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Synthesis and Characterization of Ruthenium Hydride Complexes Containing the Bulky Diphosphine 1,2-Bis(diisopropylphosphino)ethane (dippe). Crystal Structure of $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$

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The bulky diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe) reacts with $[RuCl_2(PPh_3)_3]$ to yield $[RuCl_2(dippe)_2]$ (**1**), from which the complex *cis*-$[RuH_2(dippe)_2]$ (**2**) can be prepared by reaction with $Na[BH_4]$. The hydrido–chloride complex $[RuHCl(dippe)_2]$ (**3**) is obtained by displacement of triphenylphosphine ligands in $[RuHCl(PPh_3)_3]$ by dippe. Complex **3** dissociates one chloride ligand in methanolic or ethanolic solutions generating the 16-electron, five-coordinate species $[RuH(dippe)_2]^+$, which can be isolated as the tetraphenylborate salt (**4**). This compound does not react with dinitrogen or ethylene, but it reacts with CO, $CNBu^t$, or nitriles yielding the corresponding 18-electron *trans*-octahedral derivatives $[RuH(L)(dippe)_2][BPh_4]$ (L = CO (**5**), $CNBu^t$ (**6**), PhCN (**7**), or MeCN (**8**)). **2** also reacts with dihydrogen yielding $[RuH(H_2)(dippe)_2][BPh_4]$ (**9**), which is only stable under a dihydrogen atmosphere. Both **2** and **9** react with dioxygen to form the hydridodioxygen complex $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$ (**10**), which is a rare example of dioxygen coordination at a dihydrogen-binding site. The crystal structure of **10** has been determined. Crystal data: Monoclinic system, space group $P2_1/n$, $a = 16.698(2)$ Å, $b = 15.498(2)$ Å, $c = 20.635(4)$ Å, $\beta = 103.40(1)°$, and $Z = 4$. It represents the first structural report of a hydrido–dioxygen complex. Behavior analogies of ruthenium–dippe and ruthenium–dcpe (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) complexes are also discussed.

Introduction

We have recently started a research program dealing with the effects of bulky ligands in the binding and activation of small molecules by transition metal complexes. Tertiary phosphines, either mono-, bi-, or polydentate are a common class of co-ligands in adducts of small molecules such as dinitrogen,[1] CO_2,[2] dihydrogen,[3] etc., with transition metals. For this reason we have chosen the bulky, strongly electron-releasing diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe), which is known to stabilize coordinatively unsaturated species, such as the 14-electron dialkyls $[FeR_2(dippe)_2]$ (R = CH_2SiMe_3, CH_2Ph, CH_2CMe_2Ph, or CH_2CMe_3).[4] We eventually became interested in the chemistry of hydrides of the type $[MH_2(diphos)_2]$ (M = Fe or Ru; diphos = a bidentate phosphine ligand), which are suitable starting materials for the preparation of dihydrogen, dinitrogen, and other complexes. Attempts to obtain $[FeH_2(dippe)_2]$ have been unsuccessful, this being possibly due to the fact that the bulk of dippe prevents iron to form an octahedral species containing two of these ligands attached to the same metal center. For this reason we concentrated our attention in ruthenium hoping that, because of its larger size, it could accomodate two dippe ligands and in this way provide adequate starting materials. Here we describe the synthesis and characterisation of halide and hydride complexes of ruthenium with dippe, including hydrido(dihydrogen) and hydrido(dioxygen) derivatives. Some of this work has already been published as a prelimminary communication.[5]

Experimental Section

Procedures. All synthetic operations were performed under a dinitrogen atmosphere, following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane,[6] $[RuCl_2(PPh_3)_3]$,[7] and $[RuHCl(dcpe)_2]$[8] were prepared according to the literature. $[RuHCl(PPh_3)_3]$ was obtained following a modified procedure, and experimental details are given. 1,2-Bis(dicyclohexylphosphino)ethane was supplied by Strem. IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer, in Nujol mulls. NMR were taken on Varian Unity 400-MHz, Varian Gemini 200-MHz, or Bruker 300-MHz instruments, with chemical shifts given in ppm from $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalyses were by Dr. Manuel Arjonilla, at the CSIC-Instituto de Ciencias Marinas de Andalucía, or by Butterworth Laboratories Ltd., Middlessex, U.K.

Chlorohydridotris(triphenylphosphine)ruthenium(II). $[RuCl_2(PPh_3)_3]$ (2 g, *ca.* 2 mmol) in toluene (25 mL) was treated with the equimolar amount of $Li[HBEt_3]$ (2 mL of a 1 M solution in THF, 2 mmol). A red-purple color developed immediately. The mixture was stirred at room temperature for half an hour. Then it was concentrated, and ethanol (30–50 mL) was added, producing the precipitation of red-purple crystals. The mixture was cooled to −20 °C, and the crystals were filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. Yield: Almost quantitative. The purity was checked by NMR, being always pure enough for synthetic purposes.

Bis[bis(diisopropylphosphino)ethane]dichlororuthenium(II) (1). $[RuCl_2(PPh_3)_3]$ (1 g, *ca.* 1 mmol) was dissolved in toluene (20 mL), and dippe (0.6 mL, 2 mmol) was added. The mixture was stirred for 1 h at room temperature. A yellow precipitate was formed during this time. The solid was filtered, washed with petroleum ether, and dried *in vacuo*. It was recrystallized from dichloromethane-/ethanol. Yield: 0.59 g, 84%. Anal. Calcd for $C_{28}H_{64}Cl_2P_4Ru$: C, 48.3; H, 9.19; P, 17.8; Cl, 10.2. Found: C, 48.6; H, 9.10; P, 17.4; Cl, 10.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 44.3 (s, br).

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(1) Hills, A.; Hughes, D. L.; Jiménez Tenorio, M.; Leigh, G. J. *J. Organomet. Chem.* **1990**, *391*, C41.

(2) Alvarez, R.; Carmona, E.; Poveda, M. L.; Sánchez-Delgado, R. *J. Am. Chem. Soc.* **1984**, *106*, 2731; Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* **1977**, 708.

(3) Michos, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4545. Bianchini, C.; Pérez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.

