Organometallics 1993, 12, 906-916

Use of the New Ligand $P(CH_2CH_2PCy_2)_3$ in the Synthesis of Dihydrogen Complexes of Iron(II) and Ruthenium(II)

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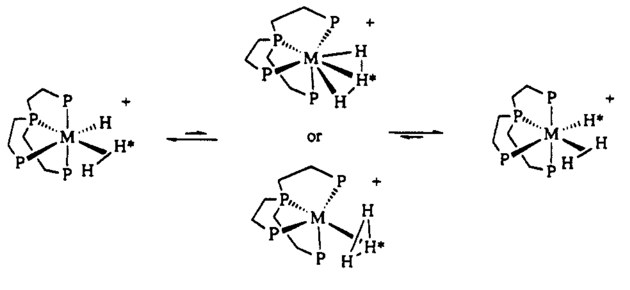
Received September 2, 1992

The novel bulky and basic tetradentate ligand $P(CH_2CH_2PCy_2)_3$ (PP_3Cy) is synthesized by the $LiN(i\text{-}Pr)_2$-catalyzed addition reaction of dicyclohexylphosphine ($HPCy_2$) to $P(CH{=}CH_2)_3$. Treatment of $RuCl_2(PPh_3)_3$ with PP_3Cy produces the five-coordinate square-pyramidal complex $[RuCl(PP_3Cy)]Cl$, which is converted into $[RuCl(PP_3Cy)]BPh_4$ when treated with $NaBPh_4$. Similarly, $FeCl_2$ reacts with PP_3Cy to give $[FeCl(PP_3Cy)]Cl$. The structure of the tetraphenylborate salt $[FeCl(PP_3Cy)]BPh_4$ is trigonal bipyramidal around Fe(II); crystals are monoclinic, space group $P2_1/c$, with $a = 12.699(4)$ Å, $b = 29.046(16)$ Å, $c = 17.026(7)$ Å, $\beta = 103.14(3)°$, and $V = 6116(5)$ Å^3 for $Z = 4$; $R = 0.065$. Reaction of $[RuCl(PP_3Cy)]Cl$ with excess $NaBH_4$ in THF yields *mer*-$RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)$, where the tetraphosphine is bound via three P atoms to ruthenium and the BH_3 is bound to a dangling terminal PCy_2 group of the tetraphosphine. The monohydride complex $RuHCl(PP_3Cy)$ is obtained from the reaction of $[RuCl(PP_3Cy)]Cl$ with excess NaOMe in refluxing THF. The η^2-dihydrogen complex $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ is synthesized by treating $[RuCl(PP_3Cy)]BPh_4$ with 1 equiv of $NaBH_4$ under an atmosphere of dihydrogen. The analogous iron complex is also described. The nonclassical structures of $[MH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ (M = Fe, Ru) are established by ^1H, ^{31}P, and T_1 NMR measurements and the observation of a $^1J(HD)$ coupling constant of 28 Hz in the isotopomer $[RuD(HD)(PP_3Cy)]^+$. Despite the steric bulk of the ligand, the complexes adopt an octahedral geometry, $[MH(H_2)(PP_3Cy)]^+$, instead of a trigonal-bipyramidal ligand geometry with an H_3 ligand.

Introduction

Polydentate phosphines are important ligands for control of the stereochemistry of coordination complexes and soluble metal catalysts. One of the polyphosphines that has attracted the most attention is the potentially tetradentate polyphosphine $P(CH_2CH_2PPh_2)_3$ (or PP_3 hereafter), partly because of the characteristic geometric features it imposes on a metal complex[2] and partly because of its activating effect on catalysts for reactions that do not require too many open sites at the metal center.[3-7] Bianchini et al. have shown that PP_3 stabilizes η^2-dihydrogen complexes, for example, $[RuH(\eta^2\text{-}H_2)(PPP_3)]^+$,[8] $[FeH(\eta^2\text{-}H_2)(PP_3)]^+$,[9,10] and $[Co(\eta^2\text{-}H_2)(PP_3)]^+$.[6] They have postulated that H atom exchange in the complexes $[M(\eta^2\text{-}H_2)(H)(PP_3)]^+$ (M = Fe, Ru) proceeds via a trihydrogen intermediate or transition state (Scheme I; the Ph groups on the terminal phosphorus atoms are not shown).

Scheme I



Trihydrogen ligands have been the subject of much speculation but have never been positively identified.[8,9,11] Heinekey and co-workers have shown that some complexes of Ir,[12,13] Ru,[14] and Nb[15] which were first thought to be trihydrogen complexes on the basis of large H–H coupling constants are in fact trihydrides which exhibit the interesting phenomenon of quantum-mechanical exchange coupling. There is some evidence for an attraction in $Fe(\eta^2\text{-}H_2)(H)_2(PEtPh_2)_3$ between a cis hydride and a hydrogen of a dihydrogen ligand at a distance of 1.86 Å which might be regarded as incipient formation of a trihydrogen ligand.[16] The complex $[Fe(\eta^2\text{-}H_2)(H)(P(CH_2CH_2CH_2PMe_3)_3)]^+$, which contains Dahlenberg's tetraphos ligand,[17]

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0276-7333/93/2312-0906$04.00/0

has NMR properties that make it appear to have a trihydrogen ligand, but it does not.[18]

We have been interested in dihydrogen complexes of the iron triad of the type $[MH(\eta^2\text{-}H_2)L_2]^+$ (M = Fe, Ru, Os; L = diphosphine or L_2 = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$) and have demonstrated how sensitive the properties of the H_2 ligand are to changes in the substituents of the diphosphine.[19,20] The chemistry of metal hydride complexes containing potentially tetradentate polyphosphines of the type $[MH_3(P(CH_2CH_2PR_2)_3)]^+$ (M = Fe, Ru, Os) might be particularly interesting. If the R group were bulky enough, a complex containing the ligand $P(CH_2CH_2PR_2)_3$ would be forced to adopt a trigonal-bipyramidal geometry owing to steric interactions between the R groups and possibly force the three hydrogen atoms close together to form a stable trihydrogen complex.

