization by rotation around the C(1)–C(1′) axis. In contrast, in the monodentate R-dim–metal interaction the H_β atom is further away from the metal. This is especially so when the two N=C systems are coplanar.

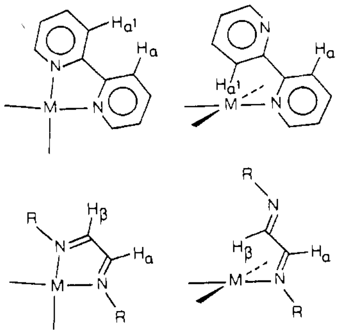

Figure 5. Comparison of the structural features of the metal–R-dim and metal–bpy interaction.

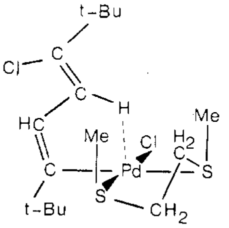

Figure 6. Molecular geometry of chloro(2,5-dithiahexane){1-(1,3-di-*tert*-butyl-4-chlorobutadienyl)}palladium.[29]

Moreover, in this conformation H_β is part of a five-membered ring system $\overline{MN{=}CH_\alpha CH_\beta{=}N}$ which from a steric point of view would be more stable than the six-membered arrangement in a monodentate bpy–metal interaction having the two aromatic nuclei coplanar. Unambiguous evidence for the preference of a coplanar N=CC=N skeleton in R-dim–metal complexes was found in the molecular structure of [{PtCl$_2$(PBu$_3$)}$_2$(*t*-Bu-dim)]; see Figure 1.[23] This structure furthermore shows that as a result of the planar N=CC=N skeleton the H_β protons reside above the respective PtPBu$_3$Cl$_2$N coordination planes. The calculated Pt···H_β distance amounts to 2.6 Å which is within the distance of 3.2 Å expected for van der Waals contacts.

The observed large downfield shift of H_β in the monodentate and fluxional R-dim–metal complexes indicates that these structural features of the R-dim ligand as well as the short M···H distance are also predominant in solution. Whether in these structures a M···H interaction is responsible for the planar N=CC=N skeleton in the anti configuration is uncertain, because it is only in this configuration that the lone pair of the free N site and the filled metal d_{z^2} orbital are apart from each other. However, examples of square-planar metal d^8 complexes containing a stabilized ligand configuration as a result of an intramolecular five-membered M···H interaction have been reported, i.e., *trans*-[PtCl$_2$(dialkylsulfur diimine)-L],[25] Pd and Pt azo and azomethine complexes,[26] [{Et$_2$B-(Pz)$_2$}Mo(CO)$_2$(η^3-allyl)],[27] and [Pd{PPh(*t*-Bu)$_2$}$_2$].[28]

Of particular interest is the Pd compound reported by Maitlis[29] containing a substituted 1,3-butadiene ligand, which is isostructural with the R-dim molecule (see Figure 6). The configuration of the 1,3-butadiene ligand which is monodentate bonded via a σ carbon–palladium bond is such that H_β resides above the Pd-coordination plane (Pd···H = 2.6 Å). Also in this case the NMR resonance of H has undergone a large downfield shift.

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[24] (a) Rotation around the Pt–N bond alone would cause a change of the chemical shift position of the respective multiplets. (b) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Am. Chem. Soc.*, **92**, 1511 (1970).

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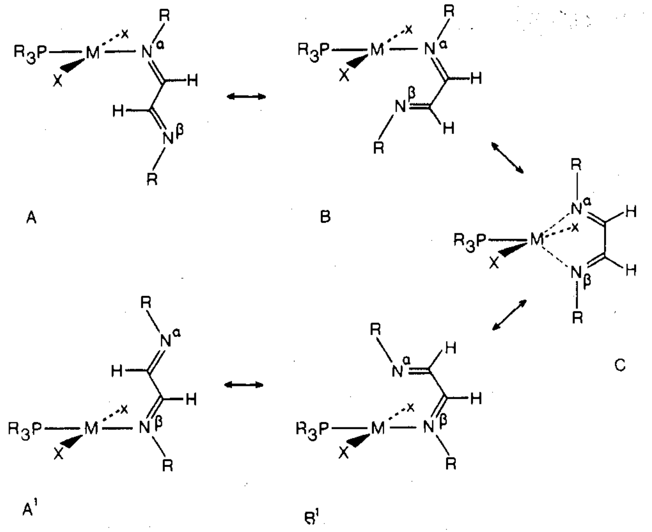

Figure 7. Proposed mechanism for the fluxional behavior of the [MCl$_2$PR$_3$(R-dim)] compounds in solution.

The large downfield shifts of H$_\beta$ in the present R-dim–metal complexes are diagnostic for the dynamic behavior of the R-dim ligand. Removal of H$_\beta$ out of the area above the metal will cause a strong upfield shift of the H$_\beta$ resonance.[24b] Accordingly, it can be concluded that in [PdCl$_2$(R-dim)$_2$] neither rotation around the Pd–N or the C$_\alpha$–C$_\beta$ bonds nor exchange of the point of attachment of the palladium atom to the R-dim ligand takes place (vide infra) on the NMR time scale because the H$_\beta$ resonance appeared to be invariant with temperature. Furthermore in the series [PdX$_2$(*t*-Bu-dim)$_2$] the deshielding of the H$_\beta$ resonance decreases more rapidly in the series Cl, Br, and I than the resonance of H$_\alpha$ (see Table II). Moreover, this variation in δ is identical with the variation found for the olefin proton residing above the Ni coordination plane in [NiX(PEt$_3$)$_2$(alkenylaryl)] (X = Cl, Br, I).[24b,25]