(4) Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763.

(5) Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1993**, *115*, 9794.

(6) Burt, T. A.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

(7) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(8) Mezzetti, A.; Del Zotto, A.; Rigo, P.; Pahor, N. B. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

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***cis*-Bis[bis(diisopropylphosphino)ethane]dihydridoruthenium (II) (2).** To a slurry of 1 (0.4 g, ca.0.6 mmol) in THF (20 mL) was added a solution of Na[BH_4] (0.1 g, 2.6 mmol) in 10 mL of ethanol. The slurry mixture was gently heated with the help of a hairdryer for 5 min and then stirred at room temperature for another hour. The resulting mixture was filtered through Celite or centrifuged. The pale yellow solution was concentrated, ethanol (15 mL) added, and the mixture cooled to -20 °C. White crystals were obtained, which were recrystallized from petroleum ether. Yield: 0.21 g, 56%. Anal. Calcd for $C_{28}H_{66}P_4Ru$: C, 53.5; H, 10.5. Found: C, 52.9; H, 10.2. IR: ν(RuH) 1940, 1913, 1896 cm^{-1}. NMR (C_6D_6, 298 K): ^1H δ -12.83 (multiplet, XX′ part of an AA′MM′XX′ spin system, $^2J_{HA} = 66.5$ Hz, $^2J_{HA'} \approx {}^2J_{HM} = {}^2J_{HM'} = 25.3$ Hz, RuH_2); $^{31}P\{^1H\}$ δ 96.5 (triplet), 70.4 (triplet) ($^2J_{AM} = 13.2$ Hz).

***trans*-Bis[bis(diisopropylphosphino)ethane]chlorohydridoruthenium(II) (3).** [$RuHCl(PPh_3)_3$] (0.92 g, 1 mmol) in toluene (20 mL) was treated with dippe (0.6 mL, 2 mmol), and the mixture was heated under reflux for 15 min. During this time, a color change from red-purple to pale yellow-green was observed. The resulting solution was concentrated, and the product was precipitated by addition of petroleum ether. The white crystalline solid was filtered, washed with petroleum ether, and dried in vacuo. The pure product was obtained by recrystallization from petroleum/dichloromethane. Yield: 0.5 g, 76%. Anal. Calcd for $C_{28}H_{65}ClP_4Ru$: C, 50.7; H, 9.82. Found: C, 50.5; H, 9.90. IR: ν(RuH) 2016 cm^{-1}. NMR (C_6D_6, 298 K): ^1H δ -21.61 (quintet, $^2J_{HP} = 19.3$ Hz, RuH); $^{31}P\{1H\}$ δ 71.82 (s).

Bis[bis(diisopropylphosphino)ethane]hydridoruthenium(II) Tetraphenylborate (4). Complex 3 (0.66 g, 1 mmol) was dissolved in MeOH, yielding an orange solution, to which solid Na[BPh_4] (0.4 g, 1.17 mmol, slight excess) was added. This resulted in the immediate formation of an orange crystalline precipitate which was filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. The product was recrystallized from a dioxygen-free acetone/ethanol mixture. Yield: 0.81 g, 86. Anal. Calcd for $C_{52}H_{85}BP_4Ru$: C, 66.0; H, 8.99. Found: C, 66.1; H, 9.12. IR: ν(RuH) 2188 cm^{-1}; NMR (acetone-d_6, 298 K): ^1H δ -32.01 (quintet, $^2J_{HP} = 19.2$ Hz, RuH); $^{31}P\{^1H\}$ 78.90 (s); no changes were observed at 228 K, apart from broadening of the signal on the $^{31}P\{^1H\}$ spectrum.

Bis[bis(diisopropylphosphino)ethane]carbonylhydridoruthenium(II) Tetraphenylborate (5). Method A. A solution of **4** (0.7 g, 0.75 mmol) in acetone (20 mL) was stirred under 1 atm of CO. In a few seconds, the orange solution became colorless. Then, it was concentrated and ethanol added. Colorless crystals were obtained upon cooling to −20 °C, which were isolated by filtration, washed with petroleum ether and dried *in vacuo*. Yield: 0.55 g, 75%.

Method B. A solution of **3** (0.66 g, 1 mmol) in MeOH was stirred under 1 atm of CO. The resulting colorless solution was treated with solid Na[BPh_4] (0.4 g, 1.1 mmol), and a white precipitate was formed. It was filtered, washed with ethanol and petroleum, and dried *in vacuo*. The product was recrystallized from THF/EtOH. Yield: 0.79 g, 81%. Anal. Calcd for $C_{53}H_{85}BOP_4Ru$: C, 65.4; H, 8.73. Found: C, 65.6; H, 8.72. IR: ν(CO) 1972; ν(RuH) 1886 cm^{-1}. NMR ($CDCl_3$, 298 K): ^1H δ -9.01 (quintet, $^2J_{HP} = 19.8$ Hz, RuH); $^{31}P\{^1H\}$ δ 71.6 (s).

Bis[bis(diisopropylphosphino)ethane]hydrido(*tert*-butyl isocyanide)ruthenium(II) Tetraphenylborate (6). Method A. **4** (0.46 g, 0.5 mmol) in acetone was treated with $CNBu^t$ (0.07 mL, 0.5 mmol). The solution became colorless. Concentration and addition of ethanol yielded white crystals. Yield: 0.4 g, 77%.

Method B. To a solution of **3** (0.46 g, 0.7 mmol) in MeOH, $CNBu^t$ (0.1 mL, 0.7 mmol) was added. Then, solid Na[BPh_4] was added to the colorless solution, and a white precipitate was obtained. It was filtered, washed with EtOH and petroleum ether, and dried *in vacuo*. The product was recrystallized from THF/EtOH or acetone/EtOH. Yield: 0.64 g, 89%. Anal. Calcd for $C_{57}H_{94}NBP_4Ru$: C, 66.5; H, 9.14; N, 1.36. Found: C, 66.7; H, 9.20; N, 1.3. IR: ν(CN) 2090 cm^{-1}; ν(RuH) not observed. NMR ($CDCl_3$, 298 K): ^1H δ -11.28 (quintet, $^2J_{HP} = 20.0$ Hz, RuH), 1.33 (s, CNC(CH_3)$_3$); $^{31}P\{^1H\}$ δ 72.2 (s).

