Synthesis and Reactivity of Ru(II)/Chloro/Hydrido/Carbonyls with Cis Bulky Phosphines: An Unsaturated Ru(II) Monohydride

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Received February 19, 1999

$[RuCl_2(CO)_2(d^tbpe)]$, $d^tbpe = {}^tBu_2PCH_2CH_2P^tBu_2$ is synthesized as a mixture of two isomers and is converted to $[RuHCl(CO)_2(d^tbpe)]$, then $[Ru(H)_2(CO)_2(d^tbpe)]$. The chloride trans to hydride in $[RuHCl(CO)_2(d^tbpe)]$ can be replaced by BF_4^- or PF_6^-, and reaction with $NaB(3,5\text{-}(CF_3)_2C_6H_3)_4$ gives authentic, five-coordinate $[RuH(CO)_2(d^tbpe)]^+$, characterized structurally by X-ray diffraction, which reveals the lack of agostic interactions. $[Ru(H)_2(CO)_2(d^tbpe)]$ reacts under mild conditions with CO to give $[Ru(CO)_3(d^tbpe)]$, with ethylene to give C_2H_6 and $[Ru(C_2H_4)(CO)_2(d^tbpe)]$, and with D_2 to give some $[Ru(H)(D)(CO)_2(d^tbpe)]$. These results are interpreted in terms of relatively facile dissociation of one end of d^tbpe from the metal.

Introduction

The chemistry of Ru(II) complexes $[RuX_2(CO)_n(P)_2]$ (X = H, Cl; n = 1,2) with P donors in trans position is well-known and widely explored.[1] In particular, complexes bearing bulky phosphines such as P^tBu_2Me or P^iPr_3 are currently receiving considerable interest because of their ability to form coordinatively unsaturated complexes with unique properties.[2−5] Surprisingly, the chemistry of the analogous cis phosphine complexes is barely explored and the number of known compounds is very small.[6−9] Therefore, we investigated the properties and reactivity of $[RuX_2(CO)_n(PP)]$ (X = H, Cl; n = 1,2) with P donors occupying cis positions. To enforce the cis position of the P atoms and to stabilize potential coordinatively unsaturated complexes, we choose the bulky chelate ligand d^tbpe ($^tBu_2PC_2H_4P^tBu_2$).[10]

Experimental Section

General. All manipulations were carried out with standard Schlenk and glovebox techniques under purified argon. Benzene, toluene, Et_2O, and pentane were dried over sodium benzophenone ketyl, distilled, and stored in gastight solvent bulbs. Dichloromethane was dried over CaH_2, distilled, and stored in a gastight solvent bulb. Ethanol and methanol were degassed and used without further purification. Benzene-d_6, toluene-d_8, dichloromethane-d_2, and acetone-d_6 were dried by appropriate methods and vacuum-distilled prior to use. $AgBF_4$, $AgPF_6$, and $LiBEt_3H$ (1 molar in THF) were purchased from Aldrich and used without further purification. CO was purchased from Air Products and D_2 from Cambridge Isotopes, and both were used as received. $[RuCl_2(CO)_2]_2$,[8] $Na[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ ($NaBAr^F{}_4$),[11] and d^tbpe (1,2-bis(di-*tert*-butyl-phosphino)ethane)[12] were synthesized as reported. ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer (^1H, 300 MHz; ^{31}P, 122 MHz; ^{19}F, 282 MHz; ^{13}C, 75 MHz) or on a Varian INOVA 400 spectrometer (^1H, 400 MHz; ^{31}P, 161 MHz; ^{19}F, 376 MHz; ^{13}C, 100 MHz). ^1H NMR chemical shifts are reported in ppm downfield of tetramethylsilane with use of residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. ^{19}F NMR chemical shifts are externally referenced to CF_3COOH/C_6D_6. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer at Indiana University. The mass spectrum used a Kratos MS80 spectrometer.

$[Ru(Cl)_2(CO)_2(d^tbpe)]$ (1). A yellow suspension of $[Ru(Cl)_2(CO)_2]_2$ (300 mg, 0.66 mmol) and d^tbpe (419 mg, 1.32 mmol) in EtOH (30 mL) was heated under reflux while a gentle stream of CO gas was bubbled through the suspension. After 15 min a clear yellow solution formed, which was cooled to room temperature and reduced in volume to ca. 5 mL. Adding Et_2O (30 mL) gave a yellow precipitate which was separated, washed with Et_2O (20 mL), and dried in vacuo. Yield: 413 mg (58%). Anal. Calcd for $C_{20}H_{40}Cl_2O_2P_2Ru$: C, 43.96; H, 7.38. Found: C, 43.83; H, 7.75. IR (CH_2Cl_2, cm^{-1}): 2066, 2014, 1983 (νCO). ^1H NMR (CD_2Cl_2): δ 1.38 (d, 9 H, C**H**$_3$, J(HP) = 13 Hz), 1.43 (d, 36 H, C**H**$_3$, J(HP) = 13 Hz), 1.48 (d, 9 H, C**H**$_3$, J(HP) = 13 Hz), 1.49 (d, 9 H, C**H**$_3$, J(HP) = 13 Hz), 1.51 (d, 9 H, C**H**$_3$, J(HP) = 13 Hz); signals for 4 CH_2 protons are overlapped by ^{t}Bu signals, 1.72 (m, 2 H, C**H**$_2$), 2.15 (m, 2 H, C**H**$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.08 (m, P**C**), 24.13 (m, P**C**), 30.61−31.40 (m, **C**H$_3$), 38.32−41.73 (m, **C**H$_2$), 190.52 (dd, **C**O, $J(CP_{trans})$ = 111 Hz, $J(CP_{cis})$ = 10 Hz), 198.67 (t, **C**O, J(CP) = 11 Hz), 200.99 (t, **C**O, J(CP) = 10 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 103.29 (d, J(PP) = 10 Hz), 100.76 (s), 72.09 (d, J(PP) = 10 Hz).

