Oxidative Addition of Carbon−Chloride Bonds to Rhodium(I) Complexes Containing Terdentate Nitrogen Ligands. X-ray Analyses of Rhodium(I) Chloride and Rhodium(III) Chloromethyl Complexes

Hendrikus F. Haarman,† Jan M. Ernsting,† Mirko Kranenburg,†
Huub Kooijman,‡ Nora Veldman,‡ Anthony L. Spek,‡
Piet W. N. M. van Leeuwen,† and Kees Vrieze*,†

J. H. van't Hoff Research Instituut, Laboratorium voor Anorganische Chemie, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Bijvoet Centre for Biomolecular Research, Vakgroep Kristal- en Structuurchemie, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received September 3, 1996⊗

Potentially terdentate hemilabile 2,6-bis(R^2-carbaldimino)pyridine and 2,6-bis(R^2-ethylidyneimino)pyridine ligands (2,6-($C(R^1){=}NR^2)_2C_5H_3N$; R^1 = H, R^2 = *i*-Pr (**1**), *t*-Bu (**2**), cyclohexyl (**3**), *p*-anisyl (**4**); R^1 = Me, R^2 = *p*-anisyl (**5**), *i*-Pr (**6**)) have been used to prepare in high yields the novel and highly nucleophilic complexes [RhCl(2,6-($C(R^1){=}NR^2)_2C_5H_3N$)] (R^1 = H, R^2 = *i*-Pr (**7**), *t*-Bu (**8**), cyclohexyl (**9**), *p*-anisyl (**10**); R^1 = Me, R^2 = *p*-anisyl (**11**), *i*-Pr (**12**)) with $[RhCl(alkene)_2]_2$ (alkene = ethene, cyclooctene) as starting material. X-ray analyses of **7**, **8**, and **12** show severe steric interactions between the R^2 group and the equatorial chloride atom, leading to out-of-plane bending of the chloride atom. The angle between the N−N−N plane and the Rh−Cl axis is 5.34(16)° for **7**, 11.73(11)° for **8**, and 10.04(11)° for **12**. Reaction of the Rh(I) complexes with CH_2Cl_2, $CHCl_3$, benzyl chloride, and α,α-dichlorotoluene led to Rh(III) complexes by C−Cl bond rupture. The Rh−C bonds of the chloromethyl complexes [$RhCl_2(CH_2Cl)$(2,6-($C(R^1){=}NR^2)_2C_5H_3N$)] (R^1 = H, R^2 = *i*-Pr (**13**), cyclohexyl (**15**)) are all short (2.052(5)−2.059(3) Å), while the C−Cl bonds (range 1.728(4)−1.790(5) Å) are rather long, which indicates the contribution of a $Rh{=}CH_2^+Cl^-$ resonance form. In solution all Rh(III) complexes exist as one isomer with the ligand bonded in a terdentate fashion (both ^1H and ^{13}C NMR), except for the complexes [$RhCl_2(R^3)$(2,6-($C(Me){=}N$-*i*-$Pr)_2C_5H_3N$)] (R^3 = CH_2Cl (**18**), CH_2Ph (**24**), CHClPh (**27**), Cl (**33**)), which all contain two interconverting isomers; one five-coordinate Rh(III) isomer has a ligand which coordinates in a bidentate manner, while the other six-coordinate isomer has a ligand which coordinates in a terdentate fashion, as evidenced by low-temperature NMR measurements. Molecular modeling has shown that the formation of the five-coordinate Rh(III) species is caused by the axial ligands, which force the equatorial Cl atom into the N−N−N plane, resulting in an increased steric interaction of R^2 and R^1. Reaction of the chloromethyl and dichloromethyl complexes **13**−**21** in boiling water with oxygen gave the trichloride complexes [$RhCl_3$(2,6-($C(R^1){=}NR^2)_2C_5H_3N$)] (R^1 = H, R^2 = *i*-Pr (**28**), *t*-Bu (**29**), cyclohexyl (**30**), *p*-anisyl (**31**); R^1 = Me, R^2 = *p*-anisyl (**32**), *i*-Pr (**33**)), while the chlorotolyl complex [$RhCl_2$(CHClPh)(2,6-($C(Me){=}N$-*i*-$Pr)_2C_5H_3N$)] **27** gave the complex **33**, benzaldehyde, and H_2O_2.

Introduction

The oxidative addition of carbon halides to low-valent metal complexes is of paramount interest. It is a key step in a number of industrially important catalytic processes, such as the carbonylation of methanol to acetic acid[1,2] catalyzed by rhodium and HI, for which the kinetics have been elucidated largely by the work of Maitlis et. al.[3−6] Another example is the oxidative addition of aryl halides in the cross-coupling and carbonylation reactions homogeneously catalyzed by palladium and platinum complexes.[7−14] Oxidative addition is also a general synthetic method for formation of carbon−metal σ-bonds.[15]

To elucidate the mechanism of the oxidative addition of carbon−halide bonds, a considerable amount of work

---

* To whom correspondence should be adressed.

† Universiteit van Amsterdam.

‡ Universiteit Utrecht.

⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Forster, D.; Singleton, T. C. *J. Mol. Catal.* **1982**, *17*, 299.

(2) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255.

(3) Ellis, P. R.; Pearson, J. M.; Haynes, A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1994**, *13*, 3215.

(4) Fulford, A.; Hickey, C. E.; Maitlis, P. M. *J. Organomet. Chem.* **1990**, *398*, 311.

(5) Haynes, A.; Mann, B. E.; Gulliver, D. J.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 8567.

(6) Hickey, C. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1609.

(7) Huser, M.; Youinou, M.-T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1386.

(8) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Öfele, K. *J. Organomet. Chem.* **1994**, *481*, 97.

(9) van Asselt, R.; Elsevier, C. J. *Organometallics* **1992**, *11*, 1999.

(10) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.

(11) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

(12) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1301.

(13) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(14) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

(15) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

S0276-7333(96)00761-3 CCC: $14.00

has been focused on zerovalent palladium and platinum complexes.[16-23] Many kinetic studies have been carried out on Ir(I) complexes, e.g. *trans*-[IrX(CO)L_2] (X = halide, L = phosphine).[17] It has become clear that no single mechanism holds for oxidative-addition reactions. In general three different mechanisms (oxidative insertion, backside nucleophilic S_N2 substitution, and radical pathways) have been observed, depending on the reactants and the conditions of the reaction.[15-23] A recent article on oxidative-addition reactions involving [IrCl(CO)L_2], MeI, H_2, and O_2 illustrates the difficulty of obtaining clear insight into the mechanisms of these reactions.[24]

When we restrict ourselves to oxidative additions of carbon halide substrates to complexes of Rh(I) and Ir(I), it has been found that, for example, additions of CH_2X_2 (X = Cl, Br, I) are generally enhanced by increasing the electron density on the metal atom. This is evidenced by the oxidative addition of CH_2I_2 to [RhCp*(CO)$_2$] (Cp* = pentamethylcyclopentadiene), affording [RhI(CH_2I)Cp*(CO)], while [RhCp(CO)$_2$] (Cp = cyclopentadiene) in contrast does not react, owing to the smaller electron donor capacity of Cp compared to Cp*.[25] The activation of dichloromethane requires even stronger donor ligands.[26-38] For example, reaction of [Rh(dmpe)$_2$]Cl containing the strongly electron donating $Me_2P(CH_2)_2PMe_2$ (=dmpe) ligands with CH_2Cl_2 afforded the complex [RhCl(CH_2Cl)(dmpe)$_2$]Cl·CH_2Cl_2.[39] Coordination of ligands with three or four nitrogen donor atoms to Rh(I) gives also strongly nucleophilic species that can activate dichloromethane. For example, reaction of a rhodium(I) complex with a tetradentate cyclic dioxime ligand with CH_2Cl_2 afforded a chloromethyl complex.[36] Reaction of [RhCl(cyclooctene)$_2$] with the terdentate nitrogen ligand bis(4,4-dimethyloxazolin-2-yl)pyridine (pybox) in dichloromethane gave the corresponding (chloromethyl)rhodium(III) complex [RhCl$_2$(CH_2Cl)(pybox)], but attempts to isolate the intermediate nucleophilic Rh(I) complexes failed.[40]

Recently, articles on the stability of a series of chloro(chloromethyl)palladium(II) and -platinum complexes in $CDCl_3$ solution (both in the absence and presence of air) were published by McCrindle et al.[41] In the case of *trans*-mono(chloromethyl)platinum(II) complexes it was found that they decompose in the presence of moisture to formaldehyde and platinum hydrides, which undergo subsequent conversion into dichlorides.[42] It was suggested, in analogy to the work of van Leeuwen et al.,[43] that metal−carbene intermediates may be involved.

In our laboratory we are investigating the influence of steric and electronic properties of bi- and terdentate nitrogen ligands on the course of a number of carbon−carbon coupling reactions mediated by palladium complexes.[44-48] In the course of these studies we have designed bidentate nitrogen ligands which are able to stabilize Pd(0), Pd(II), and Pd(IV) complexes.[44-48] These results prompted us to extend our investigations to complexes of Rh with the aim of stabilizing both Rh(I) and Rh(III) complexes and creating very nucleophilic Rh(I) species. In this article we describe the employment of the trinitrogen species 2,6-bis(R^2-carbaldimino)pyridine and 2,6-bis(R^2-ethylidyneimino)pyridine (2,6-($C(R^1)=NR^2)_2C_5H_3N$: R^1 = H, R^2 = *i*-Pr (**1**), *t*-Bu (**2**), cyclohexyl (**3**), *p*-anisyl (**4**); R^1 = Me, R^2 = *p*-anisyl (**5**), *i*-Pr (**6**)) for the isolation of novel, very reactive Rh(I) complexes. The use of these trinitrogen ligands makes it possible to form stable, strongly nucleophilic Rh(I) complexes, which undergo a fast oxidative addition of a number of substrates containing C−Cl bonds. In addition we have studied from a structural point of view the alkylidene character of the chloromethyl moieties of the Rh(III) complexes.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Benzene, diethyl ether, and pentane were distilled before use from sodium/benzophenone, dichloromethane and chloroform from calcium hydride, and acetone from $KMnO_4/Na_2CO_3$. Molecular sieves (3 Å) were activated at 180 °C *in vacuo* for 24 h. Deuteriobenzene was dried over sodium and stored under nitrogen. Deuterated chlorinated solvents were dried with

---

[16] Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

[17] Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236.

[18] Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53.

[19] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 279.

[20] Atwood, J. D. In *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; p 163.

[21] Dickson, R. S. In *Organometallic Chemistry of Rhodium and Iridium*; Academic Press: London, 1983; p 277.

[22] Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.

[23] Lukehart, C. M. In *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; p 274.

[24] Wilson, M. R.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 2044.

[25] Paul, W.; Werner, H. *Chem. Ber.* **1985**, *118*, 3032.

[26] Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* **1985**, *281*, 317.

[27] Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261.

[28] El Amane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773.

[29] Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221.

[30] Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698.

[31] Gash, R. C.; Cole-Hamilton, D. J.; Whyman, R.; Barnes, J. C.; Simpson, M. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1963.

[32] Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M. *Organometallics* **1986**, *5*, 2383.

[33] Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630.

[34] Scherer, O. J.; Jungmann, H. *J. Organomet. Chem.* **1981**, *208*, 153.

[35] Ball, G. E.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Rettig, S. J. *Organometallics* **1991**, *10*, 3767.

[36] Collman, J. P.; Murphy, D. W.; Dolcetti, G. *J. Am. Chem. Soc.* **1973**, *95*, 2687.

[37] Ciriano, M. A.; Tena, M. A.; Oro, L. A. *J. Chem. Soc. Dalton Trans.* **1992**, 2123.

[38] Fennis, P. J.; Budzelaar, P. H. M.; Frijns, J. H. G.; Orpen, A. G. *J. Organomet. Chem.* **1990**, *393*, 287.

[39] Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc. Chem. Commun.* **1987**, 1543.

[40] Nishiyama, H.; Horihata, M.; Hirai, T.; Wakamatsu, S.; Itoh, K. *Organometallics* **1991**, *10*, 2706.

[41] McCrindle, R.; Ferguson, G.; McAlees, A. J.; Arsenault, G. J.; Gupta, A.; Jennings, M. C. *Organometallics* **1995**, *14*, 2741.

[42] McCrindle, R.; Arsenault, G. J.; Gupta, A.; Hampden-Smith, M. J.; Rice, R. E.; McAlees, A. J. *J. Chem. Soc., Dalton Trans.* **1991**, 949.

[43] van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 233, 243.

[44] van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

[45] van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.

[46] van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88.

[47] Rülke, R. E.; Han, I. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F.; Zoutberg, M. C.; Wang, Y. F.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *169*, 5.

[48] Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

molecular sieves (3 Å) and stored under nitrogen. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer. The spectra were indirectly referenced to TMS using residual solvent signals. Fast atom bombardment (FAB) mass spectrometry was carried out by the Institute for Mass Spectroscopy of the University of Amsterdam using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The samples were loaded in a matrix solution (nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FABMS measurements a resolving power of 5000 (10% valley definition) was used. CsI and/or glycerol was used to calibrate the mass spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany and by our institute.

