Inorg. Chem. **1997,** *36,* 6197−6204

The Square Pyramidal Hydride Cation $[RuH(dcpe)_2]^+$, dcpe = Bis(dicyclohexylphosphino)ethane. Structures of $[RuH(dcpe)_2]^+[BPh_4]^-$ and of the Zwitterionic $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$

Rainer F. Winter* and Fridmann M. Hornung

Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany

Received May 15, 1997⊗

Two hydrido ruthenium complexes could be isolated from the reaction between $RuCl_2(DMSO)_4$ (DMSO = dimethyl sulfoxide) and the chelating 1,2-bis(dicyclohexylphosphino)ethane (dcpe) and $[BPh_4]^-$. These are $[RuH(dcpe)_2]^+[BPh_4]^-$ with a five-coordinate, 16 valence electron cation and the neutral zwitterionic 18 valence electron compound $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$. The relative amounts of these products depend on the reaction conditions. If $NaBPh_4$ is replaced by NH_4PF_6 or added after the reaction with the diphosphine has gone to completion, the 16 valence electron species $[RuH(dcpe)_2]^+$ is the only product. Reducing the size of the diphosphine chelate to 1,1-bis(dicyclohexylphosphino)methane (dcpm) has a large effect on the reaction course. Either *trans*-$RuHCl(dcpm)_2$ or *trans*-$RuCl_2(dcpm)_2$ is formed, depending on the conditions. X-ray structures of $[RuH(dcpe)_2]^+[BPh_4]^-$ (monoclinic, $P2/c$, $a = 24.936(5)$ Å, $b = 12.633(3)$ Å, $c = 25.801(5)$ Å, $\beta = 102.86(3)°$, $V = 7924(3)$ Å^3, $Z = 4$, $R = 0.062$, $R_w = 0.1694$) and $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ (monoclinic, $P2_1/n$, $a = 14.321(5)$ Å, $b = 19.716(7)$ Å, $c = 17.100(5)$ Å, $\beta = 107.60°$, $V = 4602(3)$ Å^3, $Z = 4$, $R = 0.0648$, $R_w = 0.1873$) have been determined. A nearly planar arrangement of the four P atoms exists around Ru in the five-coordinate cation, implying a distorted square pyramid. This structural motif has not been observed previously for a d^6 RuL_5 system with a P_4X donor set. $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ represents an example for the noninnocent behavior of the "noncoordinating" $[BPh_4]^-$ anion. The coordinated six-membered ring displays a boatlike distortion with the BPh_3 "substituent" and the *para*-carbon of the coordinated ring displaced away from the metal.

Introduction

There has been a long-standing interest in the structures of five-coordinate complexes and the factors governing the preference of either the trigonal bipyramidal (tbp) or the square pyramidal (sqp) structure type. While the tbp coordination mode should be generally favored for steric reasons, the specific requirements of the ligands and/or electronic effects arising from the metal d electron configuration or the ligand properties may stabilize the sqp structure type.[1,2] The balance between these isomeric forms is often quite delicate, as exemplified by the occasional observation of both configurations present in the same solid state material[3] or the dependence of the preferred structure type on the counterion[4] and even the solvent of crystallization.[5]

Special attention has been paid to five-coordinate complexes with a d^6 configuration of the metal center, particularly in view of their high reactivity arising from electronic and steric unsaturation. While ruthenium complexes of the type $Ru(PR_3)_3XY$ are relatively common,[6−9] it is only recently that a comparable number of examples of $[MX(L_2)_2]^+$ are known, where L_2 represents a chelating diphosphine and X a unidentate monoanionic ligand.[10−17] They possess a P_4X donor set around the metal center and are frequently generated by dissociation of an anionic ligand Y^- from saturated six-coordinate precursors. The readiness with which $MXY(L_2)_2$ complexes undergo such a ligand dissociation was found to depend on several factors such as the steric bulk and the electronic properties of the chelating diphosphine and the ligand X^-, the ring size of the chelate formed, the solvent employed, or which of the two possible isomers (*cis* or *trans*) of the starting material is used. To only briefly illustrate some of these points, *trans*-$RuCl_2(Ph_2P(CH_2)_3PPh_2)_2$ was reported to react with $NaBPh_4$ or $NaPF_6$ in ethanol to give $[RuCl(Ph_2P(CH_2)_3PPh_2)_2]^+$, while the methyl substituted derivative *trans*-$RuCl_2(Me_2P(CH_2)_3PMe_2)$ does not.[10,11,14] Likewise, $RuBr_2(dcpe)_2$ (dcpe = bis(dicyclohexylphosphino)ethane) spontaneously dissociates a bromide ion upon dissolution in dichloromethane, whereas the dichloro derivative requires refluxing of the starting material in ethanol in the presence of a noncoordinating counterion.[12] The effect of the chelate ring size may be inferred from the fact that *trans*-

---

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) (a) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365. (b) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.
(2) Idrissi, I. L.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671.
(3) Raymond, K. N.; Corfield, P. W. R.; Ibers J. A. *Inorg. Chem.* **1968**, *7*, 1362.
(4) Terzis, A.; Raymond, K. N.; Spiro, T. G. *Inorg. Chem.* **1970**, *9*, 2415.
(5) Stalick, J. K.; Corfield, P. W. R.; Meek, D. W. *Inorg. Chem.* **1973**, *12*, 1668.
(6) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) Hallmann, P. S.; Mc Garvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.
(7) Hoffmann, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.
(8) Cotton, F. A.; Matusz, M. *Inorg. Chim. Acta* **1987**, *131*, 213.
(9) (a) La Placa, S. A.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778. (b) Skapski, A. C.; Troughton P. G. H. *Chem. Comm.* **1968**, 1230.
(10) Bressan, M.; Rigo, P. *Inorg. Chem.* **1975**, *14*, 2286.
(11) Briggs, J. C.; McAuliffe, C. A.; Dyer, G. *J. Chem. Soc., Dalton Trans.* **1984**, 423.
(12) Mezzetti, A.; Del Zotto, A.; Rigo, P.; Pahor R. B. *J. Chem. Soc., Dalton Trans.* **1989**, 1045.
(13) Batista, A. A.; Cordeiro, L. A. C.; Oliva, G. *Inorg. Chim. Acta* **1993**, *203*, 185.
(14) Bressan, M.; Morvillo, A. *Inorg. Chim. Acta* **1987**, *132*, 1.
(15) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.
(16) Polam, J. R.; Porter, C. L. *J. Coord. Chem.* **1993**, *29*, 109.
(17) (a) Bianchini, C.; Peruzzini, M.; Zanello, P. *Gazz. Chim. Ital.* **1994**, *124*, 372. (b) Bianchini, C.; Peruzzini, M.; Ceccanti, A.; Laschi, F.; Zanello, P. *Inorg. Chim. Acta* **1997**, *259*, 61.

S0020-1669(97)00583-1 CCC: $14.00

$RuCl_2(Ph_2P(CH_2)_nPPh_2)_2$ reacts with $NaPF_6$ in refluxing ethanol to yield five-coordinate compounds when $n = 3$,[10,13] whereas no such reaction is observed for $n = 2$.[15] The more reactive *cis*-isomer of the latter complex, however, dissociates a chloride anion under the above reaction conditions.[15]

As far as their structures in the solid state are concerned, the five-coordinate d^6 ruthenium complexes fall into two distinct categories. Those with a P_3XY donor set around the metal adopt a sqp structure with one P atom at the apical position. The basal plane accommodates the two remaining P atoms as well as X and Y which are mutually trans to each other.[8,9] In the case of a P_4X donor set the structures were predicted to depend on the electronic properties of the ligand X.[2] For $X = Cl^-$ (or any other σ acceptor/π donor) the antibonding interaction between the filled π orbital of the ligand and the d_{xy} orbital on the metal renders a tbp structure with Cl^- in the equatorial plane and an acute angle between the two remaining equatorial ligands as the energy minimum. This arrangement was indeed found for all examples hitherto known[12,13,16] with the notable exception of $[RuPP_3Cl]^+$ ($PP_3 = P(C_2H_4PPh_2)_3$), which possesses a sqp structure with the Cl^- ligand in a basal position.[17a] Most interestingly, the Os analogue of this latter compound is reported to be isostructural, whereas the corresponding Fe complex is trigonal bipyramidal with two unpaired electrons.[17b] In ref 13 the authors have communicated the structure of $[RuCl(Ph_2P(CH_2)_3PPh_2)_2]$ as square pyramidal, but a closer inspection and a comparison with the other known structures reveals that a distorted trigonal bipyramidal structure is in much better agreement with the actual data. For $X = H^-$, both the tbp and the sqp structures were calculated to be true minima, the latter being favored by about 29 kJ/mol.[2] Although some hydrides of this type (X = H) were prepared,[12,15,18−20] no X-ray structures have been available. Their spectroscopic data suggest a sqp structure in solution for $[RuH(BINAP)_2]^+$ (BINAP = *R*-bis(diphenylphosphino)-1,1′-binaphthyl)[19a] but rather a tbp structure for the corresponding complex with dcpe (dcpe = bis(dicyclohexylphosphino)ethane).[12]