$[Ru(Cl)_2(CO)(d^tbpe)]_2$ (2). A yellow suspension of $[Ru(Cl)_2(CO)_2]_2$ (72 mg, 0.16 mmol) and d^tbpe (100 mg, 0.31 mmol) in EtOH (15 mL) was heated under reflux for 1 h. The resulting yellow solution was

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10.1021/ic9902020 CCC: $18.00
Published on Web 10/13/1999

cooled to room temperature and all volatiles were removed in a vacuum. The remaining yellow residue was extracted with Et_2O (20 mL) and dried in vacuo. Yield: 100 mg (61%). Anal. Calcd for $C_{38}H_{80}Cl_4O_2P_4Ru_2$: C, 44.02; H, 7.78. Found: C, 43.40; H, 7.94. IR (EtOH, cm^{-1}): 1975 (νCO). ^1H NMR (CD_2Cl_2): δ 1.20−2.10 (m/br, C**H**$_2$, C**H**$_3$); all proton signals are broad and only poorly resolved, so a more accurate assignment is not possible. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 99.15 (s; rel int., 1), 98.75 (s; rel int., 2); FAB−MS (NBA): m/z = 1003 [[Ru(Cl)$_2$(CO)(d^{t}bpe)]$_2$ − Cl]$^+$ (100%).

[Ru(Cl)$_2$(CO)(CH$_3$CN)(d^{t}bpe)] (3). CH_3CN (0.5 mL) was added to a yellow solution of **2** (40 mg, 0.039 mmol) in CH_2Cl_2 (8 mL), and the mixture was stirred at room temperature. After 12 h, all volatiles were removed in a stream of nitrogen and the remaining yellow residue was dried in vacuo. Yield: 39 mg (90%). IR (CH_2Cl_2, cm^{-1}): 1954 (νCO). ^1H NMR (CD_2Cl_2): δ 1.41 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz), 1.44 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz), 1.85 (br, 4 H, C**H**$_2$), 2.08 (s, 3 H, C**H**$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 94.69 (s).

[RuHCl(CO)$_2$(d^{t}bpe)] (4). A yellow suspension of [Ru(Cl)$_2$(CO)$_2$]$_2$ (300 mg, 0.66 mmol) and d^{t}bpe (419 mg, 1.32 mmol) in EtOH (30 mL) was heated under reflux while a gentle stream of CO gas was bubbled through the suspension until a clear solution formed (ca. 15 min). The treatment with CO gas was stopped and a solution of NaOEt (90 mg, 1.32 mmol) in EtOH (10 mL) was added to the hot solution via cannula. The mixture was heated under reflux for another 45 min, resulting in an orange solution and some white precipitate. All volatiles were removed in a vacuum and the orange residue dissolved in CH_2Cl_2 (15 mL). The cloudy solution was filtered through a plug of Celite (2 cm) and the filtrate was evaporated in vacuo. The remaining orange residue was washed with Et_2O (20 mL), suspended in hot MeOH (5 mL), and cooled to −40 °C. After 24 h, a colorless precipitate was separated and dried in vacuo. Yield: 430 mg (64%). Anal. Calcd for $C_{20}H_{41}ClO_2P_2Ru$: C, 46.92; H, 8.07. Found: C, 46.94; H, 8.10. IR (C_6H_6, cm^{-1}): 2033, 1973 (νCO). ^1H NMR (CD_2Cl_2): δ −15.66 (t, 1 H, Ru**H**, J(HP) = 23.1 Hz), 1.30 (d, 18 H, C**H**$_3$, J(HP) = 12 Hz), 1.41 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz), 1.90 (br, 2 H, C**H**$_2$), 2.10 (m, 2 H, C**H**$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.48 (t, P**C**, J(CP) = 16 Hz), 30.26 (s, **C**H$_3$), 30.80 (s, **C**H$_3$), 36.70 (m, P**C**H$_2$), 39.24 (m, P**C**H$_2$), 199.19 (dd, **C**O, J(CP$_{trans}$) = 86 Hz, J(CP$_{cis}$) = 18 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 96.74 (s).

[RuH(FBF$_3$)(CO)$_2$(d^{t}bpe)] (5). A gray suspension of [RuHCl(CO)$_2$(d^{t}bpe)] (**4**) (80 mg, 0.16 mmol) and $AgBF_4$ (30 mg, 0.16 mmol) in toluene (10 mL) was stirred for 2 h at 60 °C, yielding a bright yellow solution and a brown precipitate. The solution was filtered while hot, and the filtrate was reduced in volume to ca. 3 mL and cooled to −40 °C. A colorless precipitate formed, which was separated and dried in vacuo. Yield: 36 mg (41%). Anal. Calcd for $C_{20}H_{41}BF_4O_2P_2Ru$: C, 42.64; H, 7.33. Found: C, 41.36; H, 7.15. IR (C_6H_6, cm^{-1}): 2054, 1997 (νCO). ^1H NMR (C_6D_6): δ −21.79 (t, 1 H, Ru**H**, J(HP) = 21 Hz); 0.87 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz); 1.15 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz); 1.28 (m, 2 H, C**H**$_2$); 1.57 (m, 2 H, C**H**$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 99.03 (s). ^{19}F NMR (CD_2Cl_2): δ −172.54 (s).