[RhCl(cyclooctene)$_2$]$_2$,[49] [RhCl(C$_2$H$_4$)$_2$]$_2$,[50] 2,6-pyridinedicarboxaldehyde,[51] and the 2,6-bis(R^2-carbaldimino)pyridine and 2,6-bis(R^2-ethylidyneimino)pyridine ligands[52] (**1**−**6**) were synthesized according to literature procedures. The ligands were purified by either sublimation or crystallization depending on the ligand. *p*-Anisidine, isopropyl-, *tert*-butyl-, and cyclohexylamine, 2,6-diacetylpyridine, benzyl chloride, and α,α-dichlorotoluene were obtained from Aldrich and used after purification. Hoekloos oxygen 4.8 was used.

Synthesis of [RhCl(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (7−12). The following synthesis of the Rh(I) compound [RhCl(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)] (**7**) is representative for the method used. Both [RhCl(cyclooctene)$_2$]$_2$ and [RhCl(C$_2$H$_4$)$_2$]$_2$ can be used as starting materials. Complexes **10** and **11** are insoluble in benzene.

To a solution of 0.20 g of [RhCl(cyclooctene)$_2$]$_2$ (0.27 mmol) in 15 mL of C$_6$H$_6$ was added a solution of 0.13 g of the ligand **1** (0.55 mmol) in 15 mL of C$_6$H$_6$ heated to reflux for 30 min, giving a very dark green solution. The reaction mixture was concentrated to a small volume, and pentane was added, after which fast crystallization occurred. The deposit was filtered off, washed with pentane (3 × 2 mL), and dried *in vacuo*. The product could be recrystallized from a small volume of benzene at 7 °C as block-shaped, green crystals. Yield: 0.15 g (0.43 mmol), 78% of pure product. Yields of the other compounds are in the range 80−90%.

Anal. Calcd for C$_{13}$H$_{19}$ClN$_3$Rh (**7**): C, 43.90; H, 5.39; N, 11.81. Found: C, 43.74; H, 5.30; N, 11.66. Anal. Calcd for C$_{23}$H$_{23}$ClN$_3$O$_2$Rh (**11**): C, 53.97; H, 4.53; N, 8.21. Found: C, 53.88; H, 4.59; N, 8.18. Anal. Calcd for C$_{15}$H$_{23}$ClN$_3$Rh (**12**): C, 46.95; H, 6.05; N, 10.95. Found: C, 46.84; H, 6.10; N, 11.06. The spectroscopic data (^{1}H and ^{13}C NMR) for **9** are very similar to those for **7**, **11**, and **12**, and therefore, no elemental analyses were carried out. Elemental analysis of **8** and **10** did not give very satisfactory results, owing to solvent incorporation. However, FAB measurements of **8** clearly established the composition of the formed product. Complex **10** gave problems in the FAB apparatus, and no information could be obtained. FAB$^+$ (*m/z* obsd, *calcd*) **8**: (C$_{15}$H$_{23}$ClN$_3$Rh−Cl) 348.0870, *348.0940*; **9**, C$_{19}$H$_{27}$ClN$_3$Rh 435.0886, *435.0941*.

Synthesis of [RhCl$_2$(CH$_2$Cl)(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (13−18). As an example the synthesis is given for complex [RhCl$_2$(CH$_2$Cl)(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)] (**13**). A 0.14 g amount of **7** (0.39 mmol) was dissolved in 30 mL of dichloromethane at −96 °C. The dark green solution was warmed to room temperature and stirred for 16 h. The solvent was evaporated *in vacuo*, leaving a sticky solid. The solid was washed with benzene (3 × 5 mL) and pentane (3 × 5 mL). The orange powder was dried *in vacuo*. Yield: 0.17 g (0.37 mmol) 94%. The complexes could be recrystallized by slow diffusion of diethyl ether into a saturated dichloromethane solution at room temperature. Isolated yields of the other compounds are in the range 80−90%.

Anal. Calcd for C$_{14}$H$_{21}$Cl$_3$N$_3$Rh (**13**): C, 38.16; H, 4.81; N, 9.54. Found: C, 38.22; H, 4.86; N, 9.62. Anal. Calcd for C$_{22}$H$_{21}$Cl$_3$N$_3$O$_2$Rh (**16**): C, 46.46; H, 3.72; N, 7.38. Found: C, 45.37; H, 3.72; N, 7.15. Accurate elemental analyses of **14** and **17** could not be obtained, due to cocrystallization of irregular amounts of solvent. Elemental analyses of **15** and **18** were not carried out, because the spectroscopic data (^{1}H and ^{13}C NMR) for **15** and **18** are very similar to those for **13** and **16**.

FAB$^+$ (*m/z* obsd, *calcd*) **14** (C$_{16}$H$_{25}$Cl$_3$N$_3$Rh − Cl) 432.0485, *432.0473*; **15** (C$_{20}$H$_{29}$Cl$_3$N$_3$Rh − H), 518.0355, *518.0397*; **16** (C$_{22}$H$_{21}$Cl$_3$N$_3$O$_2$Rh − Cl) 532.0021, *532.0058*; **17** (C$_{24}$H$_{25}$Cl$_3$N$_3$O$_2$Rh + H) 596.0118, *596.0138*; **18** (C$_{16}$H$_{25}$Cl$_3$N$_3$Rh−H) 466.0014, *466.0084*.

Synthesis of [RhCl$_2$(CHCl$_2$)(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (19−21). A representative method is given for complex [RhCl$_2$(CHCl$_2$)(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)] (**19**). A 0.12 g portion of **7** (0.34 mmol) was dissolved in 40 mL of CHCl$_3$ at −60 °C. The green solution was warmed to room temperature. After 8 h the solution had turned yellow-orange. The reaction mixture was concentrated to a minimum volume, and cooling gave the product analytically pure as block-shaped crystals. Isolated yield: 0.11 g (0.22 mmol), 65%. The yields of the other compounds are about 70−80%.

Anal. Calcd for C$_{14}$H$_{20}$Cl$_4$N$_3$Rh (**19**): C, 35.40; H, 4.25; N, 8.85. Found: C, 35.46; H, 4.29; N, 8.78. Elemental analysis of **21** did not give very satisfactory results, owing to solvent incorporation. Elemental analysis of **20** was not carried out, since the spectroscopic data (^{1}H and ^{13}C NMR) for **20** are very similar to those for **19**.

FAB$^+$ (*m/z* obsd, *calcd*) **19** (C$_{14}$H$_{20}$Cl$_4$N$_3$Rh + Na) 495.9328, *495.9357*; **20** (C$_{16}$H$_{24}$Cl$_4$N$_3$Rh + H) 501.9820, *501.9850*; **21** (C$_{16}$H$_{24}$Cl$_4$N$_3$Rh + Na) 523.9669, *523.9670*.

Synthesis of [RhCl$_2$(CH$_2$C$_6$H$_5$)(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (22−24). The synthesis of the complex [RhCl$_2$(CH$_2$C$_6$H$_5$)(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)] (**22**) is presented as an example. To a green acetone solution (10 mL) of 0.055 g of **7** (0.15 mmol) was added 0.023 mL of benzyl chloride (0.025 g, 0.20 mmol) was added at −96 °C. The reaction mixture was warmed to room temperature and stirred for 6 h, during which the color changed to orange. Acetone was evaporated in vacuo and the sticky residue was washed with benzene (3 × 2 mL) and pentane (3 × 2 mL). The yellow powder obtained was dried *in vacuo*. Isolated yield: 0.059 g (0.12 mmol), 80%. Other compounds had yields varying from 70−85%.

Elemental analysis of **22**−**24** did not give very satisfactory results, owing to solvent incorporation. However, FAB measurements clearly established the composition of the products formed. FAB$^+$(*m/z* obsd, *calcd*) **22**: (C$_{20}$H$_{26}$Cl$_2$N$_3$Rh − HCl) 446.0903, *446.0863*; **23** (C$_{22}$H$_{30}$Cl$_2$N$_3$Rh − Cl) 474.1159, *474.1176*; **24** (C$_{22}$H$_{30}$Cl$_2$N$_3$Rh − Cl) 474.1108, *474.1176*.

Synthesis of [RhCl$_2$(CHClPh)(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (25−27). A representative synthesis is given for complex [RhCl$_2$(CHClPh)(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)] (**25**). To a green acetone solution (10 mL) of 0.14 g of **7** (0.39 mmol) was added 0.09 mL of α,α-dichlorotoluene (0.1 g, 0.7 mmol) at −96 °C. The reaction mixture was warmed to room temperature and was stirred for an additional 4 h at this temperature, during which the color changed to yellow. Acetone was evaporated *in vacuo*, leaving a sticky residue that was washed with benzene (3 × 5 mL) and pentane (3 × 5 mL). The yellow powder obtained was dried *in vacuo*. Yield: 0.14 g (0.31 mmol), 79%. The yields of the other compounds are in the range of 80−90%.

Anal. Calcd for C$_{20}$H$_{25}$Cl$_3$N$_3$Rh (**25**): C, 46.49; H, 4.88; N, 8.13. Found: C, 47.59; H, 4.92; N, 7.95. Elemental analysis of **26** and **27** did not give very satisfactory results, owing to solvent incorporation. **27** gave problems in the FAB$^+$ apparatus and no information could be obtained.

---

(49) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.

(50) Cramer, R. *Inorg. Synth.* **1990**, *28*, 86.

(51) Matsumoto, I.; Yoshizaw, J. Jpn. Patent 7,202,093; *Chem. Abstr.* **1972**, *76*, 126801.

(52) Lavery, A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1053.

FAB$^+$ (*m/z* obsd, *calcd*) **25** ($C_{20}H_{25}Cl_3N_3Rh + Na$) 538.0098, *538.0060*; **26** ($C_{22}H_{29}Cl_3N_3Rh - Cl$) 508.0807, *508.078*.

Synthesis of [RhCl$_3$(2,6-(C(R^1)=N-R^2)$_2$C$_5$H$_3$N)] (28−33). The synthesis of the complex [RhCl$_3$(2,6-(C(H)=N-*i*-Pr)$_2$C$_5$H$_3$N)]-(**28**) is given as an example. A green benzene solution (10 mL) of **7** (0.12 g, 0.33 mmol) was exposed to Cl_2 gas, giving a yellow-orange deposit. This deposit was washed with benzene (3 × 3 mL) and pentane (3 × 3 mL) and dried *in vacuo*, giving 0.12 g of pure **28** (0.28 mmol), yield 83%. The yields of the other complexes are in the range 70−90%.

Anal. Calcd for $C_{13}H_{19}Cl_3N_3Rh$ (**28**): C, 36.60; H, 4.49; N, 9.85. Found: C, 36.54; H, 4.55; N, 9.82. Elemental analysis of **33** did not give very satisfactory results, owing to solvent incorporation. Elemental analyses of **29**−**32** were not carried out, because the spectroscopic data (^{1}H and ^{13}C NMR) for **29**−**32** are very similar to those for **28** and FAB measurements of **29**, **30** and **33** clearly established the composition of the formed products. **31** and **32** gave problems in the FAB$^+$ apparatus, and no information could be obtained.

FAB$^+$ (*m/z* obsd, *calcd*) **28** ($C_{13}H_{19}Cl_3N_3Rh + Na$) 447.9655, *447.9590*; **29** ($C_{15}H_{23}Cl_3N_3Rh - Cl$): 418.0303, *418.0316*; **30** ($C_{16}H_{25}Cl_3N_3Rh - HCl$) 418.0337, *418.0317*; **33** ($C_{15}H_{23}Cl_3N_3Rh + H$) 454.0075, *454.0084*.

Reaction of 13−27 with H$_2$O and O$_2$. The reaction of complex **13** is representative. Complex **13** (0.0893 g, 0.20 mmol) was heated in 10 mL of H_2O at 100 °C for 1 h, while oxygen was bubbled through. Water and volatile products were evaporated *in vacuo*, and the residue was washed with diethyl ether (3 × 2 mL) and dried *in vacuo*. An orange-yellow product was obtained. The ^{1}H NMR spectrum of the product was identical with the ^{1}H NMR spectrum of **28**. The yield is quantitative. In this manner complexes **14**−**21** and **25**−**27** could be converted into the corresponding complexes **28**−**33**. Complexes **22**−**24** could not be converted.

Identification of Benzaldehyde and H$_2$O$_2$ from Reaction of 27 with H$_2$O and O$_2$. In 10 mL of water **27** (0.084 g, 0.16 mmol) was dissolved in air at 100 °C. The reaction mixture was cooled to room temperature. The volatile products were distilled *in vacuo*, and the distillate was extracted with $CDCl_3$ (2 × 0.5 mL). The ^{1}H NMR of the extract showed only benzaldehyde as a product, as concluded from comparison with the spectrum of a sample of benzaldehyde. The amount of H_2O_2 was determined by iodometry,[53−55] which showed the formation of H_2O_2 in 80−90% yield.