A similar conclusion has been drawn from the NMR data for the structures of the [MCl$_2$(XR$_3$)(*t*-Bu-dim)] (M = Pt, Pd; X = P, As) complexes in the slow-exchange limit (see Figure 7). The fluxional process by which the metal changes its point of attachment to the R-dim ligand at higher temperature is shown in this figure. Rotation around the C$_\alpha$–C$_\beta$ axis (possibly proceeded by inversion of the free N site) leads to a conformation of the monodentate ligand in which the N lone pairs are suitably orientated for σ,σ-chelation. This results in a pentacoordinate intermediate or transition state. In this respect the bonding in this intermediate is very similar to the bonding in *cis*-[PtCl(PEt$_3$)$_2$(phen)]BF$_4$ (see Introduction). As a consequence, in each of the monodentate R-dim–metal enantiomers (A and A′) either H$_\alpha$ or H$_\beta$ resides above the coordination plane. In the pentacoordinate intermediate or transition state B the halogen atoms are in trans-position while the phosphine ligand acts as a "trans" ligand for the chelating diimine.

It is of interest to note that the trans ligand exerts a large influence on the nature of the metal–R-dim bonding mode as can be deduced from the high stability of the pentacoordinate platinum compounds [PtCl$_2$(olefin)(R-dim)][5,18,30] in which the phosphine (arsine) is substituted by an olefin.

An extensive spectroscopic study including ^{195}Pt NMR of the compounds [PtCl$_2$(PR′$_3$)(R-dim)] (monodentate/fluxional), [{PtCl$_2$(PR′$_3$)}$_2$(R-dim)] (bridged), and [PtCl$_2$(olefin)(R-dim)] or [PtCl$_2$(R-dim)] (chelating) possibly may clarify the nature of this trans effect.[30]

Registry No. *cis*-[PdCl$_2$(*i*-Pr-dim)], 72905-43-2; *cis*-[PdBr$_2$(*i*-Pr-dim)], 72905-44-3; *cis*-[PdCl$_2$(*t*-Bu-dim)], 72905-45-4; *cis*-[PdBr$_2$(*t*-Bu-dim)], 72905-46-5; *cis*-[PdCl$_2$(EtMe$_2$C-dim)], 72905-47-6; *cis*-[PdBr$_2$(EtMe$_2$C-dim)], 72905-48-7; *cis*-[PdI$_2$(*i*-Pr-dim)], 72905-49-8; *trans*-[PdCl$_2$(*t*-Bu-dim)$_2$], 72937-81-6; *trans*-[PdBr$_2$(*t*-Bu-dim)$_2$], 72905-50-1; *trans*-[PdCl$_2$(EtMe$_2$C-dim)$_2$], 72905-51-2; *trans*-[PdBr$_2$(EtMe$_2$C-dim)$_2$], 72905-52-3; *trans*-[PdI$_2$(*t*-Bu-dim)$_2$], 72905-53-4; *trans*-[PdCl$_2$(PPh$_3$)(*t*-Bu-dim)], 72905-54-5; *trans*-[PdCl$_2$(PPh$_3$)(EtMe$_2$C-dim)], 72905-55-6; *trans*-[PtCl$_2$(PPh$_3$)(*t*-Bu-dim)], 72905-56-7; *trans*-[PtCl$_2$(AsPh$_3$)(*t*-Bu-dim)], 72905-35-2; *trans*-[PdCl$_2$(PEt$_3$)(*t*-Bu-dim)], 72905-36-3; *trans*-[PdCl$_2$(AsEt$_3$)(*t*-Bu-dim)], 72905-37-4; *trans*-[PtCl$_2$(PBu$_3$)(*t*-Bu-dim)], 72905-38-5; *trans*-[PdCl$_2$(PEt$_3$)(*i*-Pr-dim)], 72916-72-4; {PdCl$_2$(PEt$_3$)}$_2$, 15684-59-0; {PtCl$_2$(PBu$_3$)}$_2$, 15670-38-9; {PtCl$_2$(PPh$_3$)}$_2$, 15349-80-1; {PdCl$_2$(PPh$_3$)}$_2$, 15134-30-2; {PdCl$_2$(AsEt$_3$)}$_2$, 28103-80-2; {PtCl$_2$(AsPh$_3$)}$_2$, 39539-17-8; *i*-Pr-dim, 24764-90-7; *t*-Bu-dim, 30834-74-3; EtMe$_2$C-dim, 67122-55-8; (1,1-dimethylpropyl)amine, 594-39-8; glyoxal, 107-22-2; *trans*-[PdCl$_2$(PhC≡N)$_2$], 15617-18-2; *trans*-[PdBr$_2$(PhC≡N)$_2$], 50894-57-0; {PdCl$_2$(C$_2$H$_4$)}$_2$, 12122-75-7; {PdCl$_2$(PEt$_3$)}$_2$(*t*-Bu-dim), 72905-39-6; {PdCl$_2$(PEt$_3$)}$_2$(*i*-Pr-dim), 72925-70-3; {PtCl$_2$(PBu$_3$)}$_2$(*t*-Bu-dim), 72925-71-4; {PtCl$_2$(PPh$_3$)}$_2$(*t*-Bu-dim), 72905-40-9.

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(30) H. van der Poel and G. van Koten, to be submitted for publication.