[RuH(CO)$_2$(d^{t}bpe)]X (X = BAr$^F_4$ (6a), PF$_6$ (6b)). [RuH(CO)^2(d^{t}bpe)]BAr $^F_4$ (6a). A gray suspension of [RuHCl(CO)$_2$(d^{t}bpe)] (**4**) (50 mg, 0.098 mmol) and $AgBF_4$ (19 mg, 0.098 mmol) in toluene (10 mL) was stirred for 1 h at 60 °C, yielding a bright yellow solution and some brown precipitate. The solution was filtered while hot and the filtrate evaporated to dryness. The colorless residue was dissolved in Et_2O (10 mL), and NaBAr $^F_4$ (86 mg, 0.098 mmol) was added. A yellow solution formed, which was stirred for 1 h at room temperature. The solution was filtered and the filtrate reduced in volume to ca. 2 mL. Pentane (20 mL) was added, forming yellow micro crystals. The crystals were separated, washed with pentane (10 mL), and dried in vacuo. Yield: 78 mg (60%). Anal. Calcd for $C_{52}H_{53}BF_{24}O_2P_2Ru$: C, 46.62; H, 3.99. Found: C, 45.66; H, 3.69. IR (CH_2Cl_2, cm^{-1}): 2062, 2009 (νCO). ^1H NMR (CD_2Cl_2): δ −24.39 (t, 1 H, Ru**H**, J(HP) = 17 Hz), 1.25 (d, 18 H, C**H**$_3$, J(HP) = 14 Hz), 1.31 (d, 18 H, C**H**$_3$, J(HP) = 14 Hz), 2.23 (m, 4 H, C**H**$_2$), 7.56 (m, 4 H, C**H**), 7.72 (m, 8 H, C**H**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.27 (m, P**C**), 29.98 (m, **C**H$_3$), 37.32 (m, P**C**H$_2$), 39.21 (m, P**C**H$_2$), 117.88 (m, **C**$_{aryl}$), 124.99 (q, **C**F$_3$, J(CF) = 271 Hz), 129.28 (m, **C**$_{aryl}$), 135.20 (s, **C**$_{aryl}$), 162.16 (m, **C**B), 195.35 (dd, **C**O, J(CP$_{trans}$) = 76 Hz, J(CP$_{cis}$) = 15 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 101.75 (s). ^{19}F NMR ($CDCl_3$): δ −49.45 (s, C**F**$_3$).

[RuH(CO)$_2$(d^{t}bpe)]PF$_6$ (6b). An orange suspension of [RuHCl(CO)$_2$(d^{t}bpe)] (**4**) (200 mg, 0.39 mmol) and $AgPF_6$ (98 mg, 0.39 mmol) in CH_2Cl_2 (15 mL) was stirred for 2 h at room temperature, yielding a brown suspension. The brown precipitate was filtered off and the yellow filtrate evaporated to dryness, giving a yellow solid. Yield: 155 mg (64%). IR (CH_2Cl_2, cm^{-1}): 2045, 1983 (νCO). ^1H NMR (CD_2Cl_2): δ −24.36 (br, 1 H, Ru**H**), 1.29 (d, 18 H, C**H**$_3$, J(HP) = 10 Hz), 1.32 (d, 18 H, C**H**$_3$, J(HP) = 10 Hz), 2.10 (m, 4 H, C**H**$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 98.56 (s, Ru**P**), −144.02 (sep., **P**F$_6$).

X-ray Structure Determination of [RuH(CO)$_2$(d^{t}bpe)]B(C$_6$H$_3$(CF$_3$)$_2$)]$_4$. A preliminary peak search of an almost equidimensional crystal and analysis using the programs DIRAX and TRACER revealed a primitive monoclinic lattice (Table 1). Following intensity data collection ($6° < 2\theta < 55°$), the condition $h01$ for $h + 1 = 2n$ gave the possible choice of space groups $P2/n$ or Pn. Because the possibility existed that the space group was noncentrosymmetric and the correct absolute structure would be of interest, the data collection ($-h\ k\ \tilde{n}l$, $h\ -k\ \tilde{n}l$, and some $h\ k\ \tilde{n}l$) included a set of Friedel-related reflections which were not averaged. The choice of the noncentrosymmetric space group Pn was later confirmed by the solution and refinement of the structure. The data processing gave a set of 20 251 intensities, and R_{av} = 0.024 for the averaging of 1504 non-Friedel-related intensities. Four standards measured every 300 data showed no significant trends. No absorption correction was made (μ = 4.45 cm^{-1}). The structure was solved using a combination of direct methods (SHELXS86) and Fourier techniques. The two Ru atoms, as well as large parts of the two fluorinated anions, were located in the initial best solution. The remainder of the non-hydrogen atoms were located in iterations of a least-squares refinement, followed by a difference Fourier calculation. The asymmetric unit contained two of the Ru cations of interest and two anions. A disorder at C(8) (a *tert*-butyl group) on one cation was observed and refined. The occupancies of C(8) and C(8′) refined to 52 and 48%, respectively. Some of the hydrogen atoms were located in a difference map. All hydrogen atoms (except for the hydride atoms) were included in fixed calculated positions with isotropic thermal parameters fixed at 1.0 plus the isotropic equivalent of the parent atom. In the final cycles of refinement, the non-hydrogen atoms (except for the disorder above) were refined using anisotropic thermal parameters. The final $R(F)$ was 0.066 for 1475 total variables. The final difference map was essentially featureless; the largest peak was 0.77 e/Å^3, 1.65 Å from Ru(26), and the deepest hole was −0.76 e/Å^3. The structure shown in this report is the correct absolute structure as determined by the Flack parameter using the SHELXL-93 program. The value was 0.0635, with an esd of 0.0262 (expected values are 0, within 3esd, for the correct absolute structure and +1 for the inverse).