Computational Details. All calculations were performed using CAChe WorkSystem software[56] on an Apple Power Macintosh 9500 equipped with 2 CAChe CXP coprocessors. The molecular mechanics calculations were performed using the augmented MM2 force field.[57] Block-diagonal Newton−Raphson was used as the optimization method. As imput geometry an octahedral Rh center was used, and the N−Rh, Cl−Rh, and C−Rh bonds and the Rh−C−Cl angle were fixed at the values found in the X-ray crystal structures of **12** and **15**. The obtained structure was optimized fully. An optimized map search was performed to investigate the steric interactions around the Rh center. The torsion angles C(7)−C(6)−N−Rh and Cl(eq)−Rh−R^3 (R^3 = Cl, CH_2Cl, $CHCl_2$, CH_2Ph, CH(Ph)Cl) were rotated stepwise (15° at a time).

X-ray Structure Determination of 7, 8, 12, 13, and 15. Crystals of complex **7** were obtained in two different shapes (from different batches), which turned out to be an orthorhombic modification (**7^{ortho}**, plate-shaped crystals) and a monoclinic modification (**7^{mono}**, block-shaped crystals). Both structures were determined, although the orthorhombic modification diffracted rather poorly; only 16% of the intensity data in the θ = 25° region were above the 2.5σ(I) level due to severe solvent disorder.

Crystals suitable for X-ray diffraction were glued to the tip of a glass fiber and transferred into the cold nitrogen stream of an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Broad, highly structured reflection profiles of varying width were observed for the complex **7^{mono}**, which is indicative of a crystal consisting of several slightly misaligned individuals. The **A**-vector method[58] was used to calculate for each reflection the ψ angle for which the minimal profile width could be expected. For all structures accurate unit cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of a set of well-centered reflections (SET4[59]). Reduced-cell calculations did not indicate higher lattice symmetry.[60] Crystal data and details on data collection and refinement are collected in Table 1 for complexes **12**, **13**, and **15** and in the Supporting Information for complexes **7^{mono}**, **7^{ortho}**, and **8**. All data were collected at 150 K using Mo Kα radiation and a graphite monochromator.

Data were corrected for Lp effects and for the observed linear decay of the reference reflections. For complex **13** the standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.03I)^2$.[61] An analytical absorption correction, based on Gaussian integration techniques (ABSORB[62]), was applied for the complex **7^{ortho}**; empirical absorption correction was applied for compounds **8**, **12**, **13**, and **15** (DIFABS[63]). No absorption correction was applied for the complex **7^{mono}**.

The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[64]).

Compound **13** was refined on F by full-matrix least-squares techniques (SHELX76[65]). All other structures were refined on F^2 using full-matrix least-squares techniques (SHELXL-93[66]); no observance criterion was applied during refinement on F^2. Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. All methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the C−C bonds.

The asymmetric unit of **15** contains two independent molecules, both of which display conformational disorder in the chloromethyl moiety. A disorder model consisting of two positions for the Cl atom and the methylene hydrogen atoms was introduced in both independent molecules. The site occupation factor of the major disorder component was refined to 0.844(4) and 0.843(5) for **15^a** and **15^b**, respectively.

A difference Fourier study of **7^{ortho}** revealed a large number of residual density peaks (~2.4 e Å^{-3}) in two sets of symmetry-related interlocking channels, both running parallel to the *ab* plane. No discrete solvent model could be refined. The BYPASS procedure,[67] as implemented in the program PLATON,[68] was used to take this electron density into account. After the application of BYPASS the refinement became more stable. A total of 54 electrons was found in each of the two

---

(53) Milas, N. A. *Encyclopedia of Chemical Technology*; Interscience: New York, 1951; Vol. 7, p 727.

(54) Vogel, A. I. *A Textbook of Qualitative Inorganic Analysis*, 3rd ed.; Wiley: New York, 1961; p 343.

(55) Barbaro, P.; Bianchini, C.; Frediani, P.; Meli, A.; Vizza, F. *Inorg. Chem.* **1992**, *31*, 1523.

(56) CAChe Worksystem version 3.7, CSI, 18700 N. W. Walker Road, Building 92-01, Beaverton, OR 97006.

(57) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(58) Duisenberg, A. J. M. *Acta Crystallogr.* **1983**, *A39*, 211.

(59) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

(60) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(61) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.

(62) Spek, A. L. *ABSORB Program for absorption correction*; Utrecht University: Utrecht, The Netherlands, 1983; p 283.

(63) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(64) Beurkens, P. T.; Admiraal, G.; Beurkens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System: Technical Report of the Crystallographic Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(65) Sheldrick, G. M. *SHELX76 Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(66) Sheldrick, G. M. *SHELXL93. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(67) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(68) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table 1. Crystallographic Data for 12, 13, and 15

	12	**13**	**15**
Crystal Data			
formula	$C_{15}H_{23}ClN_3Rh$	$C_{14}H_{21}Cl_3N_3Rh$	$C_{20}H_{29}Cl_3N_3Rh$
mol wt	383.73	440.60	520.73
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a, Å	9.5744(4)	28.461(2)	16.7524(11)
b, Å	10.9998(6)	9.0062(6)	18.3617(10)
c, Å	16.0668(6)	15.309(2)	15.3835(10)
β, deg		116.479(10)	110.336(5)
V, Å^3	1692.10(13)	3512.4(6)	4437.1(5)
D_{calc}, g cm^{-3}	1.506	1.666	1.559
Z	4	8	8
F(000)	784	1776	2128
μ, cm^{-1}	11.6 (Mo Kα)	14.1 (Mo Kα)	11.3 (Mo Kα)
cryst size, mm	0.3 × 0.5 × 0.5	0.03 × 0.20 × 0.38	0.2 × 0.4 × 0.4
Data Collection			
θ_{min}, θ_{max}, deg	2.2, 27.5	1.5, 27.5	1.1, 27.5
SET4 θ_{min}, θ_{max} deg	11.38, 13.62 (21 rflns)	10.02, 13.99 (25 rflns)	11.42, 13.97 (25 rflns)
scan type	ω	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$, deg	$0.62 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.77 + 0.35 \tan \theta$
horiz, vert, aperture, mm	$2.30 + 1.15 \tan \theta$, 4.00	3.23, 4.00	2.68, 4.00
X-ray exposure, h	11	38	59
linear instability, %	2	6	1
ref rflns	062, 251, $32\bar{4}$	$\bar{2}\bar{2}4$, $4\bar{2}3$, $7\bar{3}2$	$\bar{4}\bar{5}2$, $\bar{3}\bar{2}5$, $2\bar{4}3$
data set	−12 to +11, −14 to +14, −20 to 0	-36 to +36, −11 to 0, −19to +19	−21 to +20, −23 to 0, 0 to −19
total no. of data	7865	8866	15 319
total no. of unique data	3881	4020	10155
R_{int}	0.016	0.131	0.011
no. of obsd data	no crit applied	3334 ($I > 2.5\sigma(I)$)	no crit applied)
abs corr range	0.89, 1.16 (DIFABS)	0.67, 1.46 (DIFABS)	0.90, 1.08 (DIFABS)
Refinement			
no. of refined params	187	203	495
final $R1^a$	0.0172 (3784$I > 2\sigma$(I))	0.0481 (3334$I > 2.5\sigma$(I))	0.0274 (8825 $I > 2\sigma$(I))
final $wR2^b$	0.0419		0.0634
final $R_w{}^c$		0.0653	
goodness of fit	1.10	4.36	1.03
$w^{-1\ d}$	$\sigma^2(F^2) + (0.0242P)^2 + 0.23P$	$\sigma^2(F^2) + 0.001999F^2$	$\sigma^2(F^2) + (0.0251P)^2 + 6.11P$
Flack x param	−0.01(3)		
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.002	0.009, 0.060	0.013, 0.519
min and max residual density, e Å^{-3}	−0.22, 0.32 (near Rh)	−1.62, 1.42 (near Rh)	−0.87, 0.86 (near Rh)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. [c] $R_w = [\sum[w(||F_o| - |F_c||)^2]/\sum[w(F_o{}^2)]]^{1/2}$. [d] $P = (\mathrm{Max}\ (F_o{}^2, 0) + 2F_c{}^2)/3$.

channel systems, which had a volume of 330 Å^3 each. The channels are probably filled with benzene, which was used in crystallization.

The data set for **7$^{\mathbf{ortho}}$** did not allow for anisotropic refinement of the non-hydrogen atoms, except for the Rh atom. The non-hydrogen atoms of all other structures were refined with anisotropic thermal parameters, except for the minor disorder component Cl atoms in **13**. Hydrogen atoms of **13** were refined with one overall isotropic thermal parameter amounting to 0.034(4) Å^2. The hydrogen atoms of the other compounds were refined with a fixed isotropic thermal displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms.

The Flack x parameters,[69] derived during the final structure factor calculation of **7$^{\mathbf{mono}}$**, **8**, and **12**, indicate correctly assigned absolute structures. The data set of **7$^{\mathbf{ortho}}$** did not produce a reliable value for the x parameter.

Compound **13** was refined using neutral atom scattering factors taken from Cromer and Mann[70] with anomalous dispersion corrections from Cromer and Liberman.[71] Neutral atom scattering factors and anomalous dispersion corrections used in the other refinements were taken from ref 72. Geometrical calculations and illustrations were performed with PLATON[68] and PLUTON;[73] all calculations were performed on a DECstation 5000 cluster.

Results

General Considerations. The numbers of the synthesized compounds and the numbering used for the NMR identification are given in Tables 2 and 3, respectively. The NMR data have been collected in Table 4 (^{1}H NMR) and Table 5 (^{13}C NMR).

Synthesis of [RhCl(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (7−12). The novel complexes [RhCl(2,6-(C(R^1)=NR^2)$_2$-C$_5$H$_3$N)] (R^1 = H, R^2 = *i*-Pr (**7**), *t*-Bu (**8**), cyclohexyl (**9**), *p*-anisyl (**10**); R^1 = Me, R^2 = *p*-anisyl (**11**), *i*-Pr (**12**)) were prepared by a ligand displacement reaction in benzene from [RhCl(cyclooctene)$_2$]$_2$ or [RhCl(C$_2$H$_4$)$_2$]$_2$ (Scheme 1, for the numbering of the complexes, see Table 2). For complete conversion the reaction mixture was heated to reflux in benzene for 30 min, after which the Rh(I) complexes crystallized from the warm benzene solutions.

^{1}H NMR (Table 4) is an excellent tool to determine the geometry of the compounds, as in most cases the signals are sufficiently separated. Coordination of the

---

(69) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(70) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(71) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(72) Wilson, A. J. C. *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

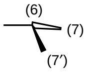
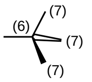
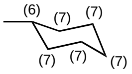
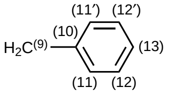
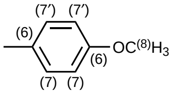
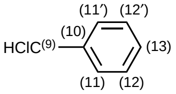
(73) Spek, A. L. *PLUTON Molecular Graphics Program*; Utrecht University: Utrecht, The Netherlands, 1995.

Table 2. Numbering of Synthesized Compounds and Ligands

ligand	R^1	R^2
1	H	*i*-Pr
2	H	*t*-Bu
3	H	cyclohexyl
4	H	*p*-anisyl
5	CH_3	*p*-anisyl
6	CH_3	*i*-Pr

complex	R^1	R^2	R^3
7	H	*i*-Pr	
8	H	*t*-Bu	
9	H	cyclohexyl	
10	H	*p*-anisyl	
11	CH_3	*p*-anisyl	
12	CH_3	*i*-Pr	
13	H	*i*-Pr	CH_2Cl
14	H	*t*-Bu	CH_2Cl
15	H	cyclohexyl	CH_2Cl
16	H	*p*-anisyl	CH_2Cl
17	CH_3	*p*-anisyl	CH_2Cl
18	CH_3	*i*-Pr	CH_2Cl
19	H	*i*-Pr	$CHCl_2$
20	H	*t*-Bu	$CHCl_2$
21	CH_3	*i*-Pr	$CHCl_2$
22	H	*i*-Pr	CH_2Ph
23	H	*t*-Bu	CH_2Ph
24	CH_3	*i*-Pr	CH_2Ph
25	H	*i*-Pr	CHClPh
26	H	*t*-Bu	CHClPh
27	CH_3	*i*-Pr	CHClPh
28	H	*i*-Pr	Cl
29	H	*t*-Bu	Cl
30	H	cyclohexyl	Cl
31	H	*p*-anisyl	Cl
32	CH_3	*p*-anisyl	Cl
33	CH_3	*i*-Pr	Cl

Table 3. Numbering for NMR Identification

R^1	R^2	R^3
$C^{(5)}H_3$		$C^{(9)}H_2Cl$
		$C^{(9)}HCl_2$
		
		

ligand for the complexes **7**−**12** can be inferred from the chemical shift differences of H(2), H(4), and H(5) when compared to H(2), H(4), and H(5) of the free ligands **1**−**6**. Pyridine coordination is clear from the 1.5 ppm high-field shift of H(2). The imine coordination is apparent from a high-field shift of 0.3 ppm for H(4). For complexes **7**−**10** a $^3J_{Rh-H}$ coupling constant on H(4) was observed of about 3.5−3.9 Hz. For complexes **11** and **12** the imine coordination is obvious from a high-field shift of 1.2 ppm for H(5). In the ^{13}C NMR spectra the high-field shift of C(4) and the $^2J_{Rh-C}$ coupling constant on C(1) are indicative of coordination of the ligand. ^{13}C NMR spectra could not be measured for complexes **10** and **11** because of their low solubility.