We describe here a simple route to the bulky ligand $P(CH_2CH_2PCy_2)_3$ (or PP_3Cy thereafter) and a few of its iron and ruthenium complexes, including the molecular dihydrogen complexes $[MH(\eta^2\text{-}H_2)(PP_3Cy)]^+$ (M = Fe, Ru).

Experimental Section

Unless otherwise noted, all manipulations were done under an Ar or H_2 atmosphere by use of Schlenk techniques. Solids were handled in a Vacuum Atmospheres drybox under N_2. All solvents were dried over appropriate reagents and distilled under N_2 before use. Reagent-grade chemicals were used as purchased from Aldrich Chemical Co. unless otherwise stated. $HPCy_2$ and PCl_3 were purchased from Strem Chemical Co. or Digital Specialty Chemicals Ltd. $RuCl_2(PPh_3)_3$[21] and $P(CH{=}CH_2)_3$[22] were prepared according to literature methods.

NMR spectra were obtained on a Varian XL 400, operating at 400.00 MHz for ^1H, 161.98 MHz for ^{31}P, and 128.4 MHz for ^{11}B, or on a Varian XL 200 operating at 200.00 MHz for ^1H and 80.98 MHz for ^{31}P. Chemical shifts refer to room-temperature conditions unless specified otherwise. All ^{31}P and ^{11}B NMR spectra were proton decoupled. ^{31}P chemical shifts were measured relative to ~1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of $\delta(P(OMe)_3)$ 140.4 ppm. ^1H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. T_1 values were measured by the inversion recovery method. ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$.

Microanalyses were performed by the Canadian Microanalytical Service Ltd., Vancouver, BC, Canada. Although the samples were handled under an inert atmosphere, acceptable elemental analyses were never obtained for the complexes $[RuCl(PP_3Cy)]Cl$, $[FeCl(PP_3Cy)]BPh_4$, and $[Ru(H_2)H(PP_3Cy)]BPh_4$.

$P(CH{=}CH_2)_3$. Freshly distilled PCl_3 (6.0 mL, 9.4 g, 69 mmol) in 10 mL of THF is dropped slowly into a stirred 1.0 M solution of $CH_2{=}CHMgBr$ in THF (210 mL, 210 mmol) cooled by dry ice. A vigorous reaction occurs immediately, and a gray-white solid forms. The reaction mixture is then warmed up to room temperature. The liquid is distilled out at 1 atm (the initial temperature of the oil bath should be controlled at ca. 70 °C and the temperature of the oil bath gradually increased to ca. 160 °C to ensure that all of the liquid is distilled) to give ca. 210 mL of a THF solution of $P(CH{=}CH_2)_3$. The concentration of $P(CH{=}CH_2)_3$ varies from 0.10 to 0.15 M from experiment to experiment. ^{31}P NMR (THF/C_6D_6): δ −19.6.

$P(CH_2CH_2PCy_2)_3$. To 100 mL of a THF solution of $P(CH{=}CH_2)_3$ (ca. 11 mmol) is added 7.0 g of $HPCy_2$ (35 mmol) and 5.0 mL of 1 M $LiN(i\text{-}Pr)_2$ in THF (5.0 mmol) to give a light orange solution. The resulting mixture is stirred at room temperature for 3 h. Because the concentrations of $P(CH{=}CH_2)_3$ vary with different experiments, it is necessary to check the reaction mixture at this stage by ^{31}P NMR spectroscopy to see if one needs to add either $HPCy_2$ or $P(CH{=}CH_2)_3$ to the reaction mixture so that the product $P(CH_2CH_2PCy_2)_3$ is the only phosphine compound present in the reaction mixture when the reaction is finished. The solvents are removed completely under vacuum. To the residue is added 30 mL of MeOH and the resulting mixture stirred for 1 h to give a white solid, which is collected by filtration, washed with a small amount of MeOH, and dried under vacuum: yield 6.0 g, 77%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ −0.2 (d, PCy_2), −16.7 (q, central P), $^3J(PP)$ = 21.4 Hz. ^1H NMR (C_6D_6): δ 1.0–1.8 (m). Anal. Calcd for $C_{42}H_{78}P_4$: C, 71.36; H, 11.12. Found: C, 71.43; H, 11.02.

$[RuCl(PP_3Cy)]Cl$. A mixture of 1.84 g of PP_3Cy (2.6 mmol) and 2.5 g of $RuCl_2(PPh_3)_3$ (2.6 mmol) in 30 mL of CH_2Cl_2 is stirred for 30 min to give a deep red-orange solution. The solvent is then removed completely. Addition of 30 mL of Et_2O to the residue gives a yellow-orange solid, which is collected by filtration, washed with Et_2O, and dried under vacuum: yield 2.0 g, 88%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 143.1 (q, central P), 66.8 (br, PCy_2), $J(PP)$ = 15.3 Hz. ^1H NMR (C_6D_6): δ 1.3–2.8 (m). Anal. Calcd for $C_{42}H_{78}Cl_2P_4Ru$: C, 57.39; H, 8.95. Found: C, 56.68; H, 9.05.

$[FeCl(PP_3Cy)]Cl$. A 0.15-g quantity of $FeCl_2$ is added to a stirred solution of 0.31 g of PP_3Cy in 20 mL of CH_2Cl_2. The mixture, which turns purple immediately, is stirred for 15 min and concentrated (in vacuo) to about 2 mL. After addition of 10 mL of Et_2O and 10 mL of hexanes, the dark purple powder is filtered off and washed with diethyl ether and hexanes: yield ca. 50%.

$[RuCl(PP_3Cy)]BPh_4$. A mixture of 1.2 g of PP_3Cy (1.7 mmol) and 1.4 g of $RuCl_2(PPh_3)_3$ (1.5 mmol) in 20 mL of CH_2Cl_2 is stirred at room temperature for 10 min. A 0.90-g amount of $NaBPh_4$ (2.6 mmol) in 40 mL of MeOH is added and the volume reduced to ca. 20 mL to give an orange solid. The solid is collected by filtration, washed with MeOH and Et_2O, and dried under vacuum: yield 1.2 g, 69%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 141.9 (q, central P), 66.3 (br, PCy_2), $J(PP)$ = 15.9 Hz. ^1H NMR (acetone-d_6): δ 1.3–2.8 (m, CH_2, CH), 6.8–7.3 (m, Ph).