Table 1. Crystallographic Data for RuH(CO)$_2$(d^{t}bpe)$^+$ in Its B[C$_6$H$_3$(CF$_3$)$_2$]$_4^-$ Salt

formula	$C_{52}H_{53}BF_{24}O_2P_2Ru$		
a, Å	12.175(1)	space group	Pn
b, Å	25.535(3)	T, °C	−168
c, Å	19.256(2)	λ, Å	0.710 69
β, Å	106.12(1)	ρ_{calcd}, g/cm^{-3}	1.547
V, Å^3	5751.02	μ(Mo Kα), cm^{-1}	4.45
Z	4	R	0.066
fw	1339.78	R_w	0.062

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

[RuH(acetone)(CO)$_2$(d^{t}bpe)]BAr$^F_4$. [RuH(CO)$_2$(d^{t}bpe)]BAr$^F_4$ (**6a**) (15 mg, 0.011 mmol) was dissolved in acetone-d_6 (0.5 mL), giving an almost colorless solution. ^1H NMR (acetone-d_6): δ −18.12 (t, 1 H, Ru**H**, J(HP) = 22 Hz), 1.32 (d, 18 H, C**H**$_3$, J(HP) = 14 Hz), 1.38 (d, 18 H, C**H**$_3$, J(HP) = 13 Hz), 2.21−2.58 (m, 4 H, C**H**$_2$), 7.61 (m, 4 H, C**H**), 7.76 (m, 8 H, C**H**). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 97.68 (s).

[RuH(CO)$_3$(d^{t}bpe)]BAr$^F_4$ (7). An NMR tube fitted with a Teflon stopcock was filled with a yellow solution of [RuH(CO)$_2$(d^{t}bpe)]BAr$^F_4$ (**6a**) (10 mg, 0.0075 mmol) in CD_2Cl_2 (0.5 mL). The solution was frozen and the headspace evacuated, and 1 atm of CO was admitted, giving a

bright yellow solution in the time of mixing. IR (CD_2Cl_2, cm^{-1}): 2106, 2058, 2046 (νCO).^{1}H NMR (CD_2Cl_2): δ −8.03 (t, 1 H, Ru**H**, *J*(HP) = 21 Hz), 1.38 (d, 18 H, C**H**$_3$, *J*(HP) = 14 Hz), 1.39 (d, 18 H, C**H**$_3$, *J*(HP) = 14 Hz), 2.01 (m, 4 H, C**H**$_2$), 7.60 (s, 4 H, C**H**), 7.75 (s, 8 H, C**H**). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 108.73 (s).

[Ru(H)$_2$(CO)$_2$(d^{t}bpe)] (8). From [RuHCl(CO)$_2$(d^{t}bpe)] (**4**): $LiBEt_3H$ (0.4 mL, 0.37 mmol) was added to a gray suspension of [RuHCl(CO)$_2$(d^{t}bpe)] (**4**) (200 mg, 0.37 mmol) in benzene (15 mL) by means of syringe, yielding an orange solution with some white precipitate. The solution was filtered and all volatiles removed in a vacuum. The remaining orange residue was recrystallized from hot MeOH at −40 °C, yielding colorless needles. Yield: 136 mg (77%). Anal. Calcd for $C_{20}H_{42}O_2P_2Ru$: C, 50.30; H, 8.86. Found: C, 50.74; H, 8.70. IR (C_6H_6, cm^{-1}): 1999, 1960 (νCO), 1896 (νRuH). ^{1}H NMR (C_6D_6): δ −8.51 (ddd, 1 H, Ru**H**, *J*(HH) = 4.5 Hz, *J*(HP) = 19 Hz, 46 Hz), −7.77 (ddd, 1 H, Ru**H**, *J*(HH) = 4.5 Hz, *J*(HP$_{cis}$) = 27 Hz, *J*(HP$_{trans}$) = 80 Hz), 1.12 (d, 9 H, C**H**$_3$, *J*(HP) = 12 Hz), 1.13 (d, 9 H, C**H**$_3$, *J*(HP) = 12 Hz), 1.15 (d, 9 H, C**H**$_3$, *J*(HP) = 12 Hz), 1.19 (d, 9 H, C**H**$_3$, *J*(HP) = 12 Hz), signals for 4 CH_2 protons are overlapped by ^{t}Bu signals. ^{13}C{^{1}H} NMR (C_6D_6): δ 23.86 (m, P**C**), 24.37 (m, P**C**), 29.85−30.42 (m, **C**H$_3$), 35.73−36.04 (m, P**C**H$_2$), 206.32 (dd, **C**O, P(CP$_{trans}$) = 76 Hz, P(CP$_{cis}$) = 8 Hz), 207.00 (m, **C**O). ^{31}P{^{1}H} NMR (C_6D_6): δ 117.84 (d, *J*(PP) = 13 Hz), 111.08 (d, *J*(PP) = 13 Hz).