The symmetric square-planar geometry is clear from the equivalency of the hydrogen and carbon atoms with and without the prime (′) mark.

Molecular Geometry and Crystal Structure of 7, 8, and 12. The structural features of **7**, **8**, and **12** are similar and are described here together. Two crystal forms of **7**, which are orthorhombic ($\mathbf{7^{ortho}}$) and monoclinic ($\mathbf{7^{mono}}$) forms were determined. Because the crystal structure of $\mathbf{7^{mono}}$ has been determined more accurately, only the structural data for $\mathbf{7^{mono}}$ is given in the Supporting Information. An ORTEP drawing of **12** along with the adopted numbering scheme is shown in Figure 1. Selected bond distances and angles for **12** are given in Table 6, while selected bond distances and angles for **8** are given in the Supporting Information.

The structure determinations show that $\mathbf{7^{mono}}$, **8**, and **12** are mononuclear, distorted-square-planar rhodium complexes with the three N atoms of the nitrogen ligand and a chloride atom coordinated to the Rh(I) atom. The deviation of the rhodium atom from the least-squares plane through N(1)−N(2)−N(3) increases from 0.024(1) Å for $\mathbf{7^{mono}}$ to 0.073(1) Å for **12** and to 0.100(1) Å for **8**. Also, the angle between the Rh−Cl(1) bond and the N(1)−N(2)−N(3) plane, (ϕ; see Figure 2) increases from 5.34(16)° for $\mathbf{7^{mono}}$ to 10.04(9)° for **12** and to 11.73(11)° for **8**. The comparable N(2)−Rh−N(3) angles of 158.08(13), 157.56(8), and 158.30(6)° for the complexes $\mathbf{7^{mono}}$, **8**, and **12**, respectively, are distorted from the ideal angle of 180° and are in the same range as those found for other metal 2,6-bis(R^2-ethylidyneimino)pyridine (R^2 = alkyl, aryl) complexes.[74−76] The Rh−N and Rh−Cl bond lengths of the complexes $\mathbf{7^{mono}}$ and **8** and the Rh−N(2) and Rh−N(3) bond lengths of the complex **12** are comparable to the lengths of the Rh−N and the equatorial Rh−Cl bonds in the Rh(III) chloromethyl complexes **13** and **15** (see Tables 6−8), while both the Rh−N(1) and the Rh−Cl bond lengths of the complex **12** are slightly shorter than those found in the Rh(III) chloromethyl complexes **13** and **15** (see Tables 6−8). The N(2)−C(6) and N(3)−C(10) bond lengths of the complexes $\mathbf{7^{mono}}$ and **8** are not different from the C−N bond lengths in the Rh(III) complexes **13** and **15**, while the N(2)−C(6) and N(3)−C(10) bond lengths of complex **12** are longer than the C−N bond lengths in the Rh(III) complexes **13** and **15** (Tables 6−8).

Steric Interactions in 7, 8, and 12. Intramolecular distances between several substituents in **7**, **8**, and **12** were compared to the van der Waals radii, to analyze possible steric interactions. In Figure 3 a space-filling model of the X-ray structure of complex **12** is shown, in which the interaction between the chloride atom and the *i*-Pr substituents is evident. The chloride atom is pressed out of the plane of the molecule by the *i*-Pr groups. The distances between the hydrogen atoms of the *i*-Pr group and the chloride in **12** are between 2.613(4) and 2.666(11) Å, which are 0.28−0.34 Å shorter than the sum of the van der Waals radii. In **7**, the values are respectively 2.777(6) and 2.932(16) Å and 0.02−0.17 Å for the monoclinic modification and 2.66(5) and 2.90-

---

[74] Alyea, E. C.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1975**, *14*, 2491.

[75] Blake, A. J.; Lavery, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans* **1989**, 965.

[76] Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500.

Table 4. ^{1}H NMR Data[a] (ppm) of Ligands and Compounds

no.	H(2)	H(3)	H(4)/H(5)	H(9)[b]	other
1[c]	8.03	7.79	8.44		H(6), 3.66 [sept, 2H]; H(7), 1.29 [d, 12H]
2[d]	8.01	7.79	8.36		H(7), 1.31 [s, 18H]
3[d]	7.98f	7.77f	8.39		H(6), 3.3 [m, 2H]; H(7), 1.1−2.0 [multi, 20H]
4[d]	8.25f	7.92f	8.67		H(7), 6.97 and 7.36 [both d, 8H]; H(8), 3.86 [s, 6H]
5[c]	8.27	7.89	2.37		H(7), 6.84 and 6.95 [both d, 8H]; H(8), 3.84 [s, 6H]
6[c]	8.06	7.68	2.40		H(6), 3.93 [sept, 2H]; H(7), 1.24 [d, 12H]
7[e]	6.54	7.65	8.02 (3.8)[f]		H(6), 4.60 [sept, 2H]; H(7), 1.65 [d, 12H]
8[e]	6.54	7.74	8.10 (3.9)[f]		H(7), 1.90 [s, 18H]
9[e]	6.61	7.68	8.02 (3.8)[f]		H(6), 4.35 [m, 2H]; H(7), 1.1−2.4 [multi, 20H]
10[e]	6.69	7.69	8.31 (3.5)[f]		H(7), 7.99 and 6.80 [both d, 8H]; H(8), 3.28 [s, 6H]
11[e]	6.80[i]	7.78	1.10		H(7), 6.80[i] and 7.43 [both d, 8H]; H(8), 3.27 [s, 6H]
12[e]	6.52	7.69	1.07		H(6), 4.48 [sept, 2H]; H(7), 1.98 [d, 12H]
13[d]	7.88	8.07	8.19 (3.2)[f]	4.47 (3.2)	H(6), 4.5 [m, 2H]; H(7), 1.55 [t, 12H]
14[d]	7.93	8.10−8.14[i]	8.10−8.14[i]	4.93 (3.3)	H(7), 1.72 [s, 18H]
15[d,g]	7.87	8.06	8.14 (2.6)[f]	4.42 (2.8)	H(6), 4.06 [m, 2H]; H(7), 1.1−2.6 [m, 24 H]
16[d]	7.98−8.11[i]	7.98−8.11[i]	8.20 (3.3)[f]	4.33 (3.1)	H(7), 6.94 and 7.70 [d, 8H]; H(8), 3.86, [s, 3H]
17[d]	8.02	8.23	2.56	4.31 (3.2)	H(7), 6.93 and 7.3 [br, 8H]; H(8), 3.83 [s, 6H]
18[d]	7.84	8.11	2.67	4.6[i]	H(6), 4.6[i] [br, 2H]; H(7), 1.57 [d, 6H], 1.64 [br, 6H]
18[d,h,j]	*7.82*,[k] *7.89*[k], 7.90	*8.13*,[l] 8.17	*2.73*,[m] *2.63*,[m] 2.63	*4.55 (3.2)*, 4.72 (3.3)	H(6), *5.47 [sept, 1H], 4.36 [sept, 1H],* 4.36 [sept, 2H]; H(7), 1.4−1.6 [m, 12H]
19[d]	7.91	8.14	8.17 (3.4)[f]	6.96[k] (3.3)	H(6), 4.64 [s, 2H]; H(7), 1.55[dd, 12H]
20[d]	7.99	8.21	8.11 (3.4)[f]	7.35[k] (3.6)	H(7), 1.67 [s, 18H]
21[d]	7.87	8.17	2.69	7.14[k] (3.5)	H(6), 4.95 [br s 2H]; H(7), 1.57 [d, 6H], 1.62 [d, 6H]
21[d,j,t]	*7.96*,[k] *7.86*,[k] 8.03	*8.22*, 8.25	*2.69*,[m] *2.61*,[m] 2.74	*7.03*[k] (*3.5*), 6.88[k] (3.2)	*H(6), 5.13 [sept, 1H], 4.29 [m, 1H];* H(6), 4.29 [m, 2H]; H(7) and*H(7), 1.56−1.43 [m, 24H]*
22[d]	7.58	7.84	7.96 (2.6)[f]	3.36 (3.3)	H(6), 4.56 [m, 2H]; H(7), 1.60 [d, 6H], 1.43 [d, 6H]; H(11), 6.54 [d, 2H]; H(12), 6.82 [t, 2H]; H(13), 6.94 [t, 1H]
23[d]	7.39	7.70	7.95 (3.5)[f]	4.06 (3.4)	H(7), 1.80 [s, 18H]; H(11), 6.49 [d, 2H]; H(12), 6.70 [t, 2H]; H(13), 6.85 [t, 1H]
24[d]	7.37	7.73	2.68	3.64	H(6), 4.9 [br, 2H]; H(7), 1.68 [br dd, 12H]; H(11), 6.41 [d, 2H]; H(12), 6.70 [t, 2H]; 7.05 [t, 1H]
24[d,n,j]	*7.37*, 7.39	*7.74*, 7.72	*2.60*, *2.53*, 2.53	*3.50 (3.2)*, 3.79 (3.2)	*H(6), 5.57 [sept, 1H], 4.43 [sept, 1H]; H(7), 1.80 [d, 3H], 1.74 [d, 2H], 1.71 [d, 2H], 1.64 [d, 2H];* H(6), 4.43 [sept, 2H]; H(7), 1.57 [d, 6H], 1.50 [d, 6H]; H(*11,12,13*,11,12,13), 6.32−6.8 [m, 10H]
25[d]	7.88,[k] 7.70[k]	8.04	8.21[k] (3.2),[f] 7.73[k] (3.0)[f]	6.53[k] (4.3)	H(6), 4.75 [sept, 1H], 3.79 [sept, 1H]; H(7), 1.65 [d, 3H], 1.62 [d, 3H], 1.42 [d, 3H], 0.87 [d, 3H]; H(11,12,13), [br. 5H]
25[d,o]	7.91,[k] 7.70[k]	8.03	8.22[k] (3.2),[f] 7.74[k] (3.2)[f]	6.42[k] (4.3)	H(6), 4.63 [sept, 1H], 3.67 [sept, 1H]; H(7), 1.55 [m, 6H], 1.33 [d, 3H], 0.84 [d, 3H]; H(11), 7.26 [ho d, 1H], 6.67 [d, 1H]; H(12), 7.06 [m, 2H]; H(13), 6.96 [ho t, 1H]
26[d]	7.97[k]7.91[k]	8.18	8.08[k] (3.4),[f] 7.93[k] (3.0)[f]	6.87[k] (4.3)	H(7), 1.78 [s, 9H], 1.08 [s, 9H]; H(11,12,13), 7.08 [br, 5H]
27[d]	7.83,[p] 7.62[q]	8.06[r]	2.70,[m] 2.42[m]	6.66[k] (3.6)	H(6), 4.9 [br, 1H], 4.70 [sept, 1H]; H(7), 1.72 [d, 3H], 1.69 [d, 3H], 1.47 [br d, 3H], 0.73 [br 3H]; H(11,12,13), 7.03 [br, 5H]
27[d,n,j]	*7.98*,[k] *7.82*,[k] 7.61,[k] 7.12[k]	*8.21*, 7.79	*2.64*,[m] *2.34*,[m] 2.69,[m] 2.34[m]	6.64 (4.5), 6.30 (4.3)	*H(6), 4.45 [sept, 1H], 5.3*[u] *[1H]; H(7), 1.81 [br d, 3H], 1.48 [d, 3H], 1.22 [d, 3H], 0.12 [d, 3H]; H(11), 7.44 [d, 1H], 7.05*[i] *[d, 1H]; H(12), 7.05i [m, 2H]; H(13), 6.54 [ho t, 1H]*; H(6), 4.34 [br, 2H]; H(7), 1.66−1.56 [br m,12H]; H(11), 7.81 [m, 2H]; H(12), 6.45 [m, 2H]; H(13), 6.60 [ho t, 1H]
28[s]	8.23	8.38	8.58 (2.4)[f]		H(6), 4.33 [sept, 2H]; H(7), 1.55 [d, 12H]
29[s]	8.27	8.42	8.47 (2.2)[f]		H(7), 1.60 [s, 18 H]
30[d]	7.95	8.15	8.13(2.6)[f]		H(6), 4.32 [br t, 2H]; H(7), 2.4−0.9 [m, 20 H]
31[s]	8.38	8.50	8.56 (2.8)[f]		H(7), 7.78 [d, 4H], 7.30 [d, 4H]; H(8), 3.99 [s, 6H]
32[s]	8.42	8.52	2.80		H(7), 7.38 [d, 4H], 7.08 [d, 4H]; H(8), 3.95 [s, 6H]
33[d]	7.95	8.22	2.72		H(6), 4.4 [br, 2H]; H(7), 1.65 [br d, 6H], 1.56 [br s, 6H]
33[d,t,j]	*2.26*,[k] *7.99*,[k] *7.93*[k]	8.01, *8.23*	2.75, *2.85*,[m] *2.75*[m]		H(6), 4.36 [sept, 2H]; H(7), 1.65 [d, 12H]; H(6), 5.73 [sept, 1H], 4.36 [sept, 1H]; H(7), 1.60 [d, 6H], 1.50 [d, 6H]
33[s]	8.36	8.49	2.94		H(6), 4.64 [sept, 2H]; H(7), 1.54 [d, 12H]

[a] Unless otherwise specified, the spectra were recorded at room temperature at 300.13 MHz. Assignments: H(2), d, 2H; H(3), t, 1H; H(4), s, 2H or with $^3J_{\mathrm{Rh-H}}$ (Hz), d, 2H; H(5), s, 6H. Abbreviations: s = singlet, d = doublet, t = triplet, dd = double doublet, sept = septet, m = multiplet, br = broad, ho = higher order. The atoms with the (prime) mark will not be mentioned if they have the same chemical shift as the atoms without the (prime) mark. If they have different values, both shifts will be given. [b] $^2J_{\mathrm{Rh-H}}$ in Hz. [c] $CDCl_3$. [d] CD_2Cl_2. [e] C_6D_6. [f] $^3J_{\mathrm{Rh-H}}$ (Hz). [g] 263 K. [h] 230 K. [i] Complicated by other signals. [j] Values for the bidentate isomer in italics. [k] d, 1H. [l] dd, 1H. [m] s, 3H. [n] 223 K. [o] 218 K. [p] br d, 1H. [q] br, 1H. [r] br t, 1H. [s] D_2O. [t] 183 K. [u] Complicated by solvent signal.