The high reactivity of these systems is of considerable interest. This point is evident from their fast reactions with anionic or neutral ligands such as CO or H_2 to yield six-coordinate 18 valence electron complexes *trans*-$[RuX(L_2)_2L']^+$,[10−12,15,18,19] their propensity for CH activation, and their potential for synthetic applications[18] or as hydrogenation catalysts.[21] As to CH activation processes, the hydrides ($X = H^-$) are probably the most powerful among the $[RuX(L_2)_2]^+$ derivatives. They may form strong agostic interactions with the hydrocarbon chelate bridges of the diphosphine ligands, provided the chelate ring is large enough to allow the alkyl chains to approach the vacant coordination site.[20,22]

In this paper we give an account of the synthesis of $[RuH(dcpe)_2]^+[A^-]$ ($A^- = BPh_4^-$ (**2a**), PF_6^- (**2b**)) and the identification of the $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ zwitterion and of the dissociatively more inert six-coordinate complexes *trans*-$RuCl_2(dcpm)_2$ (**4**) and *trans*-RuHCl(dcpm)$_2$ (**3**) (dcpm = bis(dicyclohexylphosphino)methane).

Experimental Section

General Procedures. All manipulations were performed by standard Schlenk techniques under an atmosphere of dry argon. Dichloromethane was dried by disitillation from CaH_2, and ethanol was predried with Mg and freshly distilled from CaH_2 before use. All solvents were degassed by either at least three freeze−pump−thaw cycles or saturation with argon prior to use. $RuCl_2(DMSO)_4$ (DMSO = dimethylsulfoxide) was prepared according to a literature method.[23] 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) and 1,1-bis(dicyclohexylphosphino)methane (dcpm) were obtained from Strem Chemicals and the deuterated solvents from Aldrich. All commercial materials were used as received. Infrared spectra were obtained on a Perkin-Elmer Paragon 1000 PC FT-IR instrument; ^1H (250.13 MHz), ^{13}C (62.90 MHz), and ^{31}P-NMR spectra (101.26 MHz) were recorded on a Bruker AC 250 spectrometer at 303 K (unless stated otherwise) in the solvent indicated. The spectra were referenced to the residual protonated solvent (^1H), the solvent signal itself (^{13}C), or external H_3PO_4 (^{31}P). If necessary, the assignement of ^{13}C NMR spectra was aided by appropriate DEPT experiments (DEPT = distortionless enhancement by polarization transfer). The assignments of the IR bands are based upon comparison of the IR spectra of complexes **2a** and **2b** and a comparison with the IR data of the respective diphosphine and those of BPh_4^- salts.[24] The spectral changes of the spectrum of complex **2b** in the visible region upon addition of CH_3CN were monitored by adding increasing amounts of degassed CH_3CN to a 0.83 mM solution of complex **2b** in CH_2Cl_2 in a gas-tight UV/vis cuvette under argon and recording the spectra after each addition. Elemental analyses (C, H, N) were performed at in-house facilities.

Synthesis of $\{(\eta^6\text{-}C_6H_5)BPh_3\}$RuH(dcpe) (1) and [RuH(dcpe)$_2$][BPh$_4$] (2a). Method 1. $RuCl_2(DMSO)_4$ (0.484 g, 1.0 mmol), dcpe (0.845 g, 2.0 mmol), and $NaBPh_4$ (3.422 g, 10.0 mmol) were suspended in 30 mL of ethanol, and the mixture was warmed to a gentle reflux under stirring. Within minutes the suspension cleared to a yellow solution which soon precipitated a pale orange solid. Upon further heating, this solid slowly turned dark yellow and finally orange. After 90 min, the solid was allowed to settle and the mother liquor was removed by cannula filtration. The orange residue was washed three times with 5 mL portions of ethanol by warming the mixture to a gentle reflux, allowing the solids to settle, and filtering hot as above. The resulting orange powder was dried in vacuo and extracted into CH_2Cl_2 (2 × 10 mL). The extracts were filtered by cannula to remove residual $NaBPh_4$ and were crystallized by layering the concentrated solution with ethanol. Several batches were obtained by further concentration of the respective mother liquors. The initial fractions were enriched with the white $\{(\eta^6\text{-}C_6H_5)BPh_3\}$RuH(dcpe), whereas the later ones were found to contain a higher proportion of the orange-red $[RuH(dcpe)_2]^+[BPh_4]^-$ salt. The crystals were sorted manually as far as possible, and the inseparable mixtures (partly lumps of the two different compounds baked together) recrystallized again. This procedure was repeated until further recrystallizations did only yield inseparable mixtures. Yields: $[RuH(dcpe)_2]^+[BPh_4]^-\cdot 3CH_2Cl_2$, 0.627g, 41% based on Ru; $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)\cdot 0.5CH_2Cl_2$, 0.097 g, 11% based on Ru.

Method 2. $RuCl_2(DMSO)_4$ (0.096 g, 0.20 mmol), dcpe (0.079 g, 0.187 mmol), and $NaBPh_4$ (0.638 g, 1.86 mmol) were suspended in 8 mL of ethanol, and the mixture was warmed to a gentle reflux under stirring. Within minutes the suspension cleared to a pale orange solution. Soon an almost white solid precipitated which gradually turned pale orange. After 60 min, the solid was allowed to settle and the solvent was removed by filter cannula. The resulting crude product was washed with another 4 mL portion of hot ethanol, vacuum dried, and extracted into CH_2Cl_2 (5 mL). After drying in vacuo 0.093 g of a pale orange solid was obtained, which was found to contain

---

(18) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705.

(19) (a) Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett.* **1988**, 2055. (b) Saburi, M.; Aoyagi, K.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1990**, 601.

(20) Ogasawara, M.; Saburi, M. *Organometallics* **1994**, *13*, 1911.

(21) (a) Saburi, M.; Hiroyuki, K.; Youichi, I.; Yasuzo, U. *Kenkyu Hokoku—Asahi Garasu Kogyo Gijutsu Shoreikai* **1987**, *50*, 225; CAS No., 109: 109958p. (b) Muramatsu, H.; Kawano, H.; Ishii, Y.; Saburi, M.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 769. (c) Saburi, M.; Ohnuki, M.; Ogasawara, M.; Takahashi, T.; Uchida, Y. *Tetrahedron Lett.* **1992**, *33*, 5783. (d) Saburi, M.; Takeuchi, H.; Ogasawara, M.; Tsukahara, T.; Ishii, Y.; Ikariya, T.; Takahashi, T.; Uchida, Y. *J. Organomet. Chem.* **1992**, *428*, 155.

(22) Ogasawara, M.; Aoyagi, K.; Saburi, M. *Organometallics* **1993**, *12*, 3393.

(23) Spencer, I. P.; Wilkinson G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(24) (a) Chatten, L. G.; Pernarowski, M.; Levi, L. *J. Am. Pharm. Assoc.* **1959**, *48*, 276. (b) Costa, G.; Camus, A.; Gatti, L. *J. Organomet. Chem.* **1967**, *8*, 339.

$[RuH(dcpe)_2]^+[BPh_4]^-$ and $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ in an approximate 2:3 ratio. After two recrystallizations and sorting the crystals as above $[RuH(dcpe)_2]^+[BPh_4]^-\cdot 3CH_2Cl_2$ (0.035 g, 25% based on dcpe) and $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)\cdot 0.5CH_2Cl_2$ (0.049 g, 30% based on dcpe) were obtained.