From [RuH(CO)$_2$(d^{t}bpe)]BAr$^F{}_4$ (**6a**): $LiBEt_3H$ (37 μL, 0.037 mmol; 1 M solution in THF) was added at room temperature to a solution of [RuH(CO)$_2$(d^{t}bpe)]BAr$^F{}_4$ (**6a**) (49.8 mg, 0.037 mmol) in THF (10 mL), giving a bright orange solution. The solution was evaporated to dryness and the residue extracted with benzene (10 mL). The benzene solution was filtered through a 2-cm plug of Celite and the filtrate evaporated to dryness, yielding a bright orange solid. The solid was identified by NMR and IR spectrocopies as [Ru(H)$_2$(CO)$_2$(d^{t}bpe)] (**8**).

[Ru(H)(D)(CO)$_2$(d^{t}bpe)]/[Ru(D)$_2$(CO)$_2$(d^{t}bpe)]. An NMR tube fitted with a Teflon stopcock was filled with a bright yellow solution of [RuH$_2$(CO)$_2$(d^{t}bpe)] (**8**) (10.1 mg, 0.0021 mmol) in C_6D_6 (0.5 mL). The solution was frozen and the headspace evacuated, and 1 equivalent of D_2 was admitted. After 45 min at 25 °C, the following results were observed. ^{1}H NMR (C_6D_6): δ −8.53 (apparent t, 1 H, Ru**H**, *J*(HP) = 22 Hz), −7.77 (dd, 0.74 H, *J*(HP$_{trans}$) = 80 Hz, *J*(HP$_{cis}$) = 27 Hz), 1.12−1.80 (m, 57 H, C**H**$_3$, C**H**$_2$). ^{2}H NMR (61 MHz in C_6H_6): δ = −7.76 (dd, Ru*H*, *J*(DP$_{trans}$) = 12 Hz, *J*(DP$_{cis}$) = 4 Hz); −8.55; (t, RuH, *J*(DP) = 3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 111.61 (br, **P**$_{trans}$RuH), 118.37 (d, **P**$_{cis}$RuH, *J*(PP) = 12 Hz).

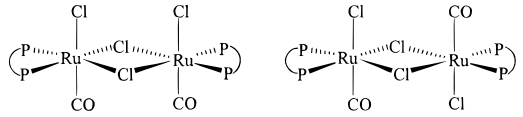
[Ru(CO)$_3$(d^{t}bpe)] (9). A yellow solution of [Ru(Cl)$_2$(CO)$_2$(d^{t}bpe)] (**1**) (103 mg, 0.19 mmol) and NEt_3 (0.2 mL, 1.43 mmol) in EtOH (10 mL) was heated under reflux to yield, initially, [Ru(H)$_2$(CO)$_2$(d^{t}bpe)] while a gentle stream of CO was bubbled through the solution. The mixture was cooled to room temperature after 1.5 h, all volatiles were removed in a vacuum, and the obtained yellow residue was extracted with benzene (10 mL). The benzene extract was evaporated to dryness and the obtained yellow solid recrystalized from hot EtOH (8 mL) at −40 °C, yielding yellow needles. Yield: 61 mg (64%). Anal. Calcd for $C_{21}H_{40}O_3P_2Ru$: C, 50.09; H, 8.01. Found: C, 50.04; H, 8.06. IR (C_6H_6, cm^{-1}): 1989, 1904, 1885 (νCO). ^{1}H NMR (acetone-d_6): δ 1.32 (d, 36 H, C**H**$_3$, *J*(HP) = 12 Hz), 1.97 (d, 4 H, C**H**$_2$, *J*(HP) = 13 Hz). ^{13}C{^{1}H} NMR (toluene-d_8): δ 24.25 (m, P**C**), 30.37 (m, **C**H$_3$), 36.60 (m, P**C**H$_2$), 215.16 (t, **C**O, *J*(CP) = 11 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 114.30 (s).

Results

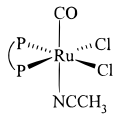
Six-Coordinate Complexes. Treatment of [RuCl$_2$(CO)$_2$]$_2$ with d^{t}bpe according to eq 1 gave [RuCl$_2$(CO)$_2$(d^{t}bpe)] (**1**). IR

$$[RuCl_2(CO)_2]_2 + 2d^tbpe \xrightarrow[78\ ^\circ C]{EtOH/CO} \underset{\mathbf{1}}{2[RuCl_2(CO)_2(d^tbpe)]} \quad (1)$$

and NMR spectra show that **1** was obtained as a mixture of two isomers, in a ratio which did not vary and which could not be separated. The IR spectrum exhibits three CO bands, the ^{31}P{^{1}H} NMR spectrum shows one singlet and two doublets, and the ^{13}C{^{1}H} NMR spectrum shows one doublet of doublets and two triplets for the CO ligands. We assign the CO bands at 2066 and 1983 cm^{-1}, the two phosphorus doublets, and the ^{13}C NMR doublet of doublets and one triplet to *all-cis*-[RuCl$_2$(CO)$_2$(d^{t}bpe)].[8] The third CO absorption at 2014 cm^{-1}, the singlet in the ^{31}P{^{1}H} NMR spectrum, and the second ^{13}C NMR triplet correspond to the *trans*-(CO)$_2$ isomer. Another possibility is the *trans*-(Cl)$_2$ isomer, but this can be excluded by means of the ^{13}C{^{1}H} NMR, which in this case should show a second doublet of doublets and not a triplet. The isolation of a *trans*-(CO)$_2$ complex is unusual because complexes with π acceptor ligands in trans positions are expected not to be thermodynamically favorable.[13,14] Heating a solution of **1** in EtOH resulted in the formation of the Cl bridged dimer [RuCl$_2$(CO)(d^{t}bpe)]$_2$ (**2**) via loss of one CO ligand. The IR spectrum of **2** exhibits one CO absorption, whose frequency is almost identical to that of [RuCl$_2$(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)]$_2$, which is another dimeric complex with chelating phosphines.[8] Further support of this assignment comes from the FAB mass spectrum, which shows the molecular ion minus one chloride with 100% intensity and the correct isotope pattern. The ^{31}P{^{1}H} NMR of **2** shows two independent signals. To explain these observations, we suggest that [RuCl$_2$(CO)(d^{t}bpe)]$_2$ (**2**) contains the *cis*-(CO)$_2$ (**A**) and the *trans*-(CO)$_2$ (**B**) isomers. Precisely this isomerism was observed recently for [RuCl$_2$(bidentate)(CO)]$_2$,[15]