(16) Å and 0.29−0.05 Å for the orthorhombic modification. In **12** the shortest distance between the hydrogen atoms of the R^1 methyl substituent (see Figure 1; the hydrogen atoms on C(11) and C(15)) and the *i*-Pr hydrogen atoms is 2.036(16) Å, which is 0.36 Å shorter than the sum of the van der Waals radii. Also, the distance of 2.052(11) Å between the *meta* hydrogen atom of the pyridine ring and the methyl substituent is 0.35 Å shorter than the sum of the van der Waals radii.

C−Cl Activation by [RhCl(2,6-(C(R^1)=NR^2)$_2$-C$_5$H$_3$N)] (7−12). The nucleophilicity of the complexes **7−12** was studied by reaction with dichloromethane, chloroform, benzylchloride, α,α-dichlorotoluene and chlorobenzene (Scheme 2, see Table 2 for numbering of the complexes). The C−Cl bond of chlorobenzene could not be activated.

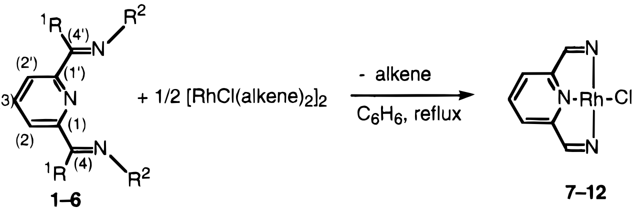
Chloromethyl Complexes [RhCl$_2$(CH$_2$Cl)(2,6-(C(R^1)=NR^2)$_2$C$_5$H$_3$N)] (13−18). The chloromethyl com-

Table 5. ^{13}C NMR Data^{a} (ppm) for Ligands and Compounds

no.	C(1)	C(2)	C(3)	C(4)	C(9)^{b}	other
1^{c}	155.1	122.6	137.5	159.6		C(6), 61.9; C(7), 24.5
2^{d}	156.0	122.0	137.6	156.8		C(6), 58.5; C(7), 30.0
3^{d}	155.6	122.4	137.5	159.9		C(6), 70.3; C(7), 25.3, 26.4, 35.0
4^{d}	155.8	123.0	137.9	158.6		C(6), 144.3, 159.9; C(7),115.2, 123.5; C(8), 56.2
5^{c}	156.8	122.7	137.3	167.9		C(5), 16.7; C(6), 144.3, 156.3; C(7),114.8, 121.4; C(8), 56.0
6^{c}	156.4	120.8	136.3	163.5		C(5), 13.1; C(6), 51.3; C(7), 23.2
7^{e}	155.4 (3)^{b}	122.6	122.5	155.8		C(6), 63.0; C(7), 22.7
8^{e}	155.1 (3)^{b}	124.1	121.8	154.8		C(6), 66.1; C(7), 29.6
9^{e}	155.6 (3)^{b}	122.5	122.5	159.9		C(6), 70.6; C(7), 25.5, 25.6, 33.3
12^{e}	156.4 (3)*b*	124.2	121.6	162.7		C(5), 15.6; C(6), 58.6; C(7), 22.4
13^{d}	157.5	128.9	140.7	165.1	41.9 (27)	C(6), 64.7; C(7), 24.5, 25.3
14^{d}	156.0	127.7	139.2	163.2	39.3 (27)	C(6), 70.0; C(7), 29.8
15^{d,f}	155.9	126.9	138.7	163.3	40.3 (27)	C(6), 70.3; C(7), 26.0, 26.1, 33.2 34.5
17^{d}	157.2	127.5^{i}	138.4	175.4	42.5(28)	C(5),19.3; C(6) and C(7), 114.3, 127.5,^{i} 139.3, 160.0; C(8),56.2
17^{d,k}	157.0	123.5	139.0	176.1	42.7 (29)	C(5), 20.3; C(6) and C(7), 113.8, 114.7, 127.8, 128.4, 139.4, 159.9; C(8), 58.4
18^{d}	158.1	126.3^{h}	138.0	172.0	40.6 (28)	C(5) and C(7), 18.2−22.5;^{i} C(6), 59.8
18^{d,g,j}	*158.3*, *157.3*, 157.7	*126.2*, *127.4*, 127.4	*138.6*, 138.8	*174.1*, *171.6*, 172.2	*40.6 (28)*, 40.9 (28)	C(5) and C(7), 17.8−22.8;^{i} C(6), *60.1*, *56.7*, 60.8
22^{d,l}	155.8	127.6	136.8	161.4	26.7 (20)	C(6), 63.3; C(7), 25.6, 23.7; C(10), 146.5; C(11,12), 128.4, 127.7; C(13), 126.1
23^{d,l}	156.9	128.0	137.9	163.4	22.9 (18)	C(6), 71.4; C(7), 31.8; C(10), 147.8; C(11,12), 129.2, 129.9; C(13), 128.0
24^{d,l}	157.7	124.4	136.2	171.2	*m*	C(5),^{m} C(6), 22.1, 23.0; C(10), 147.1; C(11,12), 128.7, 127.6; C(13), 125.7
24^{d,n,j}	*157.8*, *157.0*, 157.2	*i*	*136.6*, 136.7	*172.8*, *170.8*, 171.4	*22.9 (20)*, 21.1 (20)	*C(5)*, *22.3*, *17.8*; C(5), 18.0; *C(6)* and C(6), 23.6, 23.2, 22.6, 22.1, 21.4, 20.8 C(11,12,*11*,*12*),^{i} 128.8, 127.7, 127.5, 126.6, 125.4, 124.6

[a] Unless otherwise specified, the spectra were recorded at room temperature at 75.48 MHz. [b] $^{1}J_{\mathrm{Rh-C}}$ in Hz, given in parentheses. [c] $CDCl_3$. [d] CD_2Cl_2. [e] C_6D_6. [f] 263 K. [g] 230 K. [h] Broad. [i] Complicated by other signals. [j] Values for the second isomer given in italics. [k] 200 K. [l] 50.32 MHz. [m] Not visible. [n] 226 K.

Scheme 1. Reaction of the Ligands 1−6 with $[RhCl(alkene)_2]_2$ (Alkene = Cyclooctene, Ethene) To Yield the Rh(I) Complexes 7−12^{a}



[a] For the sake of clarity the R^{1} and R^{2} substituents have been omitted for the complexes **7**−**12**.

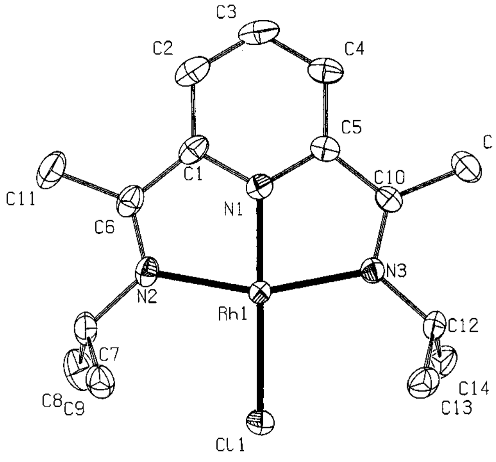


Figure 1. ORTEP[68] drawing (50% probability level) of **12**. The hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 12

Rh(1)−Cl(1)	2.3488(5)	N(2)−C(6)	1.305(3)
Rh(1)−N(1)	1.8962(16)	N(3)−C(10)	1.313(2)
Rh(1)−N(2)	2.0612(18)	C(5)−C(10)	1.455(3)
Rh(1)−N(3)	2.0644(18)	C(1)−C(6)	1.456(3)
Cl(1)−Rh(1)−N(1)	172.19(5)	N(1)−Rh(1)−N(3)	79.37(7)
Cl(1)−Rh(1)−N(2)	100.82(5)	N(2)−Rh(1)−N(3)	158.30(6)
Cl(1)−Rh(1)−N(3)	100.87(4)	N(2)−C(6)−C(1)	115.36(19)
N(1)−Rh(1)−N(2)	79.19(7)	N(3)−C(10)−C(5)	115.33(17)

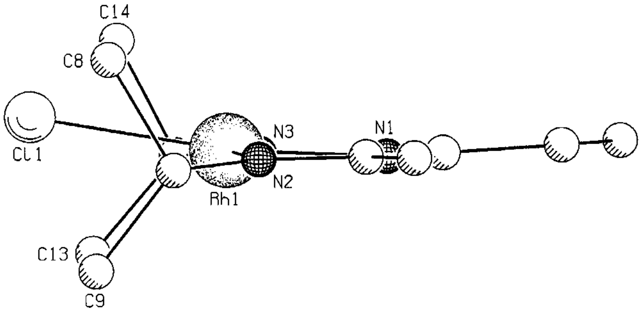


Figure 2. Side-view drawing of **12**, showing the chloride bending out of the N(1)−N(2)−N(3) plane. The angle between Rh(1)−Cl(1) and N(1)−N(2)−N(3) (=ϕ) is 10.04(9)°. Hydrogen atoms have been omitted for clarity.

plexes **13**−**18** have been prepared by dissolving the Rh(I) complexes **7**−**12** in dichloromethane at low temperature (−96 °C) followed by warming to room temperature, during which the color changed from dark green to light orange. It appeared that a clean and virtually quantitative oxidative addition of dichloromethane had taken place. The reaction is not reversible, since in deuteriodichloromethane the $Rh-CH_2Cl$ moiety remained intact. Sometimes side products $[RhCl_3(2,6\text{-}(C(R^1){=}NR^2)_2C_5H_3N)]$ (**28**−**33**) in the range of 1−10% yield have been observed owing to a reaction of the chloromethyl moiety, when insufficient care was taken to exclude water and oxygen (*vide infra*).

Characteristic of the chloromethyl complexes **13**−**18** is the proton signal of the chloromethyl moiety H(9) at δ 4.31−4.93 with a $^{2}J_{\mathrm{Rh-H}}$ coupling constant of 2.8−3.3

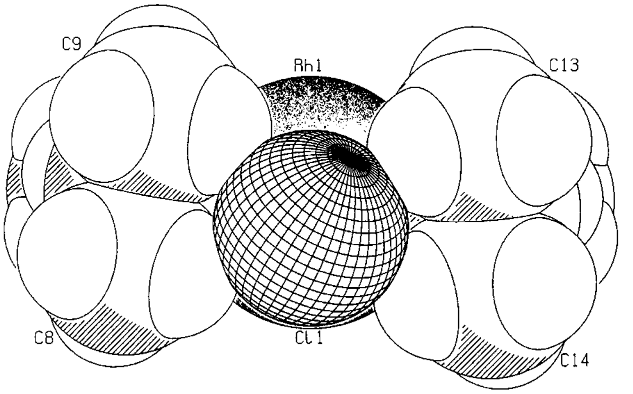
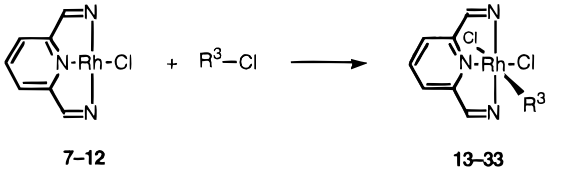


Figure 3. Space-filling model of **12** showing the steric repulsion between the *i*-Pr groups and Cl(1).

Scheme 2. Reaction of the Rh(I) Complexes 7−12 with R^3−Cl To Yield the Rh(III) Complexes 13−33[a]



7–12 **13–33**

R--Cl = CH_2Cl_2. $CHCl_3$, $PhCH_2Cl$, $PhCHCl_2$ and Cl_2

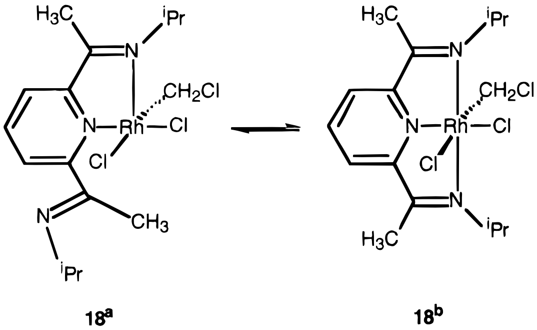
[a] For the sake of clarity the R^1 and R^2 substituents have been omitted for the complexes **7−33**.