Spectral and Analytical Data. Complex 1. ^{1}H-NMR ($CDCl_3$): δ 7.37, (2,6-H (BPh_3), d, $^3J_{H-H}$ = 7.07 Hz, 6H), 7.08 (3,5-H (BPh_3), vt, N_{H-H} = 7.32 Hz, 6H), 6.95 (4-H, (BPh_3), t, $^3J_{H-H}$ = 7.32 Hz, 3H), 5.83 (2,6-H (η^6-Ph), d, $^3J_{H-H}$ = 5.47 Hz, 2H), 5.60 (3,5-H (η^6-Ph), t, N_{H-H} = 5.50 Hz, 2H), 5.38 (4-H, (η^6-Ph), t, $^3J_{H-H}$ = 5.50 Hz, 1H), 1.18−1.79 (C_6H_{11}, m, 44H), 0.88 (PCH_2, m, 2H), 0.64 (PCH_2, m, 2H), −11.59 (RuH, t, $^2J_{P-C}$ = 36.5 Hz, 1H). ^{13}C-NMR (CD_2Cl_2): δ 160.85 (*ipso*-C, BPh_3, non-binomial quart, J_{B-C} = 60 Hz), 136.1, 125.8, 122.8 (*o, m, p*-C (BPh_3)), 92.9, 91.7, 88.9 (*o, m, p*-C (η^6-Ph)), 38.5 (*ipso*-C, (dcpe), vt, N_{P-C} = 10.3 Hz), 37.0 (*ipso*-C, (dcpe), m, N_{P-C} = 16.2 Hz), 29.2, 28.0, 27.4 (CH_2 (dcpe), all s), 27.3 (CH_2 (dcpe), vt, N_{P-C} = 3.2 Hz), 27.1 (CH_2 (dcpe), s), 26.9 (CH_2 (dcpe), vt, N_{P-C} = 4.2 Hz), 26.3 (CH_2 (dcpe), vt, N_{P-C} = 1.4 Hz), 26.1 (CH_2 (dcpe), vt, N_{P-C} = 4.4 Hz), 25.3 (CH_2 (dcpe), s), 20.9 (PCH_2 (dcpe), vt, N_{P-C} = 20.0 Hz); the resonance of the *ipso*-C atom of the coordinated phenyl ring could not be observed. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 97.2 (s). ^{31}P-NMR ($CDCl_3$): δ 97.2 (d, $^2J_{P-H}$ = 36 Hz). IR (KBr, cm^{-1}): 3057, 3037, 3001, 2984 (arene CH (BPh_4^-)), 2925, 2851 (CH_2, CH (dcpe)), 2001 (RuH), 1582, 1562, 1495, 1481 (arene CC (BPh_4^-)), 1445, 1425 (CH_2 (dcpe)), 1263 (dcpe), 852, 739, 732, 703 ($\omega(BPh_4^-)$), 661, 532. Anal. Calcd for $C_{50}H_{69}BP_2Ru\cdot 0.5CH_2Cl_2$: C, 68.43; H, 7.96. Found: C, 68.27; H, 7.94.

Complex 2a. ^{1}H-NMR ($CDCl_3$): δ 7.43 (3,5-H (BPh_4^-), m, 8H), 7.06 (2,6-H (BPh_4^-) , vt, N_{H-H} = 7.32 Hz, 8H), 6.89 (4-H, (BPh_4^-), t, $^3J_{H-H}$ = 7.32 Hz, 4H), 2.15 (*ipso*-CH (dcpe), vt, N_{H-H} = 2.18 Hz, 4H), 1.19−1.88 (C_6H_{11}, m, 84H), 0.88 (PCH_2, m, 4H), 0.77 (PCH_2, m, 4H), −32.06 (RuH, quint, $^2J_{P-C}$ = 19.2 Hz, 1H). ^{13}C-NMR (CD_2Cl_2): δ 164.5 (*ipso*-C, BPh_4^-, nonbinomial quart, J_{B-C} = 50 Hz), 136.3, 125.9 (nonbinomial quart, $^3J_{B-C}$ = 2.7 Hz), 122.0 (*p, o, m*-C (BPh_4^-)), 40.8 (*ipso*-C, (dcpe), vquint, N_{P-C} = 4.5 Hz), 40.3 (*ipso*-C, (dcpe), vquint, N_{P-C} = 6.0 Hz), 30.4, 30.3, 29.0, 28.7, 28.2, 28.0, 27.6, 26.7, 26.6 (CH_2 (dcpe), all s), 20.7 (PCH_2 (dcpe), vquint, N_{P-C} = 10.9 Hz). $^{31}P\{H\}$-NMR ($CDCl_3$): 74.2 (s), 74.0 (s). IR (KBr, cm^{-1}): 3054, 3033, 2997 (arene CH, BPh_4^-), 2928, 2850 (CH_2, CH (dcpe)), 2236 (RuH), 1579, 1481 (arene CC (BPh_4-)), 1446, 1424 (CH_2 (dcpe)), 1263 (dcpe), 850, 731, 703 ($\omega(BPh_4^-)$), 613, 533. UV/vis (CH_2Cl_2; λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 411 (2180). Anal. Calcd for $C_{76}H_{117}BP_4Ru\cdot 3CH_2Cl_2$: C, 62.37; H, 8.15 Found: C, 62.71; H, 8.20.

Synthesis of $[RuH(dcpe)_2[A^-]$ ($A^- = BPh_4^-$ (2a), PF_6^- (2b)). The procedure is given for the synthesis of the $[PF_6]^-$ salt **2b**; the analogous $[BPh_4]^-$ salt is, however, obtained in essentially the same yield by replacing NH_4PF_6 by $NaBPh_4$. $RuCl_2(DMSO)_4$ (0.175 g, 0.361 mmol) and dcpe (0.305 g, 0.721 mmol) were suspended in 9 mL of ethanol to which 1 mL of NH^iPr_2 had been added. This mixture was warmed to reflux for 3 h, and a clear orange solution formed. A solution of 0.587 g of NH_4PF_6 (3.6 mmol) in 4 mL of hot ethanol was added, and an orange precipitate immediately formed. This mixture was allowed to stir for 30 min and then filtered via a paper tipped cannula. The residue was washed with an additional 4 mL portion of hot ethanol, dried in vacuo, and extracted into 7 mL of CH_2Cl_2. The orange-red air-sensitive solution was taken to dryness and gave the analytically pure product. Large, blocklike crystals were obtained by slow concentration of a solution in CH_2Cl_2. Yield: 0.351 g, 90%.

Spectral and Analytical Data for Complex 2b. The spectral data of this compound are identical to those of the $[BPh_4]^-$ salt **2a** (*vide supra*) besides the absence of the signals due to the $[BPh_4]^-$ counterion in the ^{1}H-NMR and IR spectra and the presence of the heptet of the $[PF_6]^-$ ion in the ^{31}P-NMR spectra as well as the two characteristic bands of PF_6^- at 838 and 557 cm^{-1} in the IR. Anal. Calcd for $C_{52}H_{97}F_6P_5Ru$: C, 57.18; H, 8.95 Found: C, 57.20; H, 8.97.

Synthesis of $[RuD(dcpe)_2]^+[PF_6]^-$ (2c). The synthesis was performed as given above, but by replacing ethanol with C_2H_5OD and starting from 0.115 g (0.238 mmol) of $RuCl_2(DMSO)_4$, 0.200 g of dcpe (0.475 mmol), 0.6 mL of NH^iPr_2, and 6 mL of C_2H_5OD. Yield: 0.212 g, 88%. The spectral data for this compound were identical to those of the pure hydride, but the hydride resonance integrated to only ca. 0.5 H.

Synthesis of *trans*-RuHCl(dcpm)$_2$ (3). Method 1. $RuCl_2(DMSO)_4$ (0.160 g, 0.33 mmol) and bis(dicyclohexylphosphino)methane (dcpm) (0.271 g, 0.663 mmol) were suspended in 12.5 mL of ethanol, and 1 mL of NEt_3 was added. The pale yellow suspension was stirred under warming to a gentle reflux. Within minutes all solids dissolved to give a yellow-orange, clear solution to which $NaSbF_6$ (0.521 g, 2.0 mmol) was added as a solid. This caused an immediate color change to red-orange, and a purple precipitate appeared. The mixture was then kept at a gentle reflux for 3 h during which time the precipitate gradually turned pale orange. The volume of the reaction mixture was reduced to ca. 4 mL, and the solid collected by filtration. After drying in vacuo, the solid residue was extracted into 2 × 7 mL of CH_2Cl_2. The combined extracts were cautiously layered with 3 mL of pentane. An almost white precipitate formed overnight, which was isolated by filtration and found to contain predominantly $RuHCl(dcpm)_2$ (**3**) besides little *trans*-$RuCl_2(dcpm)_2$ (**4**). The mother liquor was further concentrated until new solids formed on the wall of the Schlenk tube and were allowed to crystallize overnight. After filtration the remaining solution contained only the product which was isolated by evaporating the solvents as a pale yellow, microcrystalline solid. The mixture obtained in the first crystallization step was dissolved in the minimum amount of hot benzene. Upon cooling, the dichloride precipitated as an orange, microcrystalline powder which was separated by cautiously syringing off the mother liquor which was in turn evaporated to yield a further crop of complex **3**. Combined yields: 0.194 g (62%) of complex **3** and 0.028g (9%) of complex **4**.