The wavelength of the CO bands of both isomers is presumably similar, so a mixture of the isomers shows only one CO absorption. The dimerization of two [RuCl$_2$(CO)(d^{t}bpe)] fragments is one significant difference between this cis chelated complex and the trans phosphine complex [RuCl$_2$(CO)(P^{t}Bu$_2$Me)$_2$], because the latter is a monomer with no tendency to dimerize.[16] This is due to the steric shielding of the entire molecule, in the case of trans phosphine complex, whereas the cis phosphine is shielded on only one side of the molecule; this enables the dimerization of two fragments. Dimer [RuCl$_2$(CO)(d^{t}bpe)]$_2$ (**2**) can be cleaved with CO to give the previously observed mixture of two [RuCl$_2$(CO)$_2$(d^{t}bpe)] (**1**) isomers. Monomeric [RuCl$_2$(L)(CO)(d^{t}bpe)] (L = CH_3CN (**3**), py) is formed by treatment of **2** with CH_3CN or pyridine, respectively. In **3** the phosphorus nuclei are equivalent, so structure **3** is indicated.



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The ligand L is only weakly bound, so isolated [RuCl$_2$(CH$_3$CN)(CO)(d^{t}bpe)] (**3**) is always contaminated by some [RuCl$_2$-

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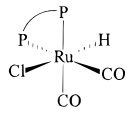
$(CO)(d^tbpe)]_2$ (**2**), and $[RuCl_2(py)(CO)(d^tbpe)]$ could only be observed in solution by its ν(CO) band at 1937 cm^{-1}. Since L is trans to CO in the structure, the weak binding of L is understandable.

Despite the fact that $[RuCl_2(CO)_2(d^tbpe)]$ (**1**) is a mixture of two isomers, the reaction of **1** with equimolar NaOEt in EtOH gave isomerically pure $[RuHCl(CO)_2(d^tbpe)]$ (**4**) in yields of more than 60%.

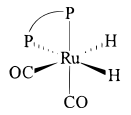


4

$[RuHCl(CO)_2(d^tbpe)]$ (**4**) in the ^1H NMR spectrum shows a triplet for the hydride and two doublets for the ^{t}Bu groups of the phosphine ligand. The $^{31}P\{^1H\}$ NMR exhibits only one singlet, and the two CO ligands appear at a single chemical shift as a doublet of doublets in the $^{13}C\{^1H\}$ NMR spectrum.

Five-Coordinate Complexes. Because of the trans effect of the hydride ligand, the Cl ligand in **4** is labile and can be removed with $AgBF_4$, $AgPF_6$, and $NaBAr^F_4$, respectively. Treatment with $AgBF_4$ gives $[RuH(FBF_3)(CO)_2(d^tbpe)]$ (**5**) in which the BF_4 ligand, with rapid fluoride site exchange, is probably only weakly coordinated. This is supported by the lack of color of the compound and the fact that the hydride signal in the ^1H NMR spectrum is shifted upfield (6.5 ppm) with respect to **4**. A larger upfield shift (ca. 9 ppm) is observed for $[RuH(CO)_2(d^tbpe)]X$ (X = BAr^F_4 (**6a**), PF_6 (**6b**)), indicating a free-coordination site trans to the hydride so that at least BAr^F_4 is not coordinated to the metal center. The differences between the NMR and IR spectra of **6a** and **6b** might be indicative of a weak interaction between the $[RuH(CO)_2(d^tbpe)]^+$ fragment and the counterion PF_6^-. Removal or exchange of the π donor ligand Cl^- in **5** and **6** also causes a shift in the averaged ν(CO) frequencies of 10−30 cm^{-1} to a higher wavelength, indicating a lower electron density at the metal center. When $[RuHCl(CO)_2(d^tbpe)]$ (**4**) was reacted directly with $NaBAr^F_4$ or $AgPF_6$, the hydride signal was often only weakly resolved and showed variable chemical shifts between −19 and −24 ppm. This probably is due to traces of water or incomplete Cl^- removal and chloride exchange between **4** and **6a**. To avoid this effect, $[RuH(CO)_2(d^tbpe)]BAr^F_4$ (**6a**) was synthesized via BF_4^- abstraction from $[RuH(FBF_3)(CO)_2(d^tbpe)]$ (**5**) with $NaBAr^F_4$, which resulted in sharp signals. The coordinatively unsaturated character of $[RuH(CO)_2(d^tbpe)]BAr^F_4$ (**6a**) is also established by X-ray structure analysis (Table 2). Compound **6a** exhibits a square-pyramidal structure, depicted in Figure 1. There are two independent cations in the asymmetric unit, but their structures differ insignificantly. The hydride ligand, which could not be detected, occupies the apical position. The free-coordination site trans to the hydride is neither stabilized by agostic interactions nor by interactions between the metal center and the counterion. The lack of any agostic interactions can be attributed to the strong trans influence of the hydride ligand. The P−Ru−P angle is 85.76(7)° and the C−Ru−C angle 90.0(4)°. The sum of angles around the Ru atom is 360°. The Ru−P distances are ca. 2.40 Å and the Ru−C distances, ca. 1.93 Å. The two independent cations show no mutual short contact, and the shortest Ru−F distances in the unit cell are 4.13 Å (Ru1) and 3.86 Å (Ru26), all of which are nonbonding.