(Benzonitrile)bis[bis(diisopropylphosphino)ethane]hydridoruthenium(II) Tetraphenylborate (7). This product was obtained following a procedure analogous to method B for the preparation of compound **6**, using an excess of PhCN instead of $CNBu^t$. Yield: 71%. Anal. Calcd for $C_{59}H_{90}NBP_4Ru$: C, 67.6; H, 8.59; N, 1.33. Found: C, 67.5; H, 8.60; N, 1.2. IR: ν(CN) 2204; ν(RuH) 2012 cm^{-1}. NMR ($CDCl_3$, 298 K): ^1H δ -17.57 (quintet, $^2J_{HP} = 19.6$ Hz, RuH); $^{31}P\{^1H\}$ δ 67.3 s.

(Acetonitrile)bis[bis(diisopropylphosphino)ethane]hydridoruthenium(II) Tetraphenylborate (8). It was obtained following a procedure analogous to that for compound **7**, using an excess of MeCN. The product was recrystallized from acetone/EtOH in the presence of an excess of added MeCN. In this way, **8** contains two molecules of ethanol of crystallization per ruthenium complex. Yield: 68%. Anal. Calcd for $C_{54}H_{88}NBP_4Ru \cdot 2C_2H_6O$: C, 64.6; H, 9.28; N, 1.29. Found: C, 64.2; H, 9.27; N, 1.3. IR: ν(CN) 2258, ν(RuH) 2021, ν(OH) 3432 cm^{-1}. NMR (acetone-d_6, 273 K): ^1H δ -18.58 (quintet, $^2J_{HP} = 19.6$ Hz, RuH), 1.780 (s, CH_3CN); $^{31}P\{^1H\}$ δ 69.7 (s).

Table 1. Summary of Data for the Crystal Structure Analysis of [RuH(O_2)(dippe)$_2$[BPh_4]

formula: $C_{28}H_{65}O_2P_4Ru$, $C_{24}H_{20}B$	$Z = 4$
fw = 978.017	$d_{calc} = 1.25$ g cm^{-3}
cryst syst: monoclinic	F(000) = 2088
space group: $P2_1/n$ (No. 14)	λ(Cu Kα) = 1.541 78 Å
cell params at 293 K	μ(Cu Kα) = 39.5 cm^{-1}
$a = 16.698(2)$ Å	2θ interval: $5° < 2\theta < 120°$
$b = 15.498(2)$ Å	no. of unique reflcns: 4853
$c = 20.635(4)$ Å	observed reflcns ($I > 3\sigma(I)$: 3022
$\beta = 103.40(1)°$	$R^a = 0.083$
$V = 5194(3)$ Å^3	R_w ($w = \sigma_F^{-2}$)^a = 0.103

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

Bis[bis(diisopropylphosphino)ethane]dihydrogenhydridoruthenium(II) Tetraphenylborate (9). Complex **9** is formed by bubbling H_2 through acetone or chloroform solutions of **4** or methanolic solutions of **3**. It was obtained as a white solid by addition of a slight excess of solid Na[BPh_4] to a solution of **3** in MeOH under dihydrogen. This product was handled under dihydrogen, turning yellow-orange when placed under an inert atmosphere of dinitrogen or argon. It was not analyzed.

NMR (acetone-d_6, 228 K): ^1H δ -11.06 (quintet, $^2J_{HP} = 18.3$ Hz, $T_1 = 160$ ms, 300 MHz, RuH(H_2)), δ -6.28 (s, br, $T_1 = 10$ ms, 300 MHz, RuH(H_2)); $^{31}P\{^1H\}$ 82.8 (s).

Bis[bis(diisopropylphosphino)ethane](dioxygen)hydridoruthenium(II) Tetraphenylborate (or Bis[bis(diisopropylphosphino)ethane]hydridoperoxoruthenium(IV) Tetraphenylborate) (10). Complex **10** was synthesized by stirring an acetone or chloroform solution of **4** in air for 15 min. The resulting brown-green solution was concentrated, ethanol added and then cooled to −20 °C. The crystals were collected by filtration, washed with petroleum ether, and dried *in vacuo*. Yield: 83%. **10** can also be obtained by stirring a methanolic solution of **3** in air for 15 min, followed by precipitation with a slight excess of Na[BPh_4]. The resulting precipitate can be recrystallized from acetone/EtOH. Anal. Calcd for $C_{52}H_{85}BO_2P_4Ru$: C, 63.9; H, 8.70. Found: C, 63.9; H, 8.68. IR: no bands attributable to ν(RuH) or dioxygen were observed. NMR (acetone-d_6, 298 K): ^1H δ -5.91 (quintet, $^2J_{HP} = 21.4$ Hz, RuH); $^{31}P\{^1H\}$ δ 71.5 (s, br). NMR (acetone-d_6, 228 K): ^1H δ -6.16 (triplet of triplets, $^2J_{HP} = 31$ Hz, $^2J_{HP'} = 11$ Hz, RuH); $^{31}P\{^1H\}$ δ 73.9 (triplet), 61.63 (triplet) ($^2J_{PP'} = 14.6$ Hz).

Bis[bis(dicyclohexylphosphino)ethane](dioxygen)hydridoruthenium(II) Tetraphenylborate (or Bis[bis(dicyclohexylphosphino)ethane]hydridoperoxoruthenium(IV) Tetraphenylborate (11). This compound was obtained following a procedure analogous to that for complex **10**, starting from [RuH(dcpe)$_2$][BPh_4] in acetone, or [RuHCl(dcpe)$_2$] in MeOH. The product was recrystallized in the same fashion as **10**. Anal. Calcd for $C_{76}H_{117}BO_2P_4Ru$: C, 70.3; H, 9.02. Found: C, 69.9; H, 8.89. IR: no bands attributable to ν(RuH) or dioxygen were observed. NMR (acetone-d_6, 298 K): ^1H δ -5.91 (quintet, $^2J_{HP} = 21.4$ Hz, RuH); $^{31}P\{^1H\}$ δ 61.0 (s, br). NMR (acetone-d_6, 228 K): ^1H δ -5.93 (triplet of triplets, $^2J_{HP} = 31.0$ Hz, $^2J_{HP'} = 11.0$ Hz, RuH); $^{31}P\{^1H\}$ 70.3 triplet, 54.0 triplet, $^2J_{PP'} = 14.0$ Hz.