Hz, which is in the range of reported values.[31,38,77] Complexes **13−16** also show a $^3J_{Rh-H}$ coupling constant of about 2.6−.3 Hz on the imine H(4) hydrogen atom.

The ^{13}C NMR spectra (Table 5) are quite difficult to measure, owing to the low solubility of all chloromethyl complexes and the long relaxation time of the chloromethyl carbon atom, which has been overcome by taking longer D_1 values. The ^{13}C NMR spectrum of **16** could not be measured.

The signals of C(1), C(2), C(3), and C(4) all show a low-field shift when compared to the corresponding signals of the free ligand. Characteristic of the chloromethyl complexes is the C(9) signal at δ 39−42 ppm with a $^1J_{Rh-H}$ coupling constant of 27−29 Hz, which is in accord with reported values.[31,38,77]

The signals for H(6), H(7), and H(9) of complex **18** are broad at room temperature but sharpen at 243 K, while at this temperature the number of signals for H(2), H(3), and H(9) are doubled. These observations indicate the presence of two isomers (**18^a** and **18^b**). The complex **18^a** (in *italics* in Table 4) contains a ligand which coordinates in a bidentate manner, which is not uncommon for 2,6-bis(R^2-ethylidyneimino)pyridine ligands,[47,78] as may be concluded from the doublet of doublets for the pyridine protons H(2), the two methyl signals H(5), and the two proton signals H(6). In complex **18^b** the ligand coordinates as a terdentate species, since there is only one singlet for the methyl hydrogen atoms H(5), one doublet for the pyridine hydrogen atoms H(2), and one signal attributable to H(6). The signals for H(7) of complexes **18^a** and **18^b** could not be used for further identification, because of overlap. Low-temperature ^{13}C NMR spectra confirmed that complex **18^a** (in *italics* in Table 5) contains a bidentate ligand, because C(1) and C(1′), C(2) and C(2′), C(4) and C(4′), and C(6) and C(6′) are inequivalent. The shifts of C(1) and C(1′), C(2) and C(2′), C(4) and C(4′), and C(6) and C(6′) of complex **18^b** are equivalent, in accord with the terdentate coordination of the nitrogen ligand.



18^a **18^b**

Figure 4. The two isomers of **18**: **18^a** and **18^b**.

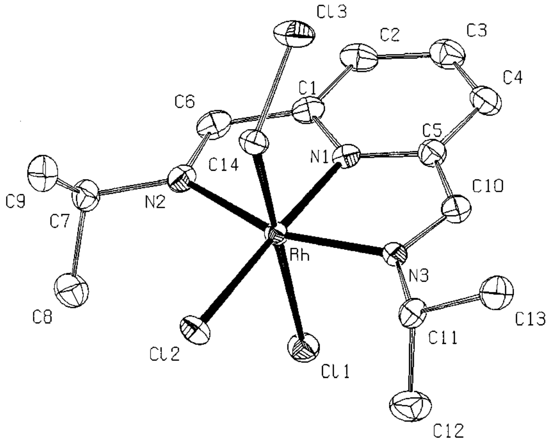


Figure 5. ORTEP[68] (50% probability level) drawing of **13**. The hydrogen atoms have been omitted for clarity.

The ratio between the isomers **18^a** and **18^b** is temperature dependent and has been measured between 183 and 243 K in CD_2Cl_2. When the temperature is lowered, the concentration of the six-coordinated Rh(III) isomer **18^b** increases with a concomitant decrease in the concentration of the five-coordinated Rh(III) isomer **18^a**. The two chloromethyl signals H(9) of **18^a** at δ 4.55 ppm and H(9) of **18^b** at δ 4.72 ppm were chosen as reporter signals. The thermodynamic parameters for the equilibrium (Figure 4) are $\Delta H° = 4.3\ (\pm\ 0.2)$ kJ/mol and $\Delta S° = 17.4\ (\pm\ 0.3)$ J/(mol K).

Molecular Geometry and Crystal Structure of 13. An ORTEP drawing of **13**, along with the adopted numbering scheme, is shown in Figure 5. Selected bond distances and angles are given in Table 7. The compound **13** is a mononuclear, distorted-octahedral rhodium complex. In the equatorial plane a chloride atom and the three N atoms of the terdentate 2,6-bis(isopropylcarbaldimino)pyridine ligand **1** are coordinated to the rhodium atom with the rhodium atom 0.055(1) Å and Cl(2) atom 0.127(1) Å out of the least-squares plane through N(1)−N(2)−N(3). The angle between the Rh−Cl(2) bond and the N(1)−N(2)−N(3) plane is 1.7(2)°. The N(2)−Rh−N(3) angle of 159.41(17)° is distorted from the ideal angle of 180° and is in the same range as found for other metal 2,6-bis(R^2-ethylidyneimino)pyridine complexes.[74−76] The chloromethyl ligand and the second chloride atom occupy the axial positions. The Rh−C(14) distance of 2.052(5) Å

---

[77] Yoshida, T.; Ueda, T.; Adachi, T.; Yamamoto, K.; Hugushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1137.

[78] Albon, J. M.; Edwards, D. A.; Moore, P. J. *Inorg. Chim. Acta* **1989**, *159*, 19.

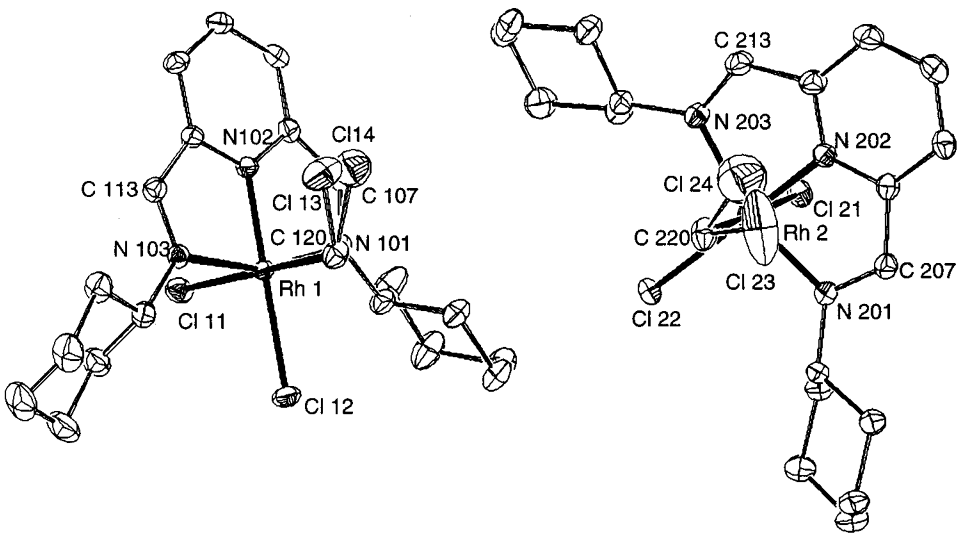


Figure 6. ORTEP[68] drawing (30% probability level) of **15**^{a} (left-hand side) and **15**^{b} (right-hand side). Atoms Cl(13) and Cl(23) represent the major disorder component; atoms Cl(14) and Cl(24) represent the minor disorder component. Hydrogen atoms have been omitted for clarity.

Table 7. Selected Bond Distances (Å) and Angles (deg) for 13

Rh−Cl(1)	2.4974(13)	C(14)−Cl(3)	1.790(5)
Rh−Cl(2)	2.3646(13)	N(2)−C(6)	1.293(7)
Rh−N(1)	1.923(4)	N(3)−C(10)	1.288(7)
Rh−N(2)	2.073(4)	C(1)−C(6)	1.467(7)
Rh−N(3)	2.041(4)	C(5)−C(10)	1.465(7)
Rh−C(14)	2.052(5)		
Cl(1)−Rh−Cl(2)	93.07(4)	N(3)−C(5)−C(10)	116.9(4)
Cl(1)−Rh−N(2)	90.06(13)	Cl(1)−Rh−N(1)	86.93(13)
Cl(1)−Rh−C(14)	178.51(16)	Cl(1)−Rh−N(3)	91.46(12)
Cl(2)−Rh−N(2)	102.70(13)	Cl(2)−Rh−N(1)	177.61(13)
Cl(2)−Rh−C(14)	85.68(15)	Cl(2)−Rh−N(3)	97.72(13)
N(1)−Rh−N(3)	79.89(18)	N(1)−Rh−N(2)	79.69(18)
N(2)−Rh−N(3)	159.41(17)	N(1)−Rh−C(14)	94.28(19)
N(3)−Rh−C(14)	87.90(18)	N(2)−Rh−C(14)	91.01(19)
N(2)−C(6)−C(1)	117.4(5)	Rh−C(14)−Cl(3)	116.9(3)

is shorter than the Rh-C distance of 2.161(2) Å found for [Rh(Cl)(CH$_2$Cl)(dmpe)$_2$]Cl.CH$_2$Cl$_2$[39] and 2.080(6) Å found for [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)].[31] The Rh−C(14)−Cl(3) angle of 116.9(3)° is in the range observed for other metal chloromethyl complexes (114.0(4)−120.4(5)°).[79] The C(14)−Cl(3) bond of 1.790(5) Å is quite long and falls at the high end of the 1.702(5)−1.803(8) Å range observed for other metal chloromethyl complexes.[79]

A possible steric interaction between the ^{i}Pr group and the chloromethyl moiety might be concluded from the H(14)−H(9) distance, which is 2.375(7) Å and thus 0.03 Å shorter than would have been expected on the basis of standard contact radii.

By comparison of the molecular geometries of the square-planar Rh(I) complex **7** and the octahedral Rh(III) complex **13**, which both have the same ligand **1** and a chloride atom coordinated in the equatorial plane, the difference in oxidation state of Rh and the influence of axial ligands in complex **13**, which are a chloride atom and a chloromethyl moiety, on the equatorial ligands could be determined. The Rh−N bond lengths of the coordinated ligand **1** and the Rh−Cl bond distance in the equatorial plane are not affected by the axially coordinated ligands or oxidation state, but the out-of-plane bending of the equatorially coordinated chloride atom is different. The angle ϕ (Figure 2) is reduced from 5.34(16)° in complex **7** to 1.7(2)° in complex **13**.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Compounds 15^{a} **and 15**^{b}

	Compound **15**^{a}		
Rh(1)−Cl(11)	2.4582(7)	Rh(1)−C(120)	2.052(3)
Rh(1)−Cl(12)	2.3669(6)	C(120)−Cl(13)[a]	1.808(3)
Rh(1)−N(102)	1.9155(18)	C(120)−Cl(14)[b]	1.668(10)
Rh(1)−N(101)	2.0493(19)	C(113)−N(103)	1.288(3)
Rh(1)−N(103)	2.0434(19)		
Cl(11)−Rh(1)−Cl(12)	93.90(2)	Cl(11)−Rh(1)−N(102)	87.50(6)
Cl(11)−Rh(1)−N(101)	85.61(6)	Cl(11)−Rh(1)−N(103)	91.49(6)
Cl(11)−Rh(1)−C(120)	178.84(8)	Cl(12)−Rh(1)−N(102)	178.56(6)
Cl(12)−Rh(1)−N(101)	99.90(5)	Cl(12)−Rh(1)−N(103)	100.09(5)
Cl(12)−Rh(1)−C(120)	85.33(8)	N(101)−Rh(1)−N(102)	79.86(8)
N(101)−Rh(1)−N(103)	159.95(7)	N(101)−Rh(1)−C(120)	93.67(10)
N(102)−Rh(1)−N(103)	80.19(8)	N(102)−Rh(1)−C(120)	93.27(10)
N(103)−Rh(1)−C(120)	89.49(10)	Rh(1)−C(120)−Cl(13)[a]	116.73(15)
C(107)−N(101)	1.288(3)	Rh(1)−C(120)−Cl(14)[b]	116.8(3)
	Compound **15**^{b}		
Rh(2)−Cl(21)	2.4774(6)	Rh(2)−C(220)	2.059(3)
Rh(2)−Cl(22)	2.3809(6)	C(220)−Cl(23)[a]	1.728(4)
Rh(2)−N(202)	1.920(2)	C(220)−Cl(24)[b]	1.771(12)
Rh(2)−N(201)	2.0481(19)	C(207)−N(201)	1.287(3)
Rh(2)−N(203)	2.0554(19)		
Cl(21)−Rh(2)−Cl(22)	96.13(2)	Cl(21)−Rh(2)−N(202)	86.37(6)
Cl(21)−Rh(2)−N(201)	90.44(5)	Cl(21)−Rh(2)−N(203)	89.51(6)
Cl(21)−Rh(2)−C(220)	179.39(8)	Cl(22)−Rh(2)−N(202)	177.44(5)
Cl(22)−Rh(2)−N(201)	100.73(6)	Cl(22)−Rh(2)−N(203)	99.48(6)
Cl(22)−Rh(2)−C(220)	84.21(10)	N(201)−Rh(2)−N(202)	79.73(8)
N(201)−Rh(2)−N(203)	159.68(8)	N(201)−Rh(2)−C(220)	89.99(9)
N(202)−Rh(2)−N(203)	79.98(8)	N(202)−Rh(2)−C(220)	93.28(11)
N(203)−Rh(2)−C(220)	89.93(9)	Rh(2)−C(220)−Cl(23)[a]	118.98(18)
C(213)−N(203)	1.286(4)	Rh(2)−C(220)−Cl(24)[b]	114.7(4)

[a] Major disorder component. [b] Minor disorder component.