Reactivity of $[RuH(CO)_2(d^tbpe)]^+$. The free-coordination site can be occupied by donor molecules such as acetone, CO, or H^-. When $[RuH(CO)_2(d^tbpe)]BAr^F_4$ (**6a**) is dissolved in acetone, a nearly colorless solution forms, and the hydride signal in the ^1H NMR spectrum is shifted ca. 6 ppm downfield with respect to **6a**. Treatment of **6a** with CO yields $[RuH(CO)_3(d^tbpe)]BAr^F_4$ (**7**), which was identified by its hydride triplet in the ^1H NMR and by three ν(CO) absorption bands in the IR spectrum. Reaction of **6a** with $LiBEt_3H$ gave the *cis*-dihydride complex $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**). However, this compound can be obtained more conveniently by treatment of $[RuHCl(CO)_2(d^tbpe)]$ (**4**) with one equivalent of $LiBEt_3H$. $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) shows inequivalent ^{31}P nuclei, 4 ^{t}Bu ^1H NMR chemical shifts, and two hydride chemical shifts, one with a large coupling to phosphorus. These spectroscopic data all indicate the following dihydride structure for $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**). This is analogous to $Ru(H)_2(CO)_2(Me_2PCH_2CH_2PMe_2)$.[9] $[RuH_2(CO)_2(d^tbpe)]$ (**8**) is stable toward loss of H_2, even at 70 °C. As has been published elsewhere, **8** reacts with C_2H_4, giving C_2H_6 and $[Ru(C_2H_4)(CO)_2(d^tbpe)]$, which is a precursor for the synthesis of $[Ru(CO)_2(d^tbpe)]_2$.[17] However, when **8** is



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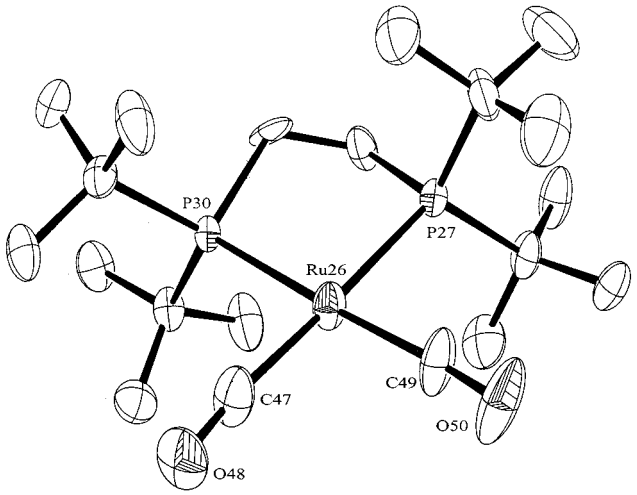

Figure 1. ORTEP drawing (30% probability level) of the nonhydrogen atoms of molecule B of $[RuH(CO)_2(^tBu_2CH_2CH_2P^tBu_2)]^+$. The hydride was not located.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	molecule A	molecule B
Ru(1)−P(2)	2.4069(20)	2.3966(23)
Ru(1)−P(5)	2.3953(23)	2.3914(21)
Ru(1)−C(22)	1.926(8)	1.930(12)
Ru(1)−C(24)	1.925(9)	1.921(9)
O(23)−C(22)	1.112(10)	1.124(12)
O(25)−C(24)	1.114(10)	1.119(11)
P(2)−Ru(1)−P(5)	85.76(7)	86.65(7)
P(2)−Ru(1)−C(22)	176.2(3)	177.7(3)
P(2)−Ru(1)−C(24)	92.07(25)	92.0(4)
P(5)−Ru(1)−C(22)	92.25(28)	91.1(3)
P(5)−Ru(1)−C(24)	177.5(3)	177.0(4)
C(22)−Ru(1)−C(24)	90.0(4)	90.3(5)
Ru(1)−C(22)−O(23)	172.8(10)	173.7(10)
Ru(1)−C(24)−O(25)	176.1(7)	175.3(11)

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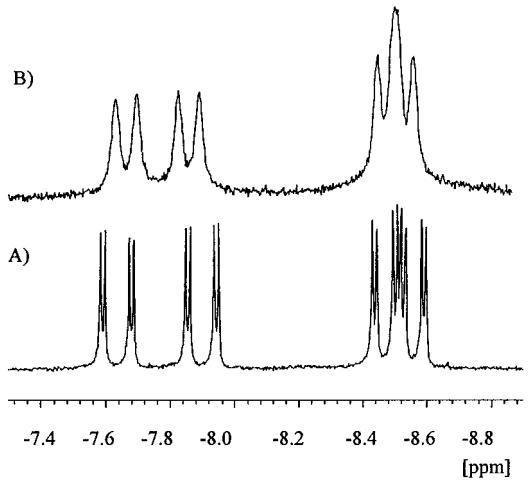