X-ray Crystal Structure Determination of 10. A summary of crystallographic data for compound **10** is given in Table 1. X-ray measurements were made on an irregularly shaped crystal of approximate dimensions 0.55 × 0.40 × 0.35 mm. The sample exhibits pleochroism, varying its color from yellow-brown to green depending on the orientation. It was mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer; Cu Kα graphite-monochromated radiation was used. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω-scan method. Lorentz and polarization corrections were applied. Decay and absorption (ψ-scan method) corrections were also applied. 3022 reflections with $I > 3\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer using the TEXSAN software system at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. The structure was solved by the Patterson method and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. The hydride atom

Table 2. Atomic Fractional Coordinates for $[RuH(O_2)(dippe)_2][BPh_4]$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru	0.32130(8)	0.19360(7)	0.02544(6)	3.51(7)
P(1)	0.2842(3)	0.3039(3)	0.0933(2)	4.0(2)
P(2)	0.2672(3)	0.1017(3)	0.0990(2)	4.2(2)
P(3)	0.3935(3)	0.2784(3)	–0.0432(2)	4.3(2)
P(4)	0.2701(3)	0.1161(3)	–0.0776(2)	4.3(2)
O(1)	0.4281(7)	0.1250(7)	0.0436(5)	5.6(6)
O(2)	0.4294(6)	0.1852(7)	0.0919(6)	5.0(6)
C(12)	0.210(1)	0.260(1)	0.1362(9)	5(1)
C(21)	0.237(1)	0.170(1)	0.1618(9)	6(1)
C(34)	0.388(1)	0.213(1)	–0.119(1)	6(1)
C(43)	0.303(1)	0.174(1)	–0.1433(8)	5(1)
C(100)	0.372(1)	0.329(1)	0.162(1)	7(1)
C(101)	0.433(1)	0.389(2)	0.140(1)	11(2)
C(102)	0.357(2)	0.351(2)	0.228(1)	11(2)
C(110)	0.236(1)	0.404(1)	0.059(1)	5(1)
C(111)	0.149(1)	0.392(1)	0.018(1)	8(1)
C(112)	0.229(2)	0.476(1)	0.113(1)	11(1)
C(200)	0.345(1)	0.032(1)	0.1526(8)	4.8(9)
C(201)	0.329(1)	0.002(1)	0.2190(9)	7(1)
C(202)	0.377(1)	–0.044(1)	0.117(1)	6(1)
C(220)	0.177(1)	0.038(1)	0.0662(8)	5(1)
C(221)	0.097(1)	0.095(1)	0.042(1)	7(1)
C(222)	0.152(1)	–0.034(1)	0.110(1)	6(1)
C(300)	0.504(1)	0.289(1)	–0.005(1)	5(1)
C(301)	0.560(1)	0.231(1)	–0.029(1)	8(1)
C(302)	0.541(1)	0.380(1)	0.001(1)	9(1)
C(330)	0.357(1)	0.386(1)	–0.0776(8)	4.7(9)
C(331)	0.264(1)	0.389(1)	–0.105(1)	7(1)
C(332)	0.398(1)	0.420(1)	–0.133(1)	8(1)
C(400)	0.160(1)	0.106(1)	–0.1108(8)	4.3(8)
C(401)	0.113(1)	0.191(1)	–0.123(1)	7(1)
C(402)	0.139(1)	0.056(1)	–0.180(1)	7(1)
C(440)	0.308(1)	0.005(1)	–0.089(1)	6(1)
C(441)	0.266(1)	–0.067(1)	–0.0582(9)	6(1)
C(442)	0.398(1)	–0.003(1)	–0.076(1)	7(1)
C(501)	0.384(1)	0.2083(9)	0.5697(8)	3.5(8)
C(502)	0.445(1)	0.228(1)	0.539(1)	6(1)
C(503)	0.440(2)	0.237(1)	0.473(1)	6(1)
C(504)	0.362(2)	0.229(1)	0.432(1)	6(1)
C(505)	0.295(1)	0.213(1)	0.457(1)	7(1)
C(506)	0.305(1)	0.202(1)	0.527(1)	6(1)
C(601)	0.472(1)	0.248(1)	0.6922(9)	3.7(9)
C(602)	0.532(1)	0.219(1)	0.744(1)	5(1)
C(603)	0.591(1)	0.268(2)	0.781(1)	7(1)
C(604)	0.594(1)	0.357(2)	0.770(1)	7(1)
C(605)	0.538(1)	0.388(1)	0.721(1)	6(1)
C(606)	0.478(1)	0.338(1)	0.681(1)	5(1)
C(701)	0.421(1)	0.084(1)	0.666(1)	4.2(9)
C(702)	0.459(1)	0.036(1)	0.623(1)	5(1)
C(703)	0.484(1)	–0.050(1)	0.638(1)	7(1)
C(704)	0.475(1)	–0.087(1)	0.697(2)	8(1)
C(705)	0.440(1)	–0.041(1)	0.739(1)	6(1)
C(706)	0.414(1)	0.043(1)	0.724(1)	6(1)
C(801)	0.313(1)	0.210(1)	0.6731(8)	3.5(8)
C(802)	0.294(1)	0.290(1)	0.6992(8)	4(1)
C(803)	0.218(2)	0.310(1)	0.7083(8)	5(1)
C(804)	0.154(1)	0.253(2)	0.694(1)	5(1)
C(805)	0.169(1)	0.174(1)	0.670(1)	6(1)
C(806)	0.245(1)	0.154(1)	0.6618(8)	5(1)
B	0.397(1)	0.189(1)	0.650(1)	4(1)
H(1)	0.2271	0.1994	0.0063	4.3

was located on a regular difference Fourier map. The other hydrogen atoms were included at idealised positions and not refined. Refinement concluded with $R = 0.083$ and $R_w = 0.103$ ($w = \sigma_F^{-2}$). Atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Results and Discussion