Method 2. $RuCl_2(DMSO)_4$ (0.091 g, 0.19 mmol), dcpm (0.147 g, 0.38 mmol), and $NaSbF_6$ (0.301 g, 1.16 mmol) were suspended in a solution of Na (0.16 g, 7 mmol) in EtOH (7.5 mL) and heated to a gentle reflux for 3 h. After the solids were allowed to settle and the solvent was removed by cannula filtration, the pale orange residue was washed with 2 portions of warm EtOH (2 mL each) and dried in vacuo. The resulting pale yellow solid was extracted into CH_2Cl_2 (2 × 5 mL) and dried. The crude product contained predominantly complex **3** along with ca. 12% of a second monohydrido complex ($^{31}P\{^1H\}$-NMR ($CDCl_3$), δ 4.0 (s); ^{31}P, ($CDCl_3$), δ 4.0 (d, $^3J_{P-H}$ = 16.2 Hz)). The latter was removed by dissolving the residue in the minimum amount of CH_2Cl_2, layering the solution with an approximately equal amount of pentane, and allowing it to stand at ambient temperature overnight. The remaining solution was separated from the precipitate and put to dryness to yield 0.088 g of pure complex **3** (0.092 mmol, 48%).

Spectral and Analytical Data for Complex 3. ^{1}H-NMR (C_6D_6): δ 3.33 (PCH_2P (dcpm), dt, $^2J_{H-H}$ = 14.50 Hz, $^2J_{P-H}$ = 2.20 Hz, 2H), 3.05 (PCH_2P (dcpm), dt, $^2J_{H-H}$ = 14.50 Hz, $^2J_{P-H}$ = 3.48 Hz, 2H), 2.98 (t, br *ipso*-CH (dcpm), $^2J_{H-H}$ = 10.5 Hz, 4H), 2.50 (m, 4H), 2.33 (m, 4H), 2.08 (m, 8H), 1.20−1.91 (m, 68H, all CH_2 (dcpm)), −17.44 (RuH, quint, $^2J_{P-H}$ = 18.71 Hz). ^{13}C-NMR (C_6D_6): δ 39.1 (*ipso*-CH, (dcpm), vquint, N_{P-C} = 4.9 Hz), 36.2 (*ipso*-CH, (dcpm), vquint, N_{P-C} = 3.4 Hz), 34.0 (PCH_2, (dcpm), vquint, N_{P-C} = 8.8 Hz), 30.6, 30.0, 29.9, 29.2, 28.1, 28.0, 26.9, 26.4 (all CH_2 (dcpm), all s). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 6.9 (s). ^{31}P-NMR (C_6D_6): δ 6.9 (d, $^3J_{P-H}$ = 18 Hz). IR (KBr, cm^{-1}): 2922, 2843 (CH_2, CH (dcpm)), 1947 (RuH), 1445, 1261, 1172, 1094, 1025, 803, 748 (dcpm). UV/vis (CH_2Cl_2; λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 381 (sh), 353 (880), 343 (1060), 315 (1090). Anal. Calcd for $C_{50}H_{93}ClP_4Ru\cdot CH_2Cl_2$: C, 58.92; H, 9.21. Found: C, 58.44; H, 9.60.

Synthesis of *trans*-RuCl$_2$(dcpm)$_2$ (4). $RuCl_2(DMSO)_4$ (0.085 g, 0.137 mmol) and dcpm (0.143 g, 0.35 mmol) were refluxed in ethanol for 1 h. A yellow solution and some yellow precipitate formed. The solvent was evaporated and the tarry residue recrystallized by slowly cooling a hot, concentrated solution in a 1:1 ethanol/chlorobenzene mixture. Well-shaped pale orange transparent crystals formed overnight which were isolated by filtration. Another batch was obtained by further concentration of the mother liquor. The combined crystal fractions were washed with cold ethanol and dried in vacuo. Yield: 0.126 g, 94%.

Spectral and Analytical Data for Complex 4. ^{1}H-NMR (C_6D_6): δ 3.54 (PCH_2 (dcpm), vquint, $^2J_{P-H}$ = 3.65 Hz, 4H), 2.70 (vt, br. *ipso*-CH (dcpm), $^2J_{H-H}$ = 10.9 Hz, 8H), 2.51 (m, 8H), 2.05 (d, br, J_{H-H} = 13.2 Hz, 8H), 1.22−1.85 (m, 64H, all CH_2 (dcpm)). ^{13}C-NMR (C_6D_6): δ 36.2 (*ipso*-C (dcpm), vquint, N_{P-C} = 4.0 Hz), 33.6 (m, PCH_2P (dcpm)), 30.8, 30.2, 30.1, 29.5, 28.4, 27.0 (C_6H_{11} (dcpm), all s). ^{31}P-

Table 1. Crystallographic Data and Data Collection Parameters for Complexes **1** and **2a**

	1	**2a**
formula	$C_{50}H_{69}BP_2Ru{\cdot}0.5CH_2Cl_2$	$C_{76}H_{117}BP_4Ru{\cdot}3CH_2Cl_2$
fw	886.34	1521.33
temp, K	188(3)	188(3)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2/c$ (No. 13)
a, Å	14.321(5)	24.936(5)
b, Å	19.716(6)	12.633(3)
c, Å	17.100(5)	25.801(5)
β, deg	107.6	102.86(3)
V, Å^3	4602(3)	7924(3)
ρ_{calc}, g cm^{-3}	1.279	1.275
wavelength, Å	0.710 73, Mo Kα	0.710 73, Mo Kα
Z	4	4
μ, mm^{-1}	0.501	0.522
final R^a indices [$I > 2\sigma(I)$]	0.0648	0.0620
$R_w{}^a$ indices (all data)	0.1873	0.1694

^{a} $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o{}^4)]\}^{1/2}$.

{^{1}H}-NMR (C_6D_6): δ −6.5 (s). IR (KBr, cm^{-1}): 2923, 2847 (CH$_2$, CH (dcpm)), 1444, 1262, 1171, 1129, 1101, 1023, 1005, 898, 891, 849, 802, 768, 742, 700 (dcpm). UV/vis (chlorobenzene; λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 500 (30), 426 (60), 329 (sh).

Crystallographic Studies. Single crystals of compound **1** were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature, whereas single crystals of compound **2a** formed upon diffusion of ethanol into a CH_2Cl_2 solution at 4 °C. Crystal, data collection, and refinement parameters are given in Table 1. The single crystals were taken from the mother liquors, separated under nujol, and sealed in a glass capillary. The data collection was performed on a Siemens-P4 four-circle diffractometer. The structures of **1** and **2a** were solved by direct methods, using the SHELXTL-Plus[25] package. Refinement was carried out with SHELXL-93,[26] employing full-matrix least squares methods. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were constrained using a riding model with isotropic thermal parameters fixed at 20% greater than that of the bonded atom. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. They can be ordered free of charge from the following: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, GB (telefax, +44 1223/336-033; e-mail, teched@chemcrys.cam.ac.uk).