$[FeCl(PP_3Cy)]BPh_4$. A 0.15-g quantity of $FeCl_2$ is added to a stirred solution of 0.31 g of PP_3Cy in 20 mL of CH_2Cl_2. The mixture, which turns purple immediately, is stirred for 5 min, and a solution of 0.2 g of $NaBPh_4$ in 5 mL of MeOH is added. The resulting solution is stirred for 15 min and concentrated (in vacuo) to about 5 mL. After addition of 10 mL of MeOH, the dark purple powder is filtered off and washed several times with methanol and then with diethyl ether: yield ca. 60%. FAB MS: calcd for $C_{42}H_{78}{}^{56}FeClP_4$ 798, observed 798. The complex was paramagnetic and gave no ^{31}P NMR spectrum.

$RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)$. A mixture of 0.40 g of $RuCl_2(PP_3Cy)$ (0.46 mmol) and 0.10 g of $NaBH_4$ (2.9 mmol) in 30 mL of THF is stirred at 20 °C overnight to give a colorless solution. The solvent is removed completely, and the residue is extracted with benzene. The volume of the extract is reduced. Addition of MeOH produces a pale yellow solid, which is collected by filtration, washed with MeOH, and dried under vacuum. The compound should be recrystallized by vapor diffusion of MeOH into a CH_2Cl_2 solution: yield 0.30 g, 78%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 123.8 (dt, $J(PP)$ = 32, 14 Hz, central P), 78.1 (d, $J(PP)$ = 14 Hz, PCy_2), 27.7 (br, $PCy_2{\cdot}BH_3$). ^1H NMR (C_6D_6): δ − 18.2 (dt, $J(PH)$ = 36.6, 19.8 Hz, 1 H, Ru–H), −7.0 (br, 2 H, $Ru(\mu\text{-}H)_2B$), 0.8–2.8 (m, CH_2, CH, BH_3), 5.5 (br, 2 H, BH_2). $^{11}B\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 12.7 (br), −42.9 (br). Anal. Calcd for $C_{42}H_{86}B_2P_4Ru$: C, 60.19; H, 10.34. Found: C, 59.80; H, 10.03.

$RuHCl(PP_3Cy)$. Refluxing a mixture of 0.50 g of $RuCl_2(PP_3Cy)$ (0.57 mmol) and 0.10 g of NaOMe (1.9 mmol) in 30 mL of

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Table I. ^1H NMR T_1 Measurements of Metal-Bonded Hydrogens of $[MH(H_2)(PP_3Cy)]BPh_4$ (M = Fe, Ru) in the Hydride Region (CD_2Cl_2 for Ru, Acetone-d_6 for Fe, 400 MHz)

	temp, °C				
	38	20	−44	−66	−88
T_1 of $Ru(H_2)$, ms	46		26	24	26
T_1 of RuH, ms	46		37	130	135
T_1 of $Fe(H_2)$, ms		56	33	29	38
T_1 of FeH, ms		56	35	40	227

THF for 5 h gives a colorless solution. The solvent is then removed completely and the residue extracted with benzene. Removal of the benzene from the extract gives a white residue. The solid is then collected by filtration, washed with MeOH, and dried under vacuum: yield 0.41 g, 85%. The compound is recrystallized by a slow diffusion of MeOH into a CH_2Cl_2 solution. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 148.8 (q, J(PP) = 11.9 Hz, central P), 54.3 (t, J(PP) = 14.2 Hz, 2 PCy_2 trans to each other), 40.4 (br, PCy_2 trans to H). ^1H NMR (CD_2Cl_2): δ −10.7 (m, J(PH) = 96, 30, 22 Hz, Ru–H), 0.9–2.8 (m, CH_2, CH). Anal. Calcd for $C_{42}H_{79}ClP_4Ru$: C, 59.73; H, 9.43. Found: C, 58.80; H, 9.33.

$[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$. Add 0.010 g of $NaBH_4$ (0.029 mmol) to a solution of $[RuCl(PP_3Cy)]BPh_4$ (0.30 g, 0.26 mmol) in 15 mL of EtOH/15 mL of THF under an H_2 atmosphere. The reaction mixture turns from orange to light yellow. After the reaction mixture is stirred for ca. 30 min, the solvents are removed by evacuation. Ca. 20 mL of EtOH is added to the residue, and the mixture is stirred at room temperature for 30 min to give an off-white solid. The solid is collected by filtration, washed with EtOH, and dried under vacuum: yield 0.19 g, 65%. This sensitive complex did not give an acceptable elemental analysis, possibly because of decomposition; however, the spectra of freshly prepared material indicate excellent purity. $^{31}P\{^1H\}$ NMR (THF/C_6D_6, 20 °C): δ 144.4 (q, central P), 73.0 (br, J(PP) = 13.7 Hz, PCy_2). For spectra at other temperatures, see the Results and Discussion. ^1H NMR (acetone-d_6, 20 °C): δ −7.6 (br, Ru–H), 1.2–2.6 (m, CH_2, CH), 6.6–7.2 (m, Ph). For ^1H NMR T_1 data, see Table I.

$[FeH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ (under N_2). A slurry of 0.03 g of $LiAlH_4$ in 5 mL of THF is added to a stirred solution of 0.1 g of $[FeCl(PP_3Cy)]Cl$ in 20 mL of THF. After the solution is refluxed for 1.5 h, 5 mL of ethanol is added. The mixture is filtered through THF-saturated Celite, the volume reduced (in vacuo) to 10 mL, and a solution of 0.1 g of $NaBPh_4$ in 15 mL of MeOH added to the stirred solution. The pale yellow precipitate is filtered off and washed with methanol followed by diethyl ether. ^1H NMR (acetone-d_6, 293 K): δ −11.4 (br). ^{31}P NMR (acetone, 293 K): δ 174.8 (quartet, J(PP) = 28.4 Hz), 98.8 (d, J(PP) = 29.1 Hz). FAS MS: calcd for $C_{42}H_{81}{}^{56}FeP_4$ 765, observed 764 ($M^+ - H$). For ^1H NMR T_1 data, see Table I. Consistently poor yields of the complex prevented attempts at recrystallization and elemental analysis.