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[RuH(O_2)(dippe)_2][BPh_4]$

	Bond Distances		
Ru–P(1)	2.381(4)	P(2)–C(21)	1.84(2)
Ru–P(2)	2.406(5)	P(2)–C(200)	1.85(2)
Ru–P(3)	2.445(5)	P(2)–C(220)	1.80(2)
Ru–P(4)	2.419(4)	P(3)–C(34)	1.86(2)
Ru–O(1)	2.04(1)	P(3)–C(300)	1.84(2)
Ru–O(2)	2.00(1)	P(3)–C(330)	1.86(2)
Ru–H(1)	1.53	P(4)–C(43)	1.81(2)
P(1)–C(12)	1.82(2)	P(4)–C(400)	1.81(2)
P(1)–C(100)	1.83(2)	P(4)–C(440)	1.87(2)
P(1)–C(110)	1.82(2)	O(1)–O(2)	1.36(1)
	Bond Angles		
P(1)–Ru–P(2)	82.4(2)	P(1)–Ru–H(1)	73.63
P(1)–Ru–P(3)	100.7(1)	P(2)–Ru–H(1)	71.61
P(1)–Ru–P(4)	141.9(2)	P(3)–Ru–H(1)	115.71
P(1)–Ru–O(1)	127.1(3)	P(4)–Ru–H(1)	70.75
P(1)–Ru–O(2)	87.7(3)	O(1)–Ru–H(1)	151.77
P(2)–Ru–P(3)	172.6(2)	O(2)–Ru–H(1)	152.68
P(2)–Ru–P(4)	98.8(2)	Ru–O(1)–O(2)	69.0(7)
P(2)–Ru–O(1)	90.9(3)	Ru–O(2)–O(1)	71.6(7)
P(2)–Ru–O(2)	86.5(3)		
P(3)–Ru–P(4)	83.0(2)		
P(3)–Ru–O(1)	81.9(3)		
P(3)–Ru–O(2)	86.8(3)		
P(4)–Ru–O(1)	91.0(3)		
P(4)–Ru–O(2)	130.4(3)		
O(1)–Ru–O(2)	39.4(4)		

When a toluene solution of $[RuCl_2(PPh_3)_3]$ is treated with 2 equiv of dippe, a yellow precipitate is formed. Analytical data for this material indicate a composition $[RuCl_2(dippe)_2]$ (**1**). This compound is air stable in the solid state, insoluble in nonpolar solvents, but slightly soluble in tetrahydrofuran and more soluble in chlorinated solvents. The ^1H NMR spectrum of **1** consists of a series of multiplets corresponding to the different protons in the phosphine ligand, whereas the $^{31}P\{^1H\}$ NMR spectrum displays one broad singlet centered at 44.3 ppm, suggesting the equivalence of the four phosphorus atoms. This singlet remains rather broad even at 223 K. According to these data, **1** seems to have a *trans*-stereochemistry. However, a simple formulation such as *trans*-$[RuCl_2(dippe)_2]$ does not explain satisfactorily the lack of solubility of **1** in nonpolar solvents and the relative broadness of the signal on the $^{31}P\{^1H\}$ NMR spectra. A similar behavior has been previously observed for the complexes $[RuX_2(dcpe)_2]$ (X = Cl or Br),[8] and interpreted in terms of the dissociation of one of the halide ligands in solution, although the possibility of formation of oligomeric, halide-bridged species could not be discarded. A similar explanation may hold in our case.

The reaction of **1** with $Na[BH_4]$ in THF/EtOH leads to a white, crystalline, air-sensitive material identified as $[RuH_2(dippe)_2]$ (**2**). The IR spectrum of **2** displays bands at 1940, 1913, and 1896 cm^{-1}, which are attributed to ν(RuH) of the *cis* hydride ligands. This geometry is confirmed by NMR spectroscopy. The ^1H NMR spectrum of **2** displays one high-field signal for the hydridic protons with a splitting pattern that corresponds to the XX′ part of an AA′MM′XX′ spin system, as it has been observed for other *cis*-dihydride complexes.[9] The $^{31}P\{^1H\}$ NMR spectrum consists of two triplets, as expected. It is interesting to note that while **2** can be obtained using the mild $Na[BH_4]$ reagent, the preparation of other *cis*-$[RuH_2(diphos)_2]$ complexes requires the use of the much stronger reducing agent $Li[AlH_4]$.[10]

Displacement of the PPh_3 ligands in $[RuHCl(PPh_3)_3]$ by dippe affords $[RuHCl(dippe)_2]$ (**3**). This compound is a white, crystalline material, soluble in aromatic hydrocarbons and also in THF, in which solvents gives air-sensitive pale-yellow solutions. The hydride ligand gives rise to a strong ν(RuH) IR band at 2016 cm^{-1} soluble in aromatic hydrocarbons and to a ^1H NMR (C_6D_6) quintet at δ –21.61 that indicates equivalent coupling ($^2J_{HP}$ = 19.3 Hz) to the four ^{31}P nuclei. In accord with this, a singlet at δ 71.8 is observed in the $^{31}P\{^1H\}$ NMR spectrum. These data

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(9) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 75; Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991**, *30*, 3116.