Results

Synthesis of {(η^6-C_6H_5)BPh_3}RuH(dcpe)] (1) and [RuH(dcpe)$_2$]$^+$[A]$^-$ (A$^-$ = $BPh_4{}^-$ (2a), $PF_6{}^-$ (2b)). In 1989 Rigo and co-workers reported the synthesis of [RuCl(dcpe)$_2$]$^+$[BPh$_4$]$^-$ (dcpe = bis(dicyclohexylphosphino)ethane).[12] Our initial experiments to reproduce their results, however, yielded a mixture of two different products which were isolated as white and dark orange crystals, respectively, and subsequently characterized as the zwitterionic arene complex {(η^6-C_6H_5)BPh_3}-RuH(dcpe) (**1**) and the five-coordinate hydride [RuH(dcpe)$_2$]$^+$[BPh$_4$]$^-$ (**2a**). As one might expect from their different composition, the relative amounts in which these two products are formed depend on the reaction stoichiometry. Thus, if 2 equiv of the chelate ligand is present, the five-coordinate cation **2a** constitutes the major product, whereas the use of only 1 equiv of the diphosphine leads to a higher proportion of the arene complex **1**. The spectroscopic data of complex **2a** suggested a rather high cation symmetry. In its ^{31}P-NMR spectrum at 303 K two sharp singlets with almost identical chemical shifts at δ = 74.2 and 74.0 ppm are observed. The presence of the characteristic [BPh$_4$]$^-$ resonances in the ^{13}C- and ^{1}H-NMR spectra and a quintet hydride signal in the ^{1}H-NMR spectrum at δ = −32.06 ppm integrating as one proton confirmed the product identity.

With chelates that are too small to allow for agostic interactions between the vacant coordination site and the (CH$_2$)$_n$ bridges of the diphosphine ligands, rather high-field-shifted hydride resonances are generally found.[20a] We also note that such a high-field shift is not without precedence for five-coordinate hydride complexes of group 8 metals.[27] The P−H coupling constant of 19 Hz is in the usual range.[20a,21] As such, the ^{31}P-NMR data are in much better agreement with a slightly distorted, square pyramidal (sqp) structure than with a trigonal bipyramidal (tbp) one. Considerably larger differences between the chemical shifts of the axial and the equatorial sites (the shift difference $\Delta\delta$ is usually in the range of some 15−43 ppm) are to be expected in the latter case.[11,12,14,16] The fact that two narrowly spaced singlet signals with no apparent coupling rather than only one singlet are observed in the ^{31}P-NMR spectra of complexes **2a,b** most probably arises from dynamic processes. The X-ray structure of complex **2a** (*vide infra*) indicates that two of the P atoms are displaced out of the best plane RuP$_4$ toward the hydride, whereas the remaining two point away from this ligand. This might render the two pairs of P atoms slightly inequivalent. As the possibility of a fast exchange between the different sites of a tbp structure could not be ruled out, we performed a low-temperature NMR study. Upon cooling a broadening of the two signals was observed, and at T = 215 K they merged into one broad resonance. (See Note Added in Proof.) Further cooling to 190 K resulted in the appearance of two broad peaks of different heights and half-widths that were located at δ = 77.6 ($W_{1/2}$ = 168 Hz) and δ = 74.6 ppm ($W_{1/2}$ = 99 Hz). Likewise, below 215 K the hydride signal appeared as a broad resonance at δ = −32.42 ppm. The electronic spectrum shows an intense absorption band at λ_{max} = 411 nm that can be regarded as characteristic for five-coordinate d^6 systems. In accordance with the higher ligand field strength of the hydride this band exhibits a hypsochromic shift of about 50−80 nm with respect to the corresponding [RuX(L$_2$)$_2$]$^+$ (X = halogen).[10,12] To our surprise our spectroscopic data did not match those reported by Rigo for a compound of identical composition,[12] the most prominent difference being the shift of the hydride ligand (see Note Added in Proof). Therefore it seemed desirable to confirm the identity of complex **2a** by performing an X-ray analysis. This was also of significance in a different context: [RuH(L$_2$)$_2$]$^+$ are excellent precursors to powerful hydrogenation catalysts,[21] and many attempts have been made to characterize one of these five-coordinate monohydrides by crystallography. None of them has been successful until now. In part this is due to their high reactivity. Thus, crystallization of [RuH(Me-DuPhos)$_2$]$^+$ (Me-DuPhos = 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene) under N$_2$ has led to the isolation of the dinitrogen addition product.[28] The crystal structure of complex **2a** (*vide infra*) confirmed an sqp configuration of the cation.

The second product of this reaction is the arene coordinated {(η^6-C_6H_5)BPh_3}RuH(dcpe) (**1**). This species is characterized

---

(25) Sheldrick, G. M. *SHELXTL-Plus: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1989.

(26) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Determination*; Universität Göttingen: Göttingen, Germany, 1993.

(27) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(28) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, *16*, 1253.

by two distinct sets of phenyl protons and carbons, integrating to 3:1 in the ^{1}H-NMR spectrum. At 303 K, the less intense of these two subsets is comprised of two well-resolved triplets at $\delta = 5.60$ and 5.38 ppm and a doublet at $\delta = 5.83$ ppm with relative intensities of 2:1:2. As a consequence of the metal coordination these signals are shifted by approximately 1.3−1.5 ppm to higher field with respect to the protons of the uncoordinated phenyl rings. In the hydride region a triplet signal is detected at $\delta = -11.59$ ppm with a 36.5 Hz coupling constant to two identical P atoms. Likewise, the sharp singlet in the ^{31}P-NMR spectrum at $\delta = 97.2$ ppm splits into a doublet with a 36 Hz coupling constant in the proton coupled spectrum. Upon a decrease in the temperature, the ^{31}P resonance broadens considerably and almost vanishes but no decoalescence is observed down to 190 K. Larger effects are, however, observed in the ^{1}H-NMR spectrum, where at 213 K the two low-field proton signals of the coordinated phenyl ring at $\delta = 5.78$ and 5.67 ppm (CD_2Cl_2) merge into one broad resonance at $\delta = 5.61$ ppm, presumably as a consequence of a hindered rotation of the metal fragment with respect to the bulky arene substituent. At still lower temperatures down to 200 K this signal sharpens, while no coalescence with the remaining proton is found and all proton couplings within the coordinated ring are lost.

The PPh_3 derivative of complex **1**, $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(PPh_3)_2$, has briefly been mentioned in the literature, but no spectroscopic data were provided,[29] and the related $[\{(\eta^6\text{-}C_6H_5)PPh_2\}RuH(PPh_3)_2]^+[BF_4]^-$ has been obtained by thermolysis of $RuH(CO_2Me)(PPh_3)_3$ in methanol and its structure determined by X-ray analysis.[30] Complex **1** may also be compared to the cationic arene complexes $[(\eta^6\text{-arene})RuH(PR_3)_2]^+$ which were first synthesized by Werner[31] only that in the case of complex **1** the anionic nature of the arene substituent renders the molecule neutral. The isoelectronic and isostructural compounds Cp^R-$RuH(PR_3)_2$ are also well documented.[32,33] The formation of complex **1** can be rationalized from the competitive attack of a $[BPh_4]^-$ nucleophile on the $RuCl_2(DMSO)_4$ starting material or a partially substituted coordinatively unsaturated derivative thereof. Compound **1** represents one more example for the noninnocent behavior of the "noncoordinating" $[BPh_4]^-$ anion,[34] and a growing number of such structures are reported in the literature.[34b] Complex **1** is only formed if the tetraphenylborate salt is added at the beginning of the reaction. Thus, complex **2a** may be isolated in high yields and without any contamination by complex **1** if the tetraphenylborate salt is added after first allowing $RuCl_2(DMSO)_4$ to react with 2 equiv of the diphosphine for 3 h under reflux. Moreover, complex **1** seems to prevail in the early stages of the reaction since the precipitates are initially only lightly colored and become more and more intense orange with time. In separate experiments we showed that both products, once formed, are stable and do not interconvert under the reaction conditions employed. We found that complex **1** does not react to complex **2a** in the presence of excess dcpe and there is no complex **1** formed when complex **2a** is refluxed in ethanol with equimolar amounts of $RuCl_2(DMSO)_4$, $NaBPh_4$, and excess NEt_3. The $[PF_6]^-$ anion, however, does not compete with the diphosphine chelate, and complex **2b** is formed in high yields irrespective of the time at which the anion is added.