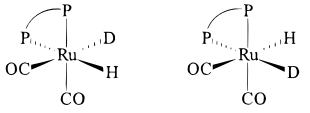
Figure 2. ^{1}H NMR spectrum (hydride region) of $[RuH_2(CO)_2(d^tbpe)]$ (**8**) (trace A) and two isotopomers of $[Ru(H)(D)(CO)_2(d^tbpe))]$ (trace B) in benzene at room temperature.

treated with a mixture of excess H_2 and $H_2C{=}CHR$ (R = H, ca. 2 eq, 6 h; Ph, ca. 5 eq, 1 week) at ca. 50 °C, the ^{1}H NMR spectra show the formation of $H_3C{-}CH_2R$ while **8** remains. Thus, $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) catalyzes the hydrogenation of $H_2C{=}CHR$ (R = H, Ph). Although we observed no loss of H_2 from $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) even at elevated temperatures, reaction of **8** with CO even at room temperature over 1 h gave clean conversion to $[Ru(CO)_3(d^tbpe)]$ (**9**) and free H_2. This led to a straightforward synthesis for $[Ru(CO)_3(d^tbpe)]$ (**9**) according to eq 2. The reaction between $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) and

$$\underset{\mathbf{1}}{[RuCl_2(CO)_2(d^tbpe)]} + NEt_3(\text{exc}) \xrightarrow[78\ ^\circ\text{C}/1.5\ \text{h}]{\text{EtOH/CO}} \underset{\mathbf{9}}{[Ru(CO)_3(d^tbpe)]} + 2HNEt_3Cl \quad (2)$$

olefins[18] or CO requires a free-coordination site at complex **8**, which is an octahedral 18e complex. The loss of H_2 from **8** and recoordination of olefin or CO can be excluded because of the observed reduction of the olefin on the metal center; hydride must remain after olefin is coordinated. To obtain a deeper insight into the reaction mechanism, $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) was reacted with approximately one equivalent of D_2. A ^{1}H NMR spectrum recorded after 45 min at room temperature shows evidence for remarkably facile exchange: the collapse of the two hydride doublets of doublets of doublets to two doublets of doublets by loss of the *J*(HH) coupling in comparison to the ^{1}H NMR of $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) (Figure 2).

The appearance of two hydride signals in the ^{1}H NMR is due to the formation of two isotopomers, **8a** and **8b**. The hydride signal at −7.8 ppm can be assigned to isomer **8a**, because of the larger $J(HP_{trans})$ coupling. The $^{31}P\{^1H\}$ NMR of the isotopomer mixture shows one resolved doublet (117.8 ppm) and one broadened signal (111.1 ppm). The broadness of the latter is due to overlapping of the *J*(PP) and $J(PD_{trans})$ coupling,



8a **8b**

and so this signal can be assigned to the P donor trans to the hydride. The formation of two H/D isotopomers requires an intermediate of composition "RuH_2D_2". The formation of such an intermediate is possible only if one ligand, either one CO or one phosphine donor, comes off the metal. Because in this case, recoordination of this donor is necessary, we favor the decoordination of one phosphine donor which is still bound to the complex via the $(CH_2)_2$ bridge and therefore not able to diffuse into the solution. The cleavage of the phosphorus donor is facilitated by the strong trans influence of the hydride or the CO ligand and the steric demand of the ^{t}Bu groups. It is thus reasonable to assume that the reaction between $[Ru(H)_2(CO)_2(d^tbpe)]$ (**8**) and olefins or CO is enabled by the same decoordination of one phosphorus donor.

Conclusion

The bulky chelate $^tBu_2PCH_2CH_2P^tBu_2$ permits access to six-coordinate $[RuCl_2(CO)_2(d^tbpe)]$, which shows a tendency to lose one CO. The resulting product is not a monomer, but rather a halide bridged dimer. The bridges in the dimer are cleaved by CO, MeCN, or pyridine. One halide of $[RuCl_2(CO)_2(d^tbpe)]$ is converted to hydride by EtOH/NaOEt, to give exclusively the isomer with H trans to Cl, and this isomer shows no tendency to lose CO. The last chloride is converted to hydride by $LiBEt_3H$, and the resulting $[Ru(H)_2(CO)_2(d^tbpe)]$, with cis hydrides, shows no tendency to lose H_2 or CO. However, CO replaces H_2 at 25 °C, to give $[Ru(CO)_3(d^tbpe)]$, and the reaction with D_2 gives rise to the formation of H/D isotopomers. Because of this scrambling, the decoordination of one phosphorus donor is suggested as a key step during the reactions of $[Ru(H)_2(CO)_2(d^tbpe)]$. This appears to be a general feature, given that it is also needed to explain the reaction of the dihydride with olefins. Chloride trans to hydride in $[RuHCl(CO)_2(d^tbpe)]$ is replaced by BF_4- or PF_6- (using $AgBF_4$ or $AgPF_6$), and an authentic five-coordinate species is formed using $NaB(3,5\text{-}(CF_3)_2C_6H_3)_4$; the five-coordinate complex binds acetone, CO, or H^- but shows no tendency for agostic ^{t}Bu donation. This lack of agostic donation contrasts with several other cases[19−21] and may result from the strong trans effect of hydride in $RuH(CO)_2(d^tbpe)^+$.

Acknowledgment. Support by NSF and DFG (T.G.G.) is gratefully acknowledged.

Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9902020

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