X-ray Crystallographic Analysis of $[FeCl(PP_3Cy)]BPh_4$. The crystals were prepared by diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the complex at −5 °C under nitrogen. The very dark purple crystals were roughly cubic with 0.20-mm edges. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. Intensities of three standard reflections measured every 2 h showed no variation. The data were corrected for absorption using the program DIFABS[23] (minimum and maximum corrections 0.865 and 1.050).

The location of the Fe atom was determined from a Patterson map, and the positions of the remaining non-hydrogen atoms were solved by subsequent Fourier and difference Fourier calculations. Refinement was by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + KF^2$, with anisotropic thermal parameters for Fe, P, and Cl atoms and isotropic thermal parameters for remaining atoms. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å, U(H) = U(C) + 0.01 Å^2). Crystal data, data collection, and least-squares parameters are listed in Table II. All calculations were performed using SHELX76,[24] SHELXS86,[25] and NRCVAX[26] on a 486-33 personal computer and an Apollo computer. Atomic coordinates are presented in Table III, and relevant bond angles and distances are given in Table IV. An ORTEP[27] diagram of the compound is presented in Figure 2.

Table II. Crystallographic Data

formula	$C_{66}H_{98}BClFeP_4$
fw	1117.5
color, habit	purple, cubic
cryst size, mm	0.15 × 0.10 × 0.25 mm
cryst system	monoclinic
space group	$P2_1/c$
a, Å	12.699(4)
b, Å	29.046(16)
c, Å	17.026(7)
β, deg	103.14(3)
V, Å^3	6116(5)
Z	4
ρ_{calc}, g/cm^3	1.214
$F(000)$	2408
μ(Mo Kα), cm^{-1}	4.3
ω scan width, deg	0.7 + 0.35 tan θ
data collected (hkl ranges)	−12 to +11, 0–27, 0–16
$2\theta_{max}$, deg	40
total no. of rflns	5940
no. of unique rflns	5701
R_{merge}	0.029
no. of rflns with $I_{net} > 2.5\sigma(I_{net})$	2689
no. of variables	354
R	0.065
R_w	0.065
weighting K	0.004
GOF	1.44
max Δ/σ (final)	0.019
resid density, e/Å^3	0.390

Results and Discussion

Preparation of Ligand. There are several possible routes to ligands of the type $P(CH_2CH_2PR_2)_3$. One of the most promising could be the coupling reaction of $P(CH_2CH_2X)_3$ (X = halide) with an organophosphide $LiPR_2$. Similar coupling reactions involving Grignard or alkali-metal organophosphide reagents with appropriate organic halides have been used extensively in syntheses of polydentate phosphine ligands.[28–33] Unfortunately, there are no simple routes to the functionalized phosphine $P(CH_2CH_2X)_3$ (X = halide or other leaving group). Our attempts to synthesize these compounds directly from readily available PCl_3, P^{3-}, or PH_3 failed (for example, the reactions

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Table III. Positional and Thermal Parameters for [FeCl(PP$_3$Cy)]BPh$_4$