Our initial guess as to why this reaction gave a totally different result in our hands (*i.e.* $[RuH(dcpe)_2]^+$ and not $[RuCl(dcpe)_2]^+$)[12] was the different procedure employed in drying the ethanol solvent. This was, however, found to have no effect on the product distribution. More specifically, ethanol itself is the most likely hydride source. We note that Ogasawara and Saburi have already suggested that ethanol is involved in the slow transformation of the monohydride cations $[RuH(L_2)_2]^+$ to their respective dihydrides (eq 1).[20]

$$[RuH(L_2)_2]^+ + CH_3CH_2OH \rightarrow RuH_2(L_2)_2 + CH_3CHO + H^+ \quad (1)$$

While no such complication was encountered in our case, the above reaction suggested to us that the monohydride might be formed by an analogous reaction via a coordinatively unsaturated intermediate. We do not know whether this intermediate is the respective chloro compound $[RuCl(dcpe)_2]^+$ that we were unable to obtain under our reaction conditions. Our results with the dcpm ligand (dcpm = $(C_6H_{11})_2PCH_2P(C_6H_{11})_2$, *vide infra*), however, make it more likely that the hydride is transferred at an earlier stage of this reaction. Irrespective of the detailed reaction sequence, the net conversion can be formulated as shown in eq 2.

$$RuCl_2(DMSO)_4 + 2dcpe + NH^iPr_2 + C_2H_5OH + NaBPh_4 \rightarrow [RuH(dcpe)_2]^+[BPh_4]^- + NaCl + NH_2{}^iPr_2Cl + CH_3CHO \quad (2)$$

We have no direct evidence for the formation of either acetaldehyde or the quaternary ammonium salt, but there are several observations which support the above reaction scheme. Thus, the presence of the amine is a necessary prerequisite in order to achieve good yields of complexes **2a,b**. In its absence the yields of isolated complexes **2a,b** dropped to typically 30−35%, while the replacement of diisopropylamine by triethylamine has no effect. The function of the amine is then to trap the protons formed upon heterolytic dissociation of H^+ from ethanol, thus preventing a detrimental protonation of the phosphine ligands. Even stronger evidence comes from the observation that the reaction run in C_2H_5OD yields an approximately 1:1 mixture of the deuterated analogue $[RuD(dcpe)_2]^+$ and the corresponding hydride. The roughly 50% incorporation of deuteride into the final product may indicate that the hydride originates statistically from the ethanol OH function and the methylene CH_2 group. We can, however, at present not exclude a H/D exchange reaction between the deuterated alcohol and the basic amine and/or D transfer to complex **2a,b** from any deuterated species present with subsequent competitive loss of a hydride or deuteride.

Description of the Structures. The X-ray crystal structure of complex **2a** reveals the presence of two crystallographically independent cations. Both possess a crystallographic 2-fold axis of symmetry through the metal center. The cations and the crystallographically unique anion pack as discrete units within the crystal lattice with no short intermolecular contacts. No unusual features are found for the $[BPh_4]^-$ anion, which warrants no further discussion. The structure of one of the cations is given in Figure 1. Crystallographic data collection parameters and selected bond distances and angles for the cations are given in Tables 1 and 2. Both exhibit a distorted square planar arrangement of the four P atoms around Ru which points to a

---

[29] Hough, J. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1972**, 371.

[30] McConway, J. C.; Skapski, A. C.; Phillips, L.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1974**, 327.

[31] Werner, H.; Werner, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 683.

[32] (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (c) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (d) Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183.

[33] (a) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980. (b) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721.

[34] (a) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

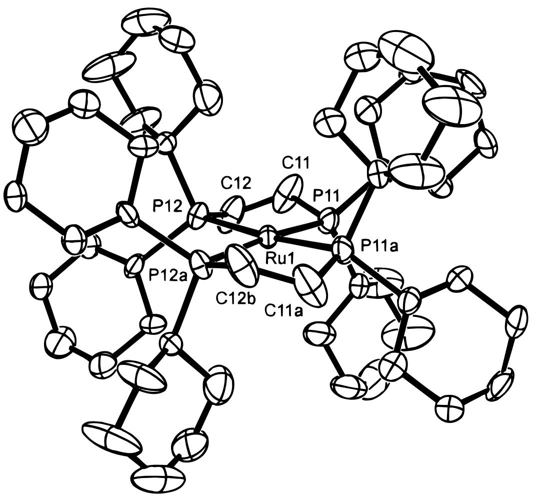

Figure 1. ORTEP diagram of the cation of complex **2a** at a 50% probability level. Hydrogen atoms are omitted for clarity. Only one of the two crystallographically unique cations is shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** and **2a** (Two Independent Cations)

	Complex **1**		
Ru−C(51)	2.374(4)	Ru−C(54)	2.301(4)
Ru−C(52)	2.288(4)	Ru−C(55)	2.234(4)
Ru−C(53)	2.272(4)	Ru−C(56)	2.253(4)
C(51)−C(52)	1.418(6)	C(54)−C(55)	1.419(7)
C(52)−C(53)	1.411(6)	C(55)−C(56)	1.406(6)
C(53)−C(54)	1.400(7)	C(51)−C(56)	1.419(6)
Ru−P(1)	2.280(1)	Ru−P(2)	2.286(2)
Ru−H(1)	1.42(5)	B−C(51)	1.661(6)
B−C(61)	1.641(6)	B−C(71)	1.644(7)
B−C(81)	1.653(7)		
P(1)−Ru−P(2)	83.95(5)	H−Ru−P(1)	79(2)
H−Ru−P(2)	80(2)	centr[a]−Ru−P(1)	134.5
centr[a]−Ru−P(2)	135.1	centr[a]−Ru−H	122.6
	Complex **2a**		
Ru(1)−P(11)	2.353(2)	Ru(2)−P(21)	2.340(2)
Ru(1)−P(12)	2.346(2)	Ru(2)−P(22)	2.341(2)
P(11)−C(11)	1.847(6)	P(21)−C(21)	1.853(9)
P(11)−C(111)	1.815(13)	P(21)−C(211)	1.856(6)
P(11)−C(121)	1.867(5)	P(21)−C(221)	1.743(11)
P(12)−C(12)	1.844(6)	P(22)−C(22)	1.838(6)
P(12)−C(131)	1.870(5)	P(22)−C(231)	1.863(6)
P(12)−C(141)	1.93(2)	P(22)−C(241)	1.805(13)
P(12)−Ru(1)−P(11)	82.61(6)	P(21)−Ru(2)−P(22)	97.90(6)
P(11)−Ru(1)−P(11a)[b]	98.40(8)	P(21)−Ru(2)−P(21b)[b]	82.52(9)
P(12)−Ru(1)−P(12a)[b]	96.94(8)	P(22)−Ru(2)−P(22b)[b]	82.63(8)
P(12)−Ru(1)−P(11a)[b]	174.37(5)	P(21)−Ru−P(22b)[b]	172.68(6)

[a] Midpoint of the coordinated arene ring C(51)−C(56). [b] Symmetry transformations to generate equivalent atoms: (a) $-x, y, -z + 1/2$; (b) $-x + 1, y, -z + 3/2$.

square pyramidal structure type. The hydride was not localized but is expected to reside in an apical position. For each cation the two independent Ru−P bond lengths differ only slightly from each other (data for the second cation are given in parantheses). Their average of 2.350 (2.341) Å lies at the lower limit of those values found for the basal P atoms in other five-coordinate, square pyramidal, 16 valence electron ruthenium compounds $RuClX(PR_3)_3$ (2.37 Å av).[8,9] Owing to crystallographic symmetry, the Ru atom is part of the best plane through the basal P atoms which in turn exhibit rather large displacements of 0.115 (0.150) Å out of the mean plane. As a consequence the angle between the equivalent pairs of *trans* P atoms is decreased to 174.37(5) (172.68(6))°. A further distortion of the pyramid base arises from the diphosphine chelate bite angles of 82.61(6) (82.52(9) and 82.63(8))°, being considerably smaller than the remaining angles of 98.40(8)° and 96.94(8) (97.90(6))° between unbridged P atoms.

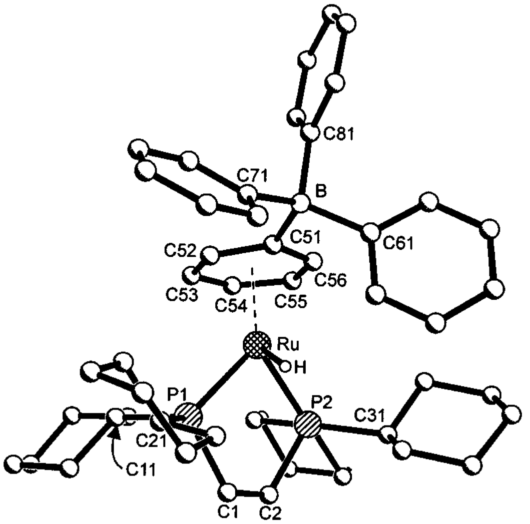

Figure 2. Perspective drawing of complex **1**.