(10) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 772, 896.

suggest that **3** exists in benzene as a discrete *trans*-octahedral species. However, when this compound is dissolved in ethanol or methanol, deep orange solutions are obtained. In accord with the behavior found for other metal–diphosphine complexes such as $[FeCl_2(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[11] $[CoCl_2(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane),[12] and also $[RuHCl(dcpe)_2]$,[8] the color change is attributed to the formation of the five-coordinate species $[RuH(dippe)_2]^+$. This complex cation can be precipitated as the tetraphenylborate salt (**4**), in the form of orange crystals, which display one weak ν(RuH) band at 2188 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of **4** (acetone-d_6) in the high-field region is identical to that of **3** when it is recorded in CD_3OD as solvent. It consists of one quintet centered at −32.01 ppm, with $^2J_{HP}$ = 19.2 Hz. No changes are observed when the spectrum is recorded at 228 K, apart from a slight broadening of the quintet. One singlet is the only signal present in the $^{31}P\{^1H\}$ NMR spectrum in the temperature range 228–293 K. This indicates the equivalence of all the phosphorus atoms in the studied range of temperatures, and it is consistent with a square-pyrammidal structure, with the hydride ligand in the apical position. No IR or NMR spectral evidence for "agostic" interactions has been detected, although the NMR effects of agostic binding would be diluted by being spread over the 48 possible ^{i}Pr protons in a fluxional, formally six-coordinate species, so this possiblility can not be completely ruled out. However, the fact that the deutero-derivative $[RuD(dippe)_2][BPh_4]$ does not present deuterium–hydrogen scrambling with the phosphine protons seems to be in support of a five-coordinate, 16-electron structure for compound **4**, with no chemically significant agostic interaction.

According to its coordinatively unsaturated character, complex **4** reacts with CO, CNBu^t and some others neutral donors to form the corresponding octahedral, 18-electron complexes (no reactivity is however observed towards dinitrogen, CS_2 or ethylene). Treatment of the orange acetone or THF solutions of **4** with CO, CNBu^t or NCR (R = Ph, Me) furnishes colorless or pale yellow solutions of the expected $[RuH(L)(dippe)_2][BPh_4]$ complexes (L = CO (**5**), CNBu^t (**6**), PhCN (**7**) or MeCN (**8**)). This contrasts with the behavior reported for the analogous species $[RuH(dcpe)_2]^+$, which has been found to be unreactive toward CO or acetonitrile[8] (see below). Compounds **5**–**8** usually display one weak IR band attributed to ν(RuH) (see Experimental Section) as well as the characteristic absorption of the L ligand. The $^{31}P\{^1H\}$ NMR spectra of complexes **5**–**7** consist of one singlet in all cases, suggesting a *trans*-stereochemistry, while in the ^1H NMR spectra a high-field quintet due to the hydride is observed. Compounds **6** and **7** show in addition signals due to the coordinated CNBu^t or PhCN respectively. However, complex **8** exhibits a somewhat different behavior. This material is a white, crystalline solid, which dissolves in acetone-d_6, yielding orange solutions that display two broad resonances in the hydride region, one centered at −32.05 ppm, the other at −18.60 ppm. These signals resolve into quintets if the temperature is lowered. The resonance at −32.05 ppm can be assigned to the hydridic proton of $[RuH(dippe)_2]^+$, whereas that at δ −18.6 may be attributed to the hydride proton in *trans*-$[RuH(MeCN)(dippe)_2]^+$. Similar observations can be made in the $^{31}P\{^1H\}$ NMR spectrum, which exhibits two broad resonances centered at 79.0 and 69.7 ppm, assigned to $[RuH(dippe)_2]^+$ and $[RuH(MeCN)(dippe)_2]^+$, respectively. These observations point out to the existence of an equilibrium in solution of the type depicted in eq 1. The dissociation of MeCN is rapid on the NMR time scale, but it can be "frozen" by lowering the temperature. The equilibrium can

$$[RuH(MeCN)(dippe)_2]^+ \rightleftarrows [RuH(dippe)_2]^+ + MeCN \qquad (1)$$

be shifted to the left by addition of MeCN and in fact, when the spectrum is recorded in CD_3CN, only signals due *trans*-$[RuH(MeCN)(dippe)_2]^+$ are observed. The equilibrium constant K for this process in acetone-d_6 at 298 K has been estimated to be 3×10^{-2} mol dm^{-3} by integration of the NMR hydride signals due to the monohydride and the hydridoacetonitrile complex in the equilibrium mixture. A similar behavior has been reported for the alkynyl–dihydrogen derivatives $[Ru(H_2)(C{\equiv}CR)(dippe)_2][BPh_4]$ (R = Ph or COOMe), which exist in solution as equilibrium mixtures with the monohydride **4** and the free alkyne.[14]

The addition of H_2 to coordinatively unsaturated metal centers is a common method for the preparation of dihydrogen complexes.[15,16] Accordingly, **4** reacts with H_2 in acetone or chloroform to yield the labile dihydrogen complex $[RuH(H_2)(dippe)_2][BPh_4]$ (**9**). This compound is also obtained by bubbling H_2 through ethanolic or methanolic solutions of **3**, followed by addition of $Na[BPh_4]$. **9** is a white solid, stable only under a dihydrogen atmosphere. The white solid, or its pale yellow acetone or chloroform solutions, becomes orange when the dihydrogen atmosphere is replaced by dinitrogen or argon. This process is accelerated by pumping *in vacuo*. The orange material has been identified as **4**, by NMR spectroscopy. Due to its lability it has not proved possible to obtain good microanalytical data for **9** but the complex has been fully characterized by NMR studies, including T_1 (longitudinal relaxation time) and $^1J_{HD}$ measurements. The ^1H NMR spectrum of **9** (acetone-d_6) at room temperature in the hydride region is almost featureless, since it consists of very broad resonances which eventually merge into the base line. As the temperature is lowered, a broad signal centered at −6.28 (Ru-H_2) and a quintet at −11.60 (Ru-H) arise. T_1 measurements yielded a minimum value of 10 and 160 ms for the dihydrogen and hydride ligands respectively (228 K, 300 MHz, acetone-d_6). The first is characteristic of a "nonclassical" hydride, as it is the $^1J_{HD}$ coupling of 30 Hz found in the isotopomer $[RuD(HD)(dippe)_2]^+$ (prepared by reaction of **4** with D_2).[17,18] The temperature dependence of the ^1H NMR spectrum can be interpreted in terms of an intramolecular exchange of hydride and hydrogen atoms in the dihydrogen ligand, as has been observed for the parent complex $[RuH(H_2)(dcpe)_2]^+$.[15] In contrast with this, the complexes $[RuH(H_2)(diphos)_2]^+$ (diphos = dppe or depe) are rigid at room temperature.[19] Hence, our results are consistent with the observation by Rigo *et al.* that the bulkiness of the substituents at phosphorus and the chelate ring size affect the dynamic behavior of these species with respect to the fast hydride–dihydrogen exchange.[15] A *trans*-stereochemistry is assigned to complex **9**, similar to that found for other $[MH(H_2)(diphos)_2]^+$ (M = Fe or Ru) complexes,[19] this being supported by the presence of only one signal in the $^{31}P\{^1H\}$ NMR spectrum.