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
Fe	0.98591(15)	0.17924(7)	0.22772(12)	2.36(10)	C52	1.3445(23)	0.1321(9)	0.3334(15)	14.1(9)
Cl	0.9565(3)	0.21713(12)	0.33491(20)	3.17(18)	C53	1.4541(16)	0.1557(7)	0.3588(12)	8.1(5)
P1	1.0184(3)	0.14118(13)	0.12304(22)	3.01(20)	C54	1.4550(19)	0.1946(8)	0.4064(14)	10.4(7)
P2	0.8092(3)	0.14867(13)	0.17849(22)	2.71(19)	C55	1.3673(23)	0.2173(9)	0.4130(15)	13.1(8)
P3	1.0458(3)	0.24286(13)	0.16230(24)	3.01(20)	C56	1.2531(13)	0.1943(6)	0.3940(10)	5.9(4)
P4	1.1160(3)	0.12739(14)	0.30060(23)	2.86(19)	C61	1.0824(10)	0.0940(5)	0.3847(8)	3.2(3)
C1	0.9095(11)	0.1034(5)	0.0755(8)	3.8(3)	C62	1.1562(14)	0.0515(6)	0.4080(11)	7.4(5)
C2	0.8026(10)	0.1263(4)	0.0760(7)	3.0(3)	C63	1.0781(12)	0.1219(5)	0.4589(9)	5.3(4)
C3	1.0430(10)	0.1777(5)	0.0421(8)	3.5(3)	C64	1.0430(12)	0.0913(5)	0.5229(9)	5.0(4)
C4	1.1045(11)	0.2213(5)	0.0787(8)	3.5(3)	C65	1.1243(13)	0.0533(6)	0.5489(10)	6.4(5)
C5	1.1367(10)	0.1027(5)	0.1483(8)	3.4(3)	C66	1.1263(14)	0.0238(7)	0.4754(12)	8.0(5)
C6	1.1376(11)	0.0819(4)	0.2313(8)	3.5(3)	B	0.2952(13)	−0.0565(6)	0.1916(10)	3.0(4)
C11	0.6896(10)	0.1870(5)	0.1614(8)	3.2(3)	C71	0.3379(10)	−0.0142(5)	0.1430(8)	3.6(3)
C12	0.5827(11)	0.1640(5)	0.1172(8)	3.8(3)	C72	0.3794(11)	0.0279(5)	0.1789(8)	4.2(4)
C13	0.4927(11)	0.2002(5)	0.0895(9)	4.8(4)	C73	0.4026(13)	0.0636(6)	0.1362(10)	5.5(4)
C14	0.4791(12)	0.2318(5)	0.1565(9)	4.8(4)	C74	0.3931(13)	0.0630(6)	0.0566(10)	5.4(4)
C15	0.5847(11)	0.2531(5)	0.2004(8)	4.3(3)	C75	0.3563(14)	0.0221(7)	0.0147(10)	7.2(5)
C16	0.6711(10)	0.2167(5)	0.2307(8)	3.2(3)	C76	0.3301(13)	−0.0157(6)	0.0595(10)	5.7(4)
C21	0.7852(11)	0.0967(5)	0.2387(8)	3.3(3)	C81	0.3073(10)	−0.1072(5)	0.1485(8)	2.9(3)
C22	0.7082(13)	0.0604(6)	0.1909(10)	6.1(4)	C82	0.3999(12)	−0.1187(5)	0.1227(9)	4.4(4)
C23	0.6986(12)	0.0187(5)	0.2476(9)	5.0(4)	C83	0.4220(12)	−0.1623(5)	0.0970(9)	4.7(4)
C24	0.6700(12)	0.0339(6)	0.3248(9)	5.5(4)	C84	0.3454(12)	−0.1954(5)	0.0967(8)	4.5(4)
C25	0.7473(13)	0.0679(6)	0.3695(10)	5.6(4)	C85	0.2507(11)	−0.1869(5)	0.1201(8)	4.2(3)
C26	0.7583(11)	0.1102(5)	0.3172(8)	3.7(3)	C86	0.2324(11)	−0.1427(5)	0.1449(8)	3.9(3)
C31	1.1570(11)	0.2794(5)	0.2209(8)	4.0(3)	C91	0.1650(10)	−0.0477(5)	0.1841(8)	3.2(3)
C32	1.2159(11)	0.3088(5)	0.1673(8)	4.5(4)	C92	0.0963(11)	−0.0315(5)	0.1148(8)	3.6(3)
C33	1.3103(13)	0.3362(6)	0.2184(10)	6.1(4)	C93	−0.0150(12)	−0.0277(5)	0.1050(9)	4.7(4)
C34	1.2755(14)	0.3638(6)	0.2809(11)	7.1(5)	C94	−0.0622(13)	−0.0397(6)	0.1662(10)	5.6(4)
C35	1.2233(14)	0.3374(6)	0.3359(10)	6.7(5)	C95	0.0008(14)	−0.0548(5)	0.2374(10)	5.8(4)
C36	1.1249(12)	0.3096(5)	0.2827(9)	5.2(4)	C96	0.1121(13)	−0.0588(5)	0.2456(9)	5.1(4)
C41	0.9433(10)	0.2860(5)	0.1140(8)	3.1(3)	C101	0.3607(11)	−0.0600(5)	0.2839(9)	3.8(3)
C42	0.8006(11)	0.3097(5)	−0.0089(8)	3.8(3)	C102	0.4422(12)	−0.0914(5)	0.3139(9)	4.7(4)
C43	0.8791(12)	0.2716(5)	0.0305(9)	4.7(4)	C103	0.4963(13)	−0.0938(6)	0.3945(11)	6.1(4)
C44	0.7249(11)	0.3237(5)	0.0440(9)	4.7(4)	C104	0.4752(13)	−0.0634(6)	0.4481(10)	5.9(4)
C45	0.7867(12)	0.3371(5)	0.1261(9)	4.8(4)	C105	0.3948(13)	−0.0311(6)	0.4249(10)	6.2(4)
C46	0.8652(11)	0.2986(5)	0.1657(8)	4.0(3)	C106	0.3435(12)	−0.0285(5)	0.3421(10)	5.3(4)
C51	1.2518(13)	0.1531(6)	0.3379(10)	5.7(4)					

of "Na_3P/K_3P"[34–36] with excess $ClCH_2CH_2Cl$ or $BrCH_2CH_2Cl$ or the reaction of PH_3 with $CH_2{=}CHOAc$).[37] An alternative route to $P(CH_2CH_2PR_2)_3$ by the reaction of PCl_3 with reagents such as $R_2PCH_2CH_2MgX$ is unlikely since the latter Grignard compounds are unstable.[30] Thus, there appears to be no simple route to the ligand $P(CH_2CH_2PR_2)_3$ via the coupling reactions between halides and nucleophiles.

Free-radical and base-catalyzed addition of P–H, As–H, and S–H groups across C═C bonds is a useful method for synthesizing polydentate phosphine ligands.[28–33] For example, $P(CH_2CH_2PPh_2)_3$ is conveniently prepared by bubbling PH_3 into a boiling THF solution of $Ph_2PCH{=}CH_2$ containing some $KOBu^t$ catalyst[32] or by addition of Ph_2PH to the double bonds in $P(CH{=}CH_2)_3$ in benzene in the presence of LiPh as a catalyst.[31]

We have found that the new tetradentate ligand $P(CH_2CH_2PCy_2)_3$ (PP$_3$Cy) can be easily prepared by the reaction of $P(CH{=}CH_2)_3$ with $HPCy_2$ in THF catalyzed by LiN-*i*-Pr$_2$ (LDA) (eq 1). The reaction is complete in less

$$P(CH{=}CH_2)_3 + 3HPCy_2 \xrightarrow[\text{THF, 3 h}]{\text{LDA}} P(CH_2CH_2PCy_2)_3 \tag{1}$$

than 3 h at room temperature. The compound can be readily isolated as a white solid from MeOH. No reaction occurs in the absence of LDA. Other bases such as KO-*t*-Bu or KOH do not initiate the reaction, possibly because they are not strong enough to react with $HPCy_2$ to generate the PCy_2^- intermediate. LDA is used because it is a sterically hindered base and a poor nucleophile, thus avoiding side reactions due to nucleophilic reaction of the base. LDA has been previously employed to generate R_2PLi in situ to synthesize polyphosphines.[38] Radical initiators such as AIBN (2,2′-azobis(isobutyronitrile)) also fail to initiate the reaction. The conditions used in synthesizing the new ligand $P(CH_2CH_2PCy_2)_3$ are milder than those in the synthesis of $P(CH_2CH_2PPh_2)_3$.[31–33]

The ^{1}H NMR spectrum of the ligand displays a broad envelope of resonances in the region 1.0–1.8 ppm. The ^{31}P NMR spectrum of the phosphine ligand $P(CH_2CH_2PCy_2)_3$ provides confirmation of the proposed structure. The signal for the central phosphorus atom is observed at −0.2 ppm as a quartet and the terminal PCy_2 group at −16.7 ppm as a doublet with a ^3J(PP) coupling constant of 21.4 Hz.