Molecular Geometry and Crystal Structure of 15. The asymmetric unit cell of **15** contains two independent molecules (hereafter referred to as **15**^{a} and **15**^{b}), both with disorder in the position of the chloromethyl group. An ORTEP drawing of both molecules is given along with the adopted numbering in Figure 6. Selected bond distances and angles are given in Table 8 for complexes **15**^{a} and **15**^{b}. Both independent molecules are distorted-octahedral Rh(III) complexes. The difference between the two molecules is the conformations of the cyclohexyl group with respect to the N−C bond. In **15**^{b} both hydrogen atoms H(6) (see Table 3) of the cyclohexyl substituent point toward the chloro-

---

(79) Friedrich, H. B.; Moss, J. R. *Adv. Organomet. Chem.* **1991**, *33*, 235.

methyl moiety. **15^a^** differs from **15^b^** only in that one of the cyclohexyl substituents is slightly rotated around the N−C bond in such a way that H(6) is pointed toward the chloride atom Cl(12), which is coordinated in the equatorial plane. In both molecules the equatorial plane contains a chloride atom and a terdentate ligand **3**. In molecule **15^a** the rhodium atom lies 0.045 Å and the chloride atom Cl(12) 0.159(1) Å out of the least-squares plane N(101)−N(102)−N(103). The angle between the Rh−Cl(12) bond and the N−N−N plane is 2.74(10)°. In molecule **15^b** the rhodium atom is situated at 0.027(1) Å and the chloride atom Cl(22) at 0.043(1) Å out of the least-squares plane through N(201)−N(202)−N(203). The angle between the Rh−Cl(22) bond and the N(201)−N(202)−N(203) plane is 1.69(9)°. The N(101)−Rh(1)−N(103) angle of 159.95(7)° and the N(201)−Rh(2)−N(203) angle of 159.68(8)° are distorted from 180° by the bite of the ligand and are in the same range as found for other metal 2,6-bis(R^2-ethylidynimino)pyridine complexes.[74−76] The chloromethyl ligand and a second chloride atom occupy the axial positions. The Rh(1)−C(120) distance is 2.052(3) Å, and the Rh(2)−C(220) distance is 2.059(3) Å. These Rh−C distances are comparable to the ones found in **13**. The Rh(1)−C(120)−Cl(13) angle of 116.73(15)° and the Rh(2)−C(220)−Cl(23) angle of 118.98(18)° are in the expected range (114.0(4)−120.4(5)°) observed for other metal chloromethyl complexes.[79] The C(120)−Cl(13) bond of 1.808(3) Å is very long with respect to the range of 1.702(5)−1.803(8) Å for other metal chloromethyl complexes.[79] The length of the C(220)−Cl(23) bond at 1.728(4) Å is as expected.[79] The large difference in distances of the CH_2Cl moieties (especially in molecule **15^a**, but also to a lesser extent in molecule **15^b** (Table 8)) is a consequence of the disorder, which is described with a limited two-site static model. We did consider a constrained refinement. Since the C−Cl bond lengths are not very reliable in both cases, we have in the end chosen for a model without an extra parameter constraint.

Synthesis of Dichloromethyl Complexes 19−21. For the synthesis of the dichloromethyl complexes **19**−**21** the same procedure as for the chloromethyl complexes was used (Scheme 2; see Table 2 for the numbering of the complexes). The reaction is virtually quantitative and not reversible in $CDCl_3$, as the Rh−$CHCl_2$ moiety remains intact. In some instances **28**−**33** were observed as side products. Owing to low solubility the dichloromethyl complexes could only be analyzed by ^{1}H NMR (Table 4), elemental analysis, and MS-FAB$^+$.

Characteristic of the complexes **19**−**21** is the ^{1}H NMR signal of Rh−$CHCl_2$ at δ 6.96−7.35 ppm with a $^2J_{Rh-H}$ coupling constant of 3.3−3.6 Hz.

At room temperature the signals H(2), H(3), H(5), H(7), and H(9) of complex **21** are sharp, that for H(6), however, is broad. At 193 K two isomers (**21^a** and **21^b**) can be identified. In complex **21^a**, which is the major isomer (90−95% abundance), the ligand coordinates as a bidentate species, as is clear from the appearance of two doublets for H(2) and H(2′), two methyl signals H(5) and H(5′), two septets of H(6) and H(6′), and four doublets of H(7). Complex **21^b**, which occurs in 5−10% abundance, contains a ligand which is coordinated as a terdentate species, since H(2) appears as one doublet while the methyl hydrogen atom H(5) appears as one singlet and H(6) appears as one septet.

For the equilibrium between **21^a** and **21^b** the thermodynamic parameters could not be measured, owing to the small temperature range available with CD_2Cl_2 as solvent.

Synthesis of Benzyl Complexes 22−24. The benzylrhodium complexes **22**−**24** could be obtained in nearly quantitative yield by adding benzyl chloride to a benzene or cold acetone solution of the rhodium(I) complexes **7**, **8**, and **12** respectively (Scheme 2; see Table 2 for the numbering of the complexes). No side products were observed. Complexes **22**−**24** are octahedral complexes with the terdentate nitrogen ligand coordinated in the equatorial plane and the η^1-benzyl ligand in the axial position, as may be concluded from the ^{1}H and ^{13}C NMR spectra. For the nitrogen ligand this may be inferred from the equivalence of the signals H/C(2) and H/C(2′), and H/C(4) and H/C(4′), respectively. In the case of **22** the H/C(7) and H/C(7′) signals are inequivalent, which is to be expected when the two axial ligands are not identical. The η^1-coordination of the benzyl ligand may be inferred from the equivalency of H/C(11) and H/C(11′) and of H/C(12) and H/C(12′). Also the chemical shifts of H(11), H(11′), H(12), H(12′), and H(13), which all resonate in the region between 6.4 and 6.9 ppm, demonstrate that the benzyl ligand is η^1-coordinated. An η^3-benzyl coordination would have resulted in a shift of one of the aromatic hydrogens H(11) to 2.5−3.0 ppm.[80] The hydrogen atom resonance H(9) of CH_2Ph lies at δ 3.36−4.06 ppm with a $^2J_{Rh-H}$ coupling constant of 3.3−3.4 Hz, while the C(9) signal at δ 22.9−26.7 ppm shows a $^1J_{Rh-C}$ coupling constant of 18−20 Hz.

The signals of H(6), H(7), and H(9) of complex **24** are broad at room temperature, while at 223 K these signals sharpen with a doubling of the number of signals of H(2), H(3), and H(9), which indicates the presence of two isomers (**24^a** and **24^b**). The complex **24^a** (values in italics in Table 4) contains a bidentate ligand, as is clear from the appearance of two methyl signals H(5) and H(5′), two septets of H(6) and H(6′), and four doublets of H(7). In complex **24^b** the ligand coordinates as a terdentate species, since the methyl hydrogen atoms H(5) appear as one singlet, H(6) appears as one septet, and H(7) appears as two doublets. Also, from low-temperature ^{13}C NMR measurements it was confirmed that complex **24^a** (values in italics in Table 5) contains a ligand which coordinates as a bidentate species, as evidenced by the inequivalence of the signals of C(1) and C(1′), C(4) and C(4′), and C(5) and C(5′). The terdentate coordination for **24^b** may be inferred from the presence of one signal for C(1)/C(1′), one signal for C(4)/C(4′), and one signal for C(5)/C(5′).

Equilibrium constants could not be derived, owing to overlap of the relevant signals.

Synthesis of α-Chlorotolyl Complexes 25−27. The α-chlorotolyl complexes **25**−**27** could be prepared in nearly quantitative yield by adding α,α-dichlorotoluene to a benzene solution of the rhodium(I) complexes **7**, **8**, and **12**, respectively, with no formation of side products (Scheme 2; see Table 2 for the numbering of the complexes). The geometry of the complexes could

---

[80] Brookhart, M.; Buck, R. C.; Danielson, E., III. *J. Am. Chem. Soc.* **1989**, *111*, 567.

be determined by ^1H NMR, while ^{13}C NMR data could not be obtained due to low solubility of the complexes **25**−**27**.

The complexes **25**−**27** are octahedral, with the nitrogen ligand coordinated in the equatorial plane and the η^1-α-chlorotolyl ligand coordinated in an axial position, as may be concluded from the ^1H patterns of the signals.

The pyridine moiety in **25**−**27** is coordinated to the metal, since H(2) and H(3) in all three cases show a low-field shift relative to the corresponding signals of the free ligand. The imine coordination of the ligand in **25** and **26** is clear from the $^3J_{Rh-H}$ coupling constant of 3.0−3.2 Hz on both H(4) and H(4′). Complex **27** shows broad ^1H NMR signals for the substituents, indicating fluxional behavior (see below).

The α-chlorotolyl ligand is η^1-coordinated in complexes **25** and **26**, because the benzylic hydrogen atom H(9) shows coupling with rhodium ($^2J_{Rh-H}$ = 4.3 Hz) and a chemical shift varying between 6.4 and 6.8 ppm. Compared to the benzylic hydrogen, H(9) of **22** and **23**, the benzylic hydrogens H(9) of **25** and **26** resonate at lower field. At 218 K sharp aromatic signals H(11,12,13) lie in the range of 6.96−7.26 ppm, which is normal for η^1-benzyl ligands.[80] At room temperature these signals are broad. The observed fluxionality is probably due to hindered rotation around the C(9)−C(10) bond, which is not observed for the benzyl group in **22** and **23**. This is obviously due to the larger steric bulk of the α-chlorotolyl ligand.

At room temperature the ^1H NMR spectrum of **27** shows broad signals, indicating fluxional behavior. At 178 K in CD_2Cl_2 the spectrum became only partially sharp and two complexes could be identified.

By comparison with the spectrum of **25** the terdentate geometry of the coordinated ligand of **27^b** could be confirmed by a triplet for H(3), two doublets for H(2), two singlets for H(5), and four doublets for H(7).

The geometry of **27^a** could not be inferred so easily from NMR, because even at 178 K the signals H(6) and H(7) of **27^a** and **27^b** are broad. In analogy to complex **18** we tentatively conclude that the ligand probably is coordinated as a bidentate species, as is indicated by two doublets for both H(2) and H(2′) and two singlets for H(5) and H(5′).

The ratio between **27^a** and **27^b** is 0.8:1 at 178 K in CD_2Cl_2, which could only be measured at this low temperature, because at higher temperatures the spectra are too broad.

Oxidative Addition of Cl_2 to 6−**12**. The yellow water-soluble complexes **28**−**33** were synthesized in benzene by reaction of **6**−**12** with Cl_2 gas (Scheme 2; see Table 2 for the numbering of the complexes). The coordination of the ligand could be determined by ^1H NMR (Table 4) as for the complexes **7**−**27**.

The ^1H NMR of complex **33** in CD_2Cl_2 at 298 K showed, in addition to sharp signals for H(3) and H(2), also broad signals for the methyl group H(5), the *i*-Pr hydrogen H(6), and the methyl groups H(7), indicating fluxional behavior. At temperatures as high as 263 K the ^1H NMR signals started to sharpen, while at 243 K a sharp spectrum was obtained which only slightly changed on further cooling to 183 K. Two isomers could be identified (**33^b** and **33^a**). Complex **33^b** contains a ligand that coordinates as a terdentate species, as could be deduced from the appearance of H(3) as a triplet, H(2) as a doublet, H(5) as a singlet, H(6) as a septet and H(7) as a doublet. Complex **33^a** contains a ligand, which coordinates in a bidentate fashion, as could be determined by the appearance of H(3) as a triplet, H(2) as two doublets, H(5) as two methyl signals, H(6) as two septets, and H(7) as two doublets. Equilibrium constants could not be calculated, owing to overlapping signals.

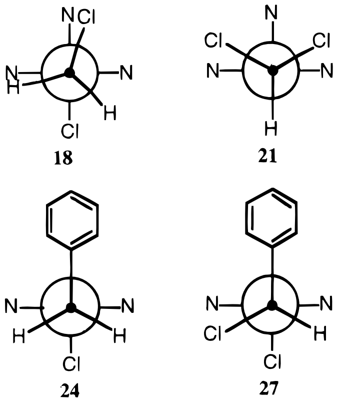
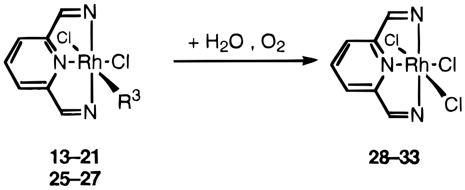


Figure 7. Minimum-energy conformations of **18**, **21**, **24**, and **27**.

Scheme 3. Reaction of the Rhodium(III) Complexes 13−21 and 25−27 with Water and Oxygen To Yield the Rhodium(III) Complexes 28−33[a]



[a] For the sake of clarity the R^1 and R^2 substituents have been omitted.