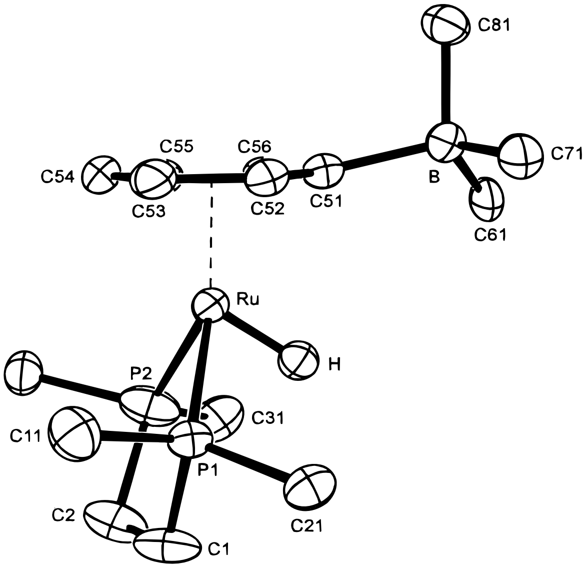

Figure 3. ORTEP diagram of a side view of complex **1** at a 50% probability level showing the boatlike distortion of the coordinated phenyl ring. The cyclohexyl substituents are omitted for clarity.

It is worth mentioning that the $[RuH(dcpe)_2]^+$ cation represents the only crystallographically characterized example of a square pyramidal five-coordinate d^6 ruthenium cation with a P_4X donor set besides $[RuCl(PP_3)]^+$,[17a] where this structural motif is induced by the rigidity of the chelating PP_3 ligand ($PP_3 = P(C_2H_4PPh_2)_3$). All other representatives belong to the type RuP_3XY; the chlorine derivatives $[RuClP_4]^+$ are trigonal bipyramidal.[13−18] These observations are in complete agreement with theoretical predictions.[2] Moreover, complex **2a** is the only example within this whole series where the metal is part of the pyramid base with *trans* pairs of basal P atoms displaced to different sides from the best plane. This is most likely due to the steric bulk of the cyclohexyl substituents and the small apical hydride. In fact, any net pyramidalization of the Ru center (*i.e.* all P atoms bending away from Ru in the *same* direction) would cause unfavorably close contacts between the cyclohexyl rings.

The arene complex **1** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and 12 molecules of CH_2Cl_2 in the unit cell. The individual molecules are well-separated, and there are no intermolecular contacts shorter than the sum of the corresponding van der Waals radii. Views of the molecule are given in Figures 2−4, and the most important bond lengths and angles are collected in Table 2 (for a listing of the crystallographic data see Table 1). The most notable feature is the

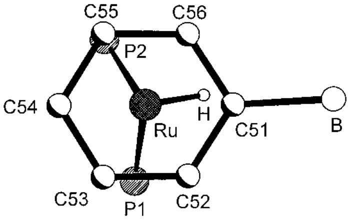

Figure 4. Top view of complex **1** showing the near ecliptic conformation of the hydride. Only the molecule skeleton is depicted.

boatlike distortion of the coordinated phenyl ring of the $[BPh_4]^-$ anion with the BPh_3^- substituted C atom C51 and the *para* C atom C54 being 0.064(6) and 0.049(7) Å above the best plane defined by the remaining four C atoms and being bent away from the metal. This distortion is evident from a side view in Figure 3 and is quantified by the interplanar angles between C51,C52,C56 or C53,C54,C55 and the mean plane through the almost coplanar C52,C53,C55,C56 of 4.8(1) and 3.9(1)°, respectively. Out-of-plane deformations are not without precedence for the coordinated $[BPh_4]^-$ anion,[35] although several other modes of distortion are known.[36] As a consequence of the metal coordination, the C−C bond lengths within the η^6 bound phenyl ring are somewhat elongated with respect to those of the free arene rings. The Ru atom is slightly shifted away from the ring center. This effect is, however, rather small as is evident from the 1.7° angle between the axis ring center Ru and the normal to the mean plane C52,C53,C55,C56 and compares well to the $[BPh_4]^-$ salt of the $[(\eta^6\text{-toluene})RuH(PPh_3)_2]^+$ cation.[37] The Ru−P bond lengths of 2.286(2) and 2.288(2) Å are basically identical and somewhat short with respect to the other crystallographically investigated $[(\eta^6\text{-arene})RuH(PPh_3)_2]^+$ cations (2.311−2.332 Å)[30,37] but somewhat longer than those in the isoelectronic $CpRuH(PR_3)_2$ derivatives (2.238−2.288 Å).[33] We were able to localize the hydride ligand at a distance of 1.42(5) Å away from the metal center but note that terminal M−H bond lengths determined by X-ray diffraction always fall short of the values determined by neutron diffraction (compare the Ru−H distances of 1.36(8) and 1.630(4) Å determined for $CpRuH(PMe_3)_2$ by X-ray and neutron diffraction, respectively).[33]

A feature common to the other $[(\eta^6\text{-arene})RuH(PPh_3)_2]^+$ cations is the T-shaped arrangement of the phosphine ligands with P−Ru−P angles of about 95−105°.[30,37] This is not the case for $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ (PRuP = 83.95(5)°) as the five-membered chelate does not allow for such an opening of this angle. The bulky cyclohexyl substituents lead to a rather large 71.3° tilt of the plane P1,Ru,P2 with respect to the best plane for the cooordinated arene ring. One more feature of this structure deserves some further comment. This is the orientation of the $RuHP_2$ unit with respect to the arene substituent. NMR-spectroscopic and crystallographic studies as well as EHMO calculations on such systems have revealed two rotameric minimum structures separated by only a small energy barrier. In the solid state complex **1** adopts one of these minimum structures with the hydride ligand nearly eccliptical to the BPh_3^-, *i.e.* the donor substituted carbon atom. The dihedral angle $B-C_{6,centr}-Ru-H$ amounts to 9.2° (Figure 4; $C_{6,centr}$ refers to the midpoint of the arene ring C(51)−C(56)). This rotameric structure also represents a general energy minimum for $[(\eta^6\text{-arene})ML_3]$ systems with monosubstituted arene rings if the ring substituent is an electron donor.[36]

Synthesis of *trans*-$RuHCl(dcpm)_2$ (3) and *trans*-$RuCl_2(dcpm)_2$ (4). We have already mentioned that the outcome of the reaction between a chelating diphosphine and a substitutionally labile Ru^{II} precursor complex critically depends *inter alia* on the chelate ring size. The relevant literature reveals the trend of a decreasing aptitude toward chloride dissociation with decreasing chelate ring size. Here we address this question with the example of two congeners of the bis(dicyclohexylphosphino)alkane (alkane = $(CH_2)_2$ (dcpe), CH_2 (dcpm)) series. If 2 equiv of the dcpm ligand are allowed to react with $RuCl_2(DMSO)_4$ in the presence of excess $NaSbF_6$ and NH^iPr_2 in refluxing ethanol, the mixed ruthenium hydrido chloride $RuHCl(dcpm)_2$ (**3**) constitutes the major product accompanied by small amounts of the corresponding dichloride **4**. Separation of these products is readily achieved on the basis of their different solubilities. Due to its dipole moment, the pale yellow, 18 valence electron monohydride **3** is much more soluble in CH_2Cl_2 and aromatic solvents such as benzene, toluene, or chlorobenzene than the almost insoluble dichloride **4**. A reviewer suggested that a more basic medium such as NaOEt in EtOH should provide a more complete conversion to the hydride complex. This is indeed the case since essentially no complex **4** is found in the crude product obtained under these conditions. However, another monohydrido species, possibly the corresponding OEt complex which is difficult to separate from complex **3**, is formed as a byproduct, thus lowering the yield of isolated complex **3**. In its ^{31}P spectrum complex **3** exhibits a sharp singlet at $\delta = 6.9$ ppm, indicative of an axial symmetry. This singlet splits into a doublet with a coupling constant of about 18 Hz in the proton coupled spectrum. The corresponding hydride resonance is found as a quintet signal at $\delta = -17.44$ ppm with a coupling constant of 18.7 Hz. In addition, a weak band at 1947 cm^{-1} in the IR spectrum of this compound can be assigned to the Ru−H stretching vibration. From the observation of both the hydrido chloride **3** and the dichloride **4** in the reaction mixture, one may assume that complex **4** is the direct precursor of complex **3** and the latter is being formed upon sodium assisted chloride dissociation and the subsequent reaction of the coordinatively unsaturated intermediate with ethanol as the hydride source (*vide supra).* In order to examine both of these points, we first investigated the reaction of $RuCl_2(DMSO)_4$ with the diphosphine ligand under conditions identical to those above, except for the shorter reaction times and the absence of the sodium salt and the amine. Indeed, the *trans*-dichloride **4** can be isolated in high yields by crystallization from a hot chlorobenzene/ethanol solution as pale orange, diamond or hexagonal shaped crystals or as a microcrystalline powder. The *trans*-stereochemistry is established by the observation of a singlet in the ^{31}P-NMR spectrum at $\delta = -6.5$ ppm. In accordance with other MCl_2P_4 derivatives of this architecture the electronic spectrum of complex **4** exhibits only weak bands in the visible region. The assumption that the *trans*-dichloride **4** is a direct precursor of complex **3** was investigated by treating isolated complex **4** with $NaSbF_6$ in refluxing ethanol to which excess NH^iPr_2 had been added. Essentially no conversion of complex **4** to the *trans*-hydrido chloride **3** was, however, observed. This leads us to believe that the incorporation of the hydride takes event at an earlier stage of this reaction and that chloride dissociation occurs from an only partially diphosphine substituted intermediate or the starting material itself.