A preliminary study shows that the method could be extended to synthesize the known tetraphosphine $P(CH_2CH_2PPh_2)_3$[31–33] and the new ligand $P(CH_2CH_2PEt_2)_3$. The characterization of $P(CH_2CH_2PEt_2)_3$ is not complete and will not be discussed here.

Preparation of [RuCl(PP$_3$Cy)]Cl and [RuCl(PP$_3$Cy)]BPh$_4$. The dichloride compound [RuCl(PP$_3$Cy)]Cl is readily synthesized by the reaction of $RuCl_2(PPh_3)_3$ with

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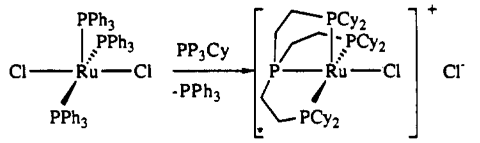
Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in [FeCl(PP$_3$Cy)]BPh$_4$

Bond Lengths (Å)			
Fe–Cl	2.235(4)	P(3)–C(4)	1.855(13)
Fe–P(1)	2.216(4)	P(3)–C(31)	1.860(13)
Fe–P(2)	2.383(4)	P(3)–C(41)	1.861(12)
Fe–P(3)	2.372(4)	P(4)–C(6)	1.838(13)
Fe–P(4)	2.364(4)	P(4)–C(51)	1.845(14)
P(1)–C(1)	1.806(13)	P(4)–C(61)	1.855(13)
P(1)–C(3)	1.822(12)	C(1)–C(2)	1.506(17)
P(1)–C(5)	1.841(12)	C(3)–C(4)	1.543(17)
P(2)–C(2)	1.846(12)	C(5)–C(6)	1.536(17)
P(2)–C(11)	1.851(12)		
P(2)–C(21)	1.890(13)		
Bond Angles (deg)			
Cl–Fe–P(1)	178.92(15)	C(2)–P(2)–C(11)	101.6(5)
Cl–Fe–P(2)	98.62(14)	C(2)–P(2)–C(21)	104.9(6)
Cl–Fe–P(3)	97.55(14)	C(11)–P(2)–C(21)	109.9(5)
Cl–Fe–P(4)	96.45(14)	Fe–P(3)–C(4)	108.7(4)
P(1)–Fe–P(2)	82.15(14)	Fe–P(3)–C(31)	118.5(4)
P(1)–Fe–P(3)	82.68(14)	Fe–P(3)–C(41)	117.8(4)
P(1)–Fe–P(4)	82.52(14)	C(4)–P(3)–C(31)	102.4(6)
P(2)–Fe–P(3)	120.17(14)	C(4)–P(3)–C(41)	104.7(5)
P(2)–Fe–P(4)	115.86(14)	C(31)–P(3)–C(41)	102.9(6)
P(3)–Fe–P(4)	118.87(14)	Fe–P(4)–C(6)	108.1(4)
Fe–P(1)–C(1)	113.7(4)	Fe–P(4)–C(51)	115.0(5)
Fe–P(1)–C(3)	114.7(4)	Fe–P(4)–C(61)	118.9(4)
Fe–P(1)–C(5)	114.0(4)	C(6)–P(4)–C(51)	104.2(7)
C(1)–P(1)–C(3)	105.1(6)	C(6)–P(4)–C(61)	102.1(6)
C(1)–P(1)–C(5)	103.6(6)	C(51)–P(4)–C(61)	106.8(7)
C(3)–P(1)–C(5)	104.6(6)	P(1)–C(1)–C(2)	108.7(9)
Fe–P(2)–C(2)	107.1(4)	P(2)–C(2)–C(1)	108.7(8)
Fe–P(2)–C(11)	120.4(4)	P(1)–C(3)–C(4)	109.0(8)
Fe–P(2)–C(21)	111.4(4)	P(3)–C(4)–C(3)	110.0(8)
		P(1)–C(5)–C(6)	106.9(8)
		P(4)–C(6)–C(5)	109.6(8)

1 equiv of PP$_3$Cy in dichloromethane (eq 2). The reaction is complete in less than 30 min at room temperature.



(2)

It is noted that preparations of other tetradentate phosphine complexes such as RuCl$_2$(PP$_3$) (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$),[8] RuCl$_2$(P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$),[39] and RuCl$_2$(*meso*-P$_4$) (P$_4$ = Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$)[40] by substitution reactions from appropriate starting materials (e.g. RuCl$_2$(PPh$_3$)$_3$, RuCl$_2$(DMSO)$_4$, RuCl$_2$(py)$_4$) require prolonged refluxing conditions. The more bulky steric characteristics of the new ligand P(CH$_2$CH$_2$PCy$_2$)$_3$ may be the origin for the higher rate of the substitution reaction.[41]

[RuCl(PP$_3$Cy)]Cl is a yellow-orange compound and can be recrystallized from a CH$_2$Cl$_2$/Et$_2$O solvent mixture. It is soluble in polar solvents such as acetone, dichloromethane, and THF and slightly soluble in alcohols but insoluble in benzene. These observations support the formulation of the compound as a 1:1 electrolyte, [RuCl(PP$_3$Cy)]Cl, in solution.