Molecular Modeling on Complexes 18, 21, 24, 27, and 33. The molecular mechanics calculations on **18**, **21**, **24**, **27**, and **33** showed that the methyl group R^1 on the imine position restricts the rotation of the ^iPr substituent R^2. In the most likely conformation of the *i*-Pr group, one of the methyls is pointing toward the axial R^3 group and the other toward the axial chloride. The substituents on the R^3 group experience a steric interaction of the methyl of the *i*-Pr group (Figure 7).

Reactivity of Complexes 13−**27 toward Oxygen in Boiling Water.** During the synthesis of the chloromethyl complexes **13**−**18** and the dichloromethyl complex **19** the formation of rhodium trichloride complexes **28**−**33** was observed in irreproducible amounts. We have found, however, that the synthesis of the chloromethyl complexes with freshly distilled dichloromethane under exclusion of air yields no trichloride complexes. To find out the cause of this side reaction, the chloromethyl compounds were made to react in boiling water with and without oxygen. Only in the presence of water and oxygen (admitted either as the pure gas or as air) the rhodium trichloride complexes could be isolated (Scheme 3; see Table 2 for the numbering of the complexes). In the absence of oxygen no stable products were isolated and formation of rhodium black was observed, while in the absence of water no reaction took place.

The dichloromethyl complexes **20** and **21** and the α-chlorotolyl complexes **25**−**27** could also be converted to the corresponding trichloride complexes by this method. In the case of **27** also benzaldehyde and H_2O_2 could be identified. The benzyl complexes **22**−**24** obviously could not be converted in boiling water in the presence of oxygen to the trichloride complexes, undoubtedly owing to the absence of a chloride atom on the organic fragment.

Discussion

In order to create a large electron density on Rh(I) with concomitant stronger nucleophilic behavior we employed hemilabile 2,6-bis(R^2-carbaldimino)pyridine and 2,6-bis(R^2-ethylidyneimino)pyridine ligands (2,6-$(C(R^1){=}NR^2)_2C_5H_3N$; for R^1 and R^2 see Table 2) with the two imine groups as flexible imine side arms. In this way the ligand, when bonded as a terdentate species, strongly donates electronic charge, while at the same time it is able to create easily accessible coordination sites on the Rh(I) atom. We have been able to prepare in high yields the complexes [RhCl(2,6-$(C(R^1){=}NR^2)_2$-C_5H_3N)] (**7**−**12**; see Table 2) by using $[RhCl(alkene)_2]_2$ containing the easily displaceable ethene or cyclooctene as the alkene (Scheme 1). It should be noted that use of $[RhCl(COD)]_2$ and $[RhCl(NBD)]_2$ (COD = 1, 5-cyclooctadiene; NBD = bicyclo[2.2.1]hepta-2,5-diene) as starting materials gives very different reaction pathways, as will be described elsewhere.[81] Also, it is essential to use benzene as a solvent with the rigorous exclusion of oxygen and water.

From Table 2 it is clear that a variety of imine R^2 substituents may be used in combination with H or Me as R^1 on the imine C atom.

In solution ^1H and ^{13}C spectra of the Rh(I) complexes **7**−**12** show that the ligands are bonded as terdentate species with no evidence of fluxionality on the NMR time scale.

The structures of **7**, **8**, **12**, **13**, and **15**, determined by X-ray analysis, show that the oxidation state of the metal has no influence on the Rh−N and the Rh−Cl bonds in the equatorial plane. The C=N bond length, which is elongated on π-back-donation[82] is between 1.295(5) and 1.313(2) Å for the Rh(I) complexes and between 1.286(4) and 1.293(7) Å for the Rh(III) complexes. Obviously the oxidation state of the metal influences the C=N bond length only slightly or not at all.

Rather unexpected in the first instance was that the chloride atom in the structures of **7**, **8**, and **12** is bending out of the plane of the molecule (Figure 2). Very interesting is the fact that the bending angle ϕ increases going from **7** to **12** to **8** from 5.34(16) to 10.04(9) and to 11.73(11)°, respectively. These distortions from planarity appear also to have a large influence on the Rh chemical shifts.[83] In the case of **12** we also observe steric interactions between R^2 (*i*-Pr) and R^1 (Me) and between the H atoms of the R^1 groups (Me) and the *meta* H atoms of the pyridine ring. The steric strain in the monovalent Rh(I) complexes is relieved by bending of the Cl atom out of plane, rather than by dissociation of one of the side arms, which would result in energetically unfavorable three-coordinate 14-electron complexes.

Reaction of these Rh(I) complexes with CH_2Cl_2, $CHCl_3$, benzyl chloride, and α,α-dichlorotoluene led to the rapid and virtually quantitative formation of Rh(III) complexes (Scheme 2), illustrating the high nucleophilicity of the Rh(I) center and therefore, the strong electron donor capacity of these N−N−N ligands. It was not possible to split the C−Cl bond of chlorobenzene, which may be rationalized by the mechanistic proposal of Milstein[10] et al., which involves as intermediate a metal centre with sufficient open space to allow binding of the chlorobenzene via both the chloride atom and the *ipso* carbon atom of the phenyl ring. This bidentate type geometry of chlorobenzene is impossible for the Rh(I) complexes at hand, even when one imine side arm would dissociate.

It is of interest to note that the Rh−C(14) bonds of **13** (2.052(5) Å) and of $\mathbf{15^a}$ (2.052(3) Å) and the Rh−C(220) bond of $\mathbf{15^b}$ (2.059(3) Å) are all rather short in comparison to the Rh−C distances for $[Rh(Cl)(CH_2Cl)(dmpe)_2]Cl{\cdot}CH_2Cl_2$ (2.161(2) Å)[39] and for $[RhCl(I)(CH_2I)(CO)(PEt_3)]$ (2.080(6) Å),[31] while the C(14)−Cl(13) bond of **13** (1.790(5) Å) and the C(120)−Cl(13) bond of the major disorder component of $\mathbf{15^a}$ (1.808(3) Å) and of $\mathbf{15^b}$ (C(220)−Cl(23) = 1.728(4) Å) are rather normal in comparison to other metal chloromethyl complexes (1.702(5)−1.803(8) Å).[79] These observations are in line with previous proposals that one should consider a metal carbene $Rh{=}C^+Cl^-$ type bonding as an important resonance form[79] of the $Rh{-}CH_2Cl$ moiety. It should be evident that the metal carbene type bonding may cause enhanced reactivity, as will be discussed later.

In solution the Rh(III) complexes exist as one isomer with a ligand that coordinates as a terdentate species, according to the ^1H and ^{13}C NMR spectra, with the exception of the compounds **18**, **21**, **24**, **27**, and **33**, which all contain two isomers as evidenced by low-temperature NMR measurements and which all have in common the combined presence of an *i*-Pr group on the R^2 position and a Me group on the R^1 position. It may be concluded from the spectra at 243 K that the isomer $\mathbf{18^a}$ contains a ligand that coordinates in a bidentate manner, while $\mathbf{18^b}$ contains a ligand that coordinates as a terdentate species. The thermodynamic parameters of the equilibrium ($\mathbf{18^b} \rightleftarrows \mathbf{18^a}$), $\Delta H° = -4.3\ (\pm 0.2)$ kJ/mol and $\Delta S° = 17.4\ (\pm 0.3)$ J/(mol K), clearly indicate that we are dealing with a low-energy intramolecular interconversion mechanism with the five-coordinated isomer **18a** increasing in concentration with increasing temperature, as would be expected on the grounds of the entropy factor. Unfortunately, it was impossible to calculate the thermodynamic parameters of the equilibria occurring for **21**, **24**, **27**, and **33**. Although precise concentration measurements could not be carried out, it is clear that in all these cases sizeable amounts of the five-coordinate isomers are present at low temperatures. It is therefore to be expected that at ambient temperatures the five-coordinate Rh(III) complexes are by far the dominant ones, while the fast exchange process makes the substituents on both imine side arms magnetically equivalent.

A very interesting observation is that the observed fluxional behavior which may involve an associative or

---

[81] Haarman, H. F.; Bregman, F. R.; Ernsting, J. M.; Veldman, N.; Spek, A. L.; Vrieze, K. *Organometallics* **1997**, *16*, 54.

[82] van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

[83] Haarman, H. F.; Kaagman, J. W. F.; Ernsting, J. M.; Wilms, M.; Vrieze, K.; Elsevier, C. J. To be submitted for publication.

a dissociative pathway, is dependent on the size of the axial ligands. We observe that the temperatures at which the fluxional process reaches the slow exchange limit is dependent on the other axial group; i.e., they decrease in the order Cl ($T = 263$ K) > CH_2Cl ($T = 243$ K) > CH_2Ph ($T = 223$ K) ≫ $CHCl_2$ ($T = 193$ K) > CHClPh ($T = 178$ K), in other words, with increasing size of the other axial group, as would be expected if steric factors play a dominant role. This point will be elaborated in more detail below.

We have carried out six single X-ray determinations in order to obtain more quantitative information on the steric interactions. First, the equatorial Cl atom of the Rh(I) complexes is increasingly forced out of the N−N−N plane with increasing steric bulk of the R^2 substituents. Second, a particularly interesting exercise is to compare the molecular structures of the Rh(I) complex **7** and the Rh(III) complex **13**, which both contain the same terdentate-bonded N−N−N ligand, i.e. with $R^1 = H$ and $R^2 = i$-Pr. An eye-catching difference is the out-of-plane bending of the equatorial Cl atom, which lies 0.243(1) Å above this plane in **7** and only 0.127(1) Å in **13**, but in the latter this bending is in the direction of the CH_2Cl fragment, indicating that of the two axial fragments the Cl atom *close* to the Rh(III) atom has a greater steric bulk than the CH_2Cl fragment. The introduction of two axial ligands in **13** pushes the equatorial Cl atom back toward the N−N−N plane, which as a result will increase the steric interaction between the R^2 and the R^1 substituents. These latter interactions will be particularly strong when R^1 is a Me group. To clarify the steric interactions, we have carried out molecular mechanics calculations (Experimental Section). In the case of the rhodium trichloride complex **33** one does observe that the rotation of the *i*-Pr group around the N−C bond is hindered by interactions of the Me (R^1) substituent with the methyl groups of the *i*-Pr group, which is sufficient to cause partial formation of a five-coordinate species. In the case where one of the axial groups is a CH_2Cl or a CH_2Ph fragment, there are also steric interactions between the Cl atom or Ph group with the *i*-Pr group (R^2). The rotation about the Rh−C bond is even more hindered in the case where one of the axial groups is a $CHCl_2$ or CHClPh fragment. These calculations nicely rationalize the observed temperature sequence at which the slow exchange limit is reached: it is highest for Cl (**33**), lower for CH_2Cl (**18**) and CH_2Ph (**24**), and the lowest for $CHCl_2$ (**21**) and CHClPh (**27**) (*vide supra*). Since in all cases the equatorial Cl atom is sterically solidly wedged between the two axial ligands, there is for the Rh(III) complex only one way to relieve the steric strain, and that is by dissociation of at least one of the side arms followed by rotation of about 90° around the C(1)−C(4) axis. In this context it is worthwhile noting that when R^1 is a Me group but R^2 is a *p*-anisyl group, i.e. for complexes **17** and **32**, there is no evidence for the formation of five-coordinate Rh(III) species. This is understandable, as the *p*-anisyl group is flat and causes less steric hindrance than an *i*-Pr group.[46]

One might also consider electronic factors with regard to the dissociation of the imine side arm, but it is unlikely that these play an important role in view of the above data. If electronic factors were dominant, we would expect the more electron withdrawing N-*p*-anisyl moiety to be less strongly bonded than the strongly electron donating N-*i*-Pr group.

A serendipitous discovery was that trichloride complexes **28**−**33** were formed as minor side products of the reaction of **7**−**12** with dichloromethane or chloroform, if insufficient care was taken to exclude air and moisture. Formation of rhodium trichloride complexes has been noted before for these substrates and has been ascribed to one-electron pathways.[31,40] Recently, McCrindle et al.[41,42] showed in the case of chloro(chloromethyl)palladium(II) complexes of sulfide and amine ligands that water and air were needed to convert the $M-CH_2Cl$ moiety to M−Cl and formaldehyde. We have now demonstrated that the Rh(III) complexes **13**−**21** and **25**−**27** could be converted to the trichloride complexes **28**−**33**, respectively (Scheme 3). In the case of the reaction of **27** with water and oxygen we could conclusively demonstrate the formation of **33**, benzaldehyde, and H_2O_2, which is understandable in view of the participation of the $Rh{=}C^+Cl^-$ resonance form to the bonding (*vide supra*), as has been noted before for Pd and Pt complexes by van Leeuwen et al.[43] and McCrindle et al.[41,42] This interesting reaction will be the subject of a separate publication.[84]

Acknowledgment. We thank Dr. H. W. F. Frühauf for stimulating discussions, K. Goubitz for assistance with the crystallographic database, and M. Torres Gomez for practical assistance. This work was supported in part (A.L.S., N.V.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: Further details of the structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters, for $\mathbf{7^{mono}}$, $\mathbf{7^{ortho}}$, **8**, **12**, **13**, and **15** (29 pages). Ordering information is given on any current masthead page.

OM9607614

---

[84] Haarman, H. F.; Bregman, F. R.; van Leeuwen, P. W. M. N.; Vrieze, K. *Organometallics*, in press.