During our investigations of compounds **4** and **9** we eventually detected ^1H NMR resonances due to another hydridic species. Thus, a small quintet at δ −5.91 was sometimes observed, together with signals due to **4** or **9**. Formulation of this species as a dinitrogen derivative, e.g. *trans*-$[RuH(N_2)(dippe)_2]^+$, can be ruled out by the lack of IR and microanalytical evidence. We soon

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(11) Hughes, D. L.; Jiménez Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 75.

(12) Basallote, M. G.; Hughes, D. L.; Jiménez Tenorio, M.; Leigh, G. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1993**, 1841.

(13) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, O.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563.

(14) Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1750.

(15) Mezzetti, A.; Del Zotto, A.; Rigo, A.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

(16) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 5581; Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(17) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(18) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124; **1988**, *110*, 4126.

(19) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.

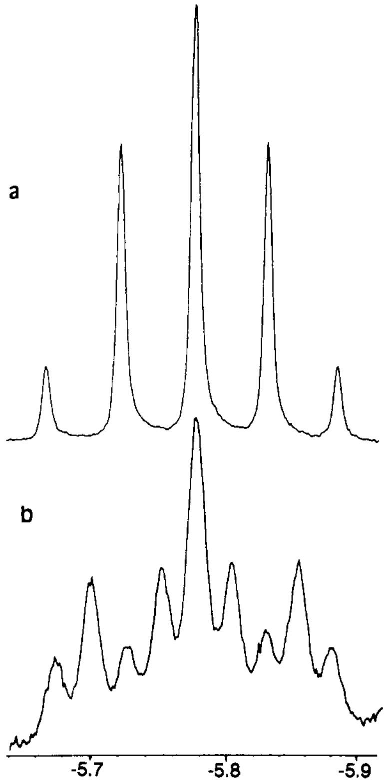

Figure 1. ^1H NMR spectra of $[RuH(O_2)(dippe)_2][BPh_4]$ (acetone-d_6) in the hydride region: (a) 293 K; (b) 228 K.

discovered that the exposure to air of acetone or chloroform solutions of **4** or methanolic solutions of **3** leads to the disappearance of the hydride resonance due to $[RuH(dippe)_2]^+$ and the rising of one unique quintet at -5.91 ppm. This transformation is quantitative and allows the isolation of complex **10**, for which a single-crystal X-ray study shows the unexpected, albeit remarkable, formulation $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$ (**10**). This compound is also obtained by reaction of the dihydrogen complex **9** with air. Systems in which dioxygen is added to a dihydrogen-binding site are rare, the only previously known example being $[OsHCl(CO)(P^iPr_3)_2]$, which reacts with both H_2 and O_2 to yield the corresponding adducts $[OsHCl(H_2)(CO)(P^iPr_3)_2]$ and $[OsHCl(O_2)(CO)(P^iPr_3)_2]$.[13] No structural data were however available for complexes containing both hydride and dioxygen ligands. The IR spectrum of **10** does not show any ν(RuH) band, and absorptions due to the dioxygen ligands are not distinguishable due to overlapping with dippe and tetraphenylborate bands. The ^1H NMR spectrum of **10** at 298 K consists of one quintet, as it has already been mentioned. As the temperature is lowered the splitting pattern changes from a quintet to a triplet of triplets (Figure 1), suggesting fluxional behavior. The dynamic process responsible for this could be the propeller-like spinning of the dioxygen ligand, similar to that found in dihydrogen complexes. This can be "frozen" by cooling the sample, and results in the nonequivalence of the phosphorus atoms in accordance with the solid-state structure for **10** (Figure 2) which shows two sets of nonequivalent phosphorus atoms. In agreement with this dynamic behavior, the $^{31}P\{^1H\}$ NMR spectrum of **10** is also temperature dependent and consists of one broad singlet at 298 K which splits in two triplets at 228 K, as expected for an A_2X_2 spin system. Everything seems to indicate that the dioxygen binding is irreversible. Thus, **10** is air-stable, and it is also stable under an inert atmosphere of argon or dinitrogen, both in the solid state and in solution. It does not lose dioxygen under vacuum in the solid state, and the dioxygen ligand is not displaced by neutral ligands such as MeCN, CO, or H_2 in solution at room temperature.

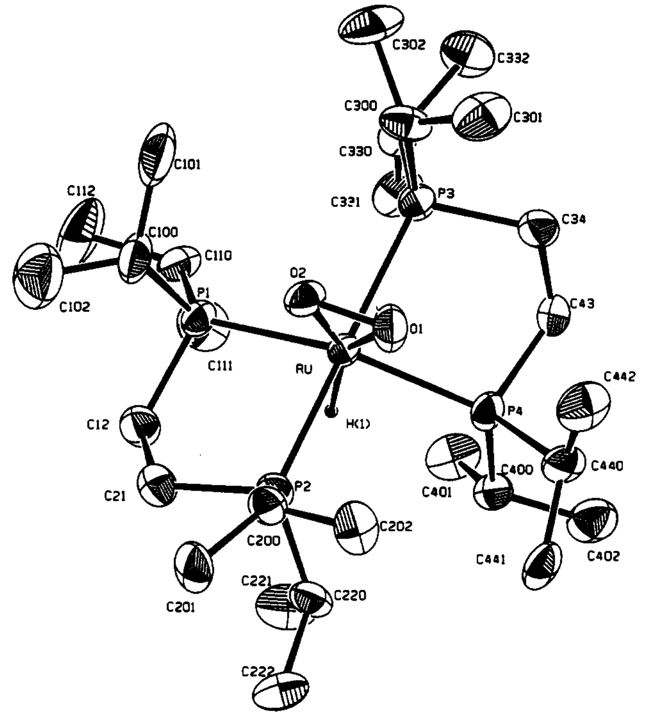

Figure 2. Molecular structure of the cation $[RuH(O_2)(dippe)_2]^+$. Hydrogen atoms, except hydride, are omitted.