---

(35) (a) Nolte, M. J.; Gafner, G.; Haines, L. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1406. (b) Ware, D. C.; Olmstead, M. M.; Wang, R.; Taube, H. *Inorg. Chem.* **1996**, *35*, 2576.

(36) (a) Substituted and *para* C atoms are closer to the metal: Albano, M.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069. (b) Only the BPh_3 substituted carbon out of plane: de Carvalho, L. C. A.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 6848. (c) Planar arene ring: Kruger, G. J.; du Preez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1302.

(37) Siedle, R. R.; Newmark, R. A.; Pignolet, L. H.; Wang, D. X.; Albright, T. A. *Organometallics* **1986**, *5*, 38.

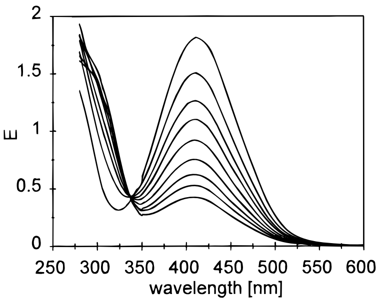

Figure 5. Spectral changes upon consecutive addition of increasing amounts of CH_3CN to a solution of complex **2b** in CH_2Cl_2. The overlay displays the absorption band of complex **2b** without added CH_3CN (upper trace) and after addition of approximately 150, 260, 370, 520, 730, 1000, 1250, and 2300 equiv of CH_3CN (lower traces).

Reaction of $[RuH(dcpe)_2]^+[A]^-$ with CH_3CN. The five-coordinate, 16 valence electron cations $[RuXP_4]^+$ (X = halogen, H), irrespective of their structure, readily add neutral two-electron donor ligands or halide anions to achieve electronic saturation at the metal center. The stability of these adducts varies with the size and the donor ability of the incoming nucleophile, and frequently equilibria are obtained.[12,15,19a] Thus, while CO forms stable six-coordinate cations, all attempts to isolate solid samples of the acetonitrile or nitromethane solvates have failed so far. $[RuH(dcpe)_2]^+[A]^-$ ($A^- = [PF_6]^-$, $[BPh_4]^-$) seems to be a remarkable exception in that no reactions with CH_3CN, CO, or N_2 have been observed[12] (see, however, Note Added in Proof). (Other $[RuH(L_2)_2]^+$ cations are nevertheless reported to be highly reactive toward CO, halogenide, and, most notably, H_2 and N_2.)[19,26] In our hands, however, rapid reactions of both the $[PF_6]^-$ and the $[BPh_4]^-$ salts with acetonitrile were found to occur. This process is conveniently monitored by UV/vis spectroscopy. Addition of increasing amounts of CH_3CN to a CH_2Cl_2 solution of complexes **2a,b** leads to a discoloration of the orange solution to a very pale orange and a leaching of the strong visible band of the five-coordinate cation at λ_{max} = 411 nm. In the near UV a new band is observed as a shoulder near λ = 300 nm. It increases in height as more acetonitrile is added and is consequently attributed to a CH_3CN containing product (Figure 5). Even in the presence of a large excess of CH_3CN there is still some remainder of the original band of the five-coordinate cation which shows that the equilibrium for this process lies quite to the left. From the UV/vis changes an equlibrium constant K_c of about 0.0023 mol^{-1} L^{-1} may be derived. In accordance with the above observation solutions of complexes **2a,b** in CH_3CN contain a strong band at 299 nm (ϵ_{max} = 1800 M^{-1} cm^{-1}) as well as an even stronger band at 230 nm (ϵ_{max} = 7000 M^{-1} cm^{-1}) but do not exhibit any absorption at 411 nm. The addition was found to be reversible as pumping off the solvent in vacuo under heating to 60 °C and redissolving the solid residue in CH_2Cl_2 regenerated the original spectrum. This lets us assume that complexes **2a,b** are generally reactive toward neutral two-electron donor molecules. At present we are investigating their interaction with terminal alkynes, and we will report our findings in due course.

Summary

In the present work we have reinvestigated the reaction between $RuCl_2(DMSO)_4$ and dcpe in the presence of either NH_4PF_6 or $NaBPh_4$ in refluxing ethanol and have shown that the coordinatively unsaturated hydride cation $[RuH(dcpe)_2]^+$ is the major and, upon slight modification of the reaction conditions, the only product. An X-ray analysis of the $[BPh_4]^-$ salt **2a** establishes this cation as belonging to the square pyramidal structure type. Low-temperature NMR studies make it very likely that this structure is also maintained in solution. In the case of the $[BPh_4]^-$ counterion we were able to identify the as yet unnoticed zwitterionic $\{(\eta^6\text{-}C_6H_5)BPh_3\}RuH(dcpe)$ as the second product which was found by X-ray analysis to feature a boat-shaped η^6-coordinated phenyl ring. Further investigations make it likely that the latter compound is formed by competitive nucleophilic attack of the $[BPh_4]^-$ anion on a coordinatively unsaturated reaction intermediate, whereas the hydride **2a** itself is inert toward this anion. The coordinatively unsaturated cations present in complexes **2a,b** readily coordinate acetonitrile.

Reducing the size of the dcpe chelate by one CH_2 unit renders six-coordinate species dissociatively stable even in the presence of a large excess of $NaSbF_6$ in boiling ethanol. Depending on the exact reaction conditions either *trans*-$RuHCl(dcpm)_2$ (**3**) or *trans*-$RuCl_2(dcpm)_2$ (**4**) are isolated in good to excellent yields. We have shown that the dichloride **4** is no direct precursor to the hydride **3** and that chloride abstraction and hydride addition take place at an earlier stage of the reaction; *i.e.* they involve intermediates that contain less than two chelating diphosphine ligands.

Note Added in Proof. We only recently became aware of previous work by M. C. Puerta and others describing the synthesis and reactivity of $[RuH(dippe)]^+[BPh_4]^-$ (dippe = bis(diisopropylphosphino)ethane),[38] an analogue to the complexes **2a**,**b** discussed here. Not only did they establish the high reactivity of this cation toward various nucleophiles but they also found, in complete agreement with our results, that the NMR data reported in ref 12 for the $[RuH(dcpe)_2]^+$ cation are erroneous and originate instead from the dioxygen adduct $[RuH(\eta^2\text{-}O_2)(dcpe)_2]^+$. This species is formed upon exposing $[RuH(dcpe)_2]^+$ to air and was fully characterized. Moreover, the dioxygen complex is substitutionally inert, which accounts for the failure of the authors of ref 12 to observe any reactivity of their samples of **2b** toward CO and CH_3CN.

Acknowledgment. We are indebted to the Fonds der Chemischen Industrie, Frankfurt am Main, Germany, and to Prof. W. Kaim for support of this work.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1** and **2a** are available on the Internet only. Access information is given on any current masthead page.

IC970583M

---

[38] Jiménez-Tenorio, J.; Puerta, M. C.; Valerga, P. *Inorg. Chem.* **1994**, *33*, 3515.