Further evidence for the formulation of the dichloride as [RuCl(PP$_3$Cy)]Cl is the easy formation of [RuCl(PP$_3$Cy)]BPh$_4$ and the similarity of the spectroscopic parameters of the two compounds. The compound [RuCl(PP$_3$Cy)]BPh$_4$ is formed from a mixture of [RuCl(PP$_3$Cy)]Cl and NaBPh$_4$ in CH$_2$Cl$_2$/MeOH and is isolated from MeOH. The ^{1}H NMR spectrum of [RuCl(PP$_3$Cy)]BPh$_4$ in acetone-d_6 exhibits, in addition to the resonance of BPh$_4^-$ in the aromatic region (6.8–7.3 ppm), the signals of the ligand in the aliphatic region (1.3–2.8 ppm); the signal shape is identical with that of [RuCl(PP$_3$Cy)]Cl. The ^{31}P NMR spectra of the two compounds are also very similar at both room temperature and low temperature. For example, the ^{31}P resonance for the bridgehead phosphorus of the PP$_3$Cy ligand was observed at 143.1 ppm (q, J(PP) = 15.5 Hz) for [RuCl(PP$_3$Cy]Cl and at 141.9 ppm (q, J(PP) = 15.9 Hz) for [RuCl(PP$_3$Cy)]BPh$_4$; the signals for the terminal PCy$_2$ groups were observed at 66.8 ppm (br) for [RuCl(PP$_3$Cy)]Cl and 66.3 ppm (br) for [RuCl(PP$_3$Cy)]BPh$_4$ in dichloromethane at room temperature.

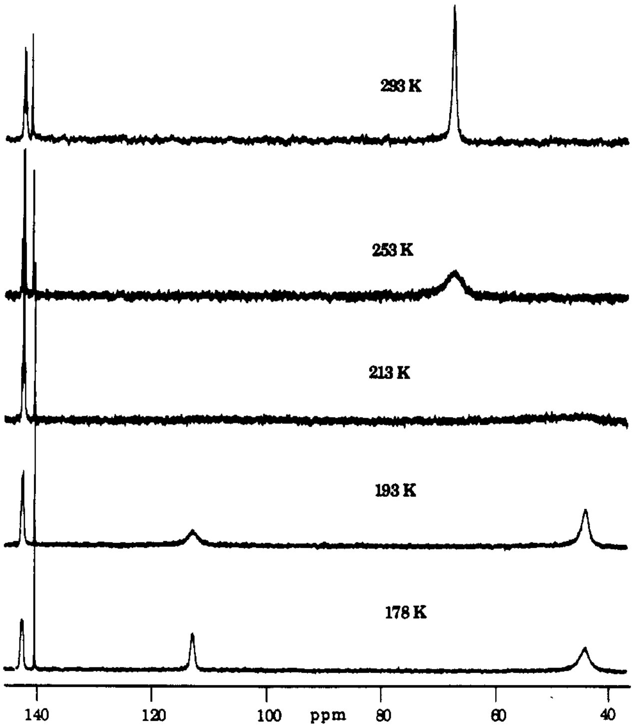


Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra for [RuCl(PP$_3$Cy)]BPh$_4$ in dichloromethane (80.98 MHz). The chemical shift scale is referenced to P(OMe)$_3$ (singlet at 140.4 ppm).

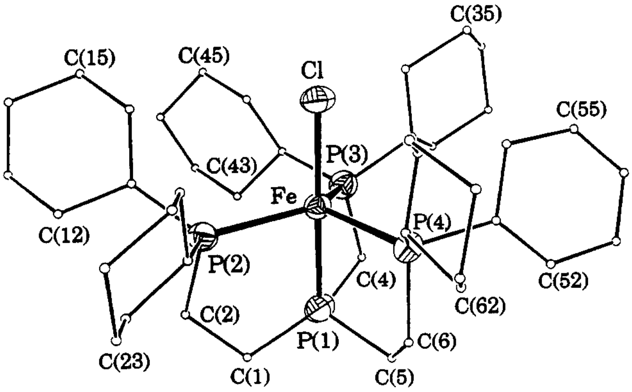


Figure 2. Molecular structure of the cation of [FeCl(PP$_3$Cy)]BPh$_4$. The hydrogen atoms are omitted for clarity.

It is interesting to note that other reported RuCl$_2$(tetraphos) complexes, such as RuCl$_2$(P(CH$_2$CH$_2$PPh$_2$)$_3$),[8] RuCl$_2$(P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$),[39] and RuCl$_2$(P(*o*-C$_6$H$_4$PPh$_2$)$_3$),[42] all exhibit AMX$_2$ splitting patterns in their ^{31}P

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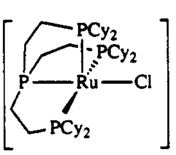
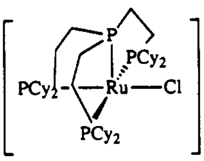
NMR spectra and are all neutral octahedral complexes. Thus, the three bulky PCy_2 groups in $P(CH_2CH_2PCy_2)_3$ forced one of the Cl^- ligands out of the coordination sphere to form the five-coordinate complex. The complex $RuCl_2$(*meso*-P_4) adopts a trans-octahedral structure[40] but behaves as a 1:1 electrolyte in dimethylacetamide.[43]