The posibility of using **10** as reagent for oxygen-transfer reactions is in any case being investigated.

The spectroscopic data obtained for complex **10** cast some doubts on those reported for $[RuH(dcpe)_2]^+$, which may instead correspond to an analogous dioxygen species, namely $[RuH(O_2)(dcpe)_2]^+$. The described quintet at δ -5.8 ppm seems in fact more in agreement with a six-coordinate, 18-electron structure than with a coordinatively unsaturated formulation, in which the hydride signal should appear at much higher field.[8,13] This quintet becomes an overlapping triplet of triplets at 213 K. These observations and temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum match exactly the spectral properties of **10** and are therefore in support of the above proposal.

In order to clarify this situation, the complex $[RuHCl(dcpe)_2]$ was prepared following the literature procedure[8] and its ^1H NMR recorded both with careful exclusion of oxygen and after exposure to air. In the first instance a quintet at δ -32.2 ppm, ($^2J_{HP} = 19.3$ Hz), attributable to $[RuH(dcpe)_2]^+$ was detected (Figure 3) whereas in the presence of air only a new quintet at δ -5.85 ppm, ($^2J_{HP} = 21.3$ Hz), coincident with the reported data,[8] could be observed. Subsequently, the dcpe–O_2 complex was isolated as the tetraphenylborate salt, $[RuH(O_2)(dcpe)_2][BPh_4]$ (**11**). It is therefore clear that both $[RuH(dippe)_2]^+$ and $[RuH(dcpe)_2]^+$ have a similar affinity for O_2. However, as far as we are aware, there is no precedent for dioxygen coordination at other ruthenium–dihydrogen binding sites such as $\{[RuH(dppe)_2]^+\}$ or $\{[RuH(depe)_2]^+\}$,[17] although there are recent examples of dioxygen coordination at ruthenium sites capable of homolytic dihydrogen splitting, such as $[Ru(\eta^5\text{-}C_5Me_5)(O_2)(dppe)][PF_6]$[20] and $[Ru(\eta^5\text{-}C_5Me_5)(O_2)(dippe)][BPh_4]$.[21]

From the results of this study it can be concluded that (1) the formation of dioxygen adducts is a possibility to be seriously considered when working with coordinatively unsaturated hydride species and (2) the steric bulkiness of the auxiliary ligand plays an important role in the stabilization of O_2 coordination at transition metal centers capable of dihydrogen binding.

X-Ray Crystal Structure of 10. The crystal structure of compound **10** was determined by single-crystal X-ray structure analysis. All atoms are located at general positions. The molecular structure of the complex cation $[RuH(O_2)(dippe)_2]^+$

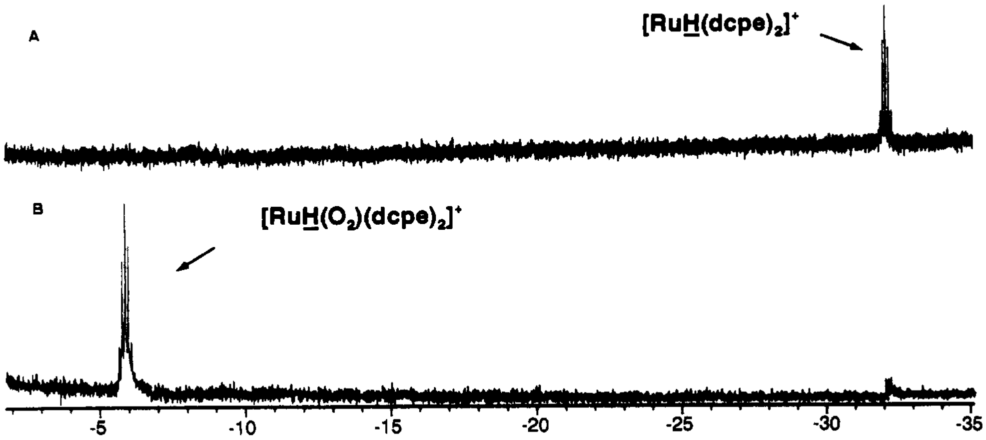

Figure 3. ^{1}H NMR spectra of [RuHCl(dcpe)$_2$] in CD_3OD at 293 K: (a) under dinitrogen; (b) upon exposure to air.

is shown in Figure 2. The coordination is distorted octahedral around the ruthenium atom, with the dioxygen bound in the side-on manner, having an O–O separation of 1.360(10) Å. As expected this distance is longer than in the free dioxygen molecule (1.2074 Å),[22] but it is slightly shorter than that in other η^2-O_2 complexes such as [Ir(O$_2$)(dppm)$_2$][PF$_6$] (dppm = 1,2-bis(diphenylphosphino)methane; *d*(O–O) = 1.453(2) Å),[23] [Rh(O$_2$)(dppe)$_2$][PF$_6$] (*d*(O–O) = 1.418(11) Å),[24] and also [Ru(η^5-C$_5$Me$_5$)(O$_2$)(dppe)][PF$_6$] (*d*(O–O) = 1.398(5) Å).[20] The hydride ligand appears *trans* to the dioxygen, with a Ru–H distance of 1.53 Å (the hydride was located on a regular difference Fourier map, selecting the only peak with reasonable bond distance and angle values, but it was not refined). The phosphorus atoms are located in the distorted equatorial plane, with two mutually *trans*-phosphorus atoms displaced away from the dioxygen and toward the hydride, possibly to minimize repulsions with the dioxygen ligand.

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Supplementary Material Available: Tables of X-ray crystallographic data, including atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters (25 pages). Ordering information is given on any current masthead page.

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(20) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1993**, 892.

(21) Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. Unpublished work.

(22) Abrahams, J. C. *Q. Rev. Chem. Soc.* **1956**, *10*, 407.

(23) Nolte, M. J.; Singleton, E.; Laing, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1979.

(24) McGinnety, J. A.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301.