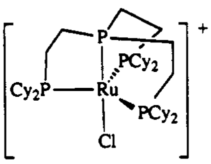
Three possible structures for the cation $[RuCl(PP_3Cy)]^+$ are shown by I–III, based on the variable-temperature ^{31}P NMR spectra (Figure 1) in dichloromethane. At room temperature an AM_3 splitting pattern is observed, which indicates that all of the terminal PCy_2 groups are equivalent. As the temperature is lowered, the signal for the terminal PCy_2 groups at 66.2 ppm broadens and then separates into two peaks, when the temperature is below −60 °C, at 111.9 and 43.2 ppm with a 1:2 ratio of intensities. The low-temperature ^{31}P NMR pattern AMX_2 suggests that the cation $[RuCl(PP_3Cy)]^+$ adopts the square-pyramidal geometry I or II. In the ^{31}P NMR spectrum at −80 °C, the signal at 141.8 ppm is assigned to the bridgehead phosphorus atom of the tripod ligand PP_3Cy. The exceptional downfield chemical shift for the bridgehead phosphorus atom is caused by the five-membered-ring effect.[44] The signals at 111.9 and 43.2 ppm are assigned, respectively, to the apical PCy_2 group and the basal PCy_2 groups in structure I. Structure I, where one of the PCy_2 groups is in the apical position, is preferred over structure II, where the central phosphorus atom is in the apical position, because of the significantly downfield chemical shift for the unique PCy_2 group. The chemical shift difference between the unique PCy_2 group and the other two equivalent mutually trans PCy_2 groups is 68.7 ppm. For comparison, the chemical shift difference between the PPh_2 group trans to a chloride (65.70 ppm) and the two mutually trans PPh_2 groups (40.40 ppm) is only 25.3 ppm in the octahedral tetraphosphine PP_3 complex $RuCl_2(PP_3)$. It has been observed that the apical phosphorus atom is significantly deshielded compared with the basal ones in several ruthenium square-pyramidal complexes.[45–48] For example, the resonance for the apical PPh_3 appears at 75.0 ppm and the basal PPh_3 at 23.3 ppm in $RuCl_2(PPh_3)_3$.[46] Fast chemical exchange of the apical and the basal PCy_2 groups in structure I may explain the room-temperature ^{31}P NMR spectrum. The undistorted-trigonal-bipyramidal structure III can be excluded because it does not explain the low-temperature ^{31}P NMR spectra; in this geometry the complex would be like the iron complex $[FeCl(PP_3Cy)]^+$, which is paramagnetic and gives no spectrum.



I



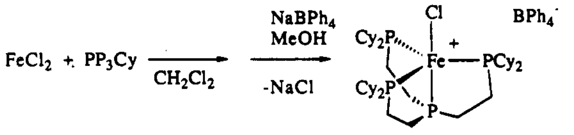
II



III

We recently learned of an X-ray structure determination of $[RuCl(PP_3)]BPh_4$ which shows that this cation has a structure intermediate between those of I and III.[49] The corresponding PP_3Cy complex probably also has this distorted-trigonal-bipyramidal structure in the solid state. This structure could be maintained in solution or there may be some slight modification, including weak coordination of CH_2Cl_2, although we have no evidence for this.

Preparation and Crystal Structure of $[FeCl(PP_3Cy)]BPh_4$. Anhydrous iron(II) chloride and PP_3Cy react in dichloromethane to give the purple complex $[FeCl(PP_3Cy)]Cl$. Anion exchange with $NaBPh_4$ gave the purple complex $[FeCl(PP_3Cy)]BPh_4$ (eq 3), which was characterized by FAB mass spectroscopy and single-crystal X-ray diffraction.



(3)

The X-ray structure of the complex shows that the coordination geometry around the iron atom is trigonal bipyramidal (TBP), with only small (<5°) deviations from the ideal 120° angles in the equatorial plane (Figure 2). However, the iron atom is displaced toward the chloride by 0.312(3) Å from the plane defined by the three equatorial phosphine atoms. Similar displacement of the metal atom toward the monodentate ligand has been observed in TBP complexes of tripod ligands such as $[Fe(SH)(PP_3)]BPh_4$ (0.334 Å out of plane),[50] $[Ni(SH)(PP_3)]BPh_4$ (0.196 Å),[50] $[Co(H_2)(PP_3)]PF_6$ (0.112 Å),[6] $Rh(XH)(PP_3)$ (X = S, Se, Te; 0.22–0.24 Å),[51] and all of the complexes of the formula $[MBr(Me_6tren)]Br$ (M = Mn, Fe, Co, Ni, Cu, Zn; Me_6tren = $N(CH_2CH_2NMe_2)_3$; 0.20–0.36 Å out of plane).[52–54] The displacement of the metal out of the plane results at least partially from the inability of the ethylene bridges to span the full 90° axial–equatorial angle. However, the displacement is not observed in the cobalt(I) complex $CoH(PP_3)$.[55]

Associated with this metal atom displacement is a shortening of the Fe–P(1) bond by 0.157 Å compared to the other Fe–P bonds in $[FeCl(PP_3Cy)]BPh_4$. Similar axial bond shortening is found in the PP_3 complexes mentioned above (e.g. 0.114–0.133 Å, for the Fe, Rh and Ni complexes) but not in the Me_6tren complexes. In octahedral and square-pyramidal PP_3 complexes as well, the bridgehead phosphorus is bound more tightly.[8,56]

The related complexes $[RuCl(dcpe)_2]^+$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) and $[FeBr(\textit{meso}\text{-}P_4)]^+$ adopt a distorted-TBP geometry, with the halide in an equatorial position trans to an equatorial P–M–P angle of less than 120° (93.1 and 105.0°, respectively).[57,58] This arrangement is not possible in the present complex because the ethylene bridges cannot span angles of greater than ~83°.

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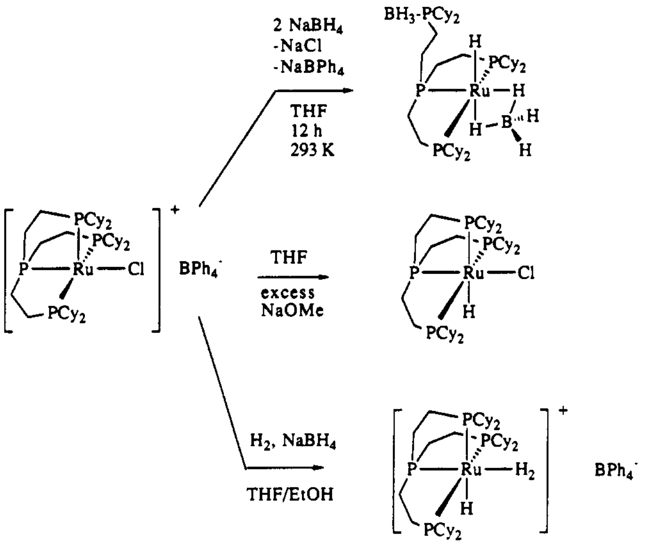
Scheme II



The Fe–Cl bond length is within the range observed for Fe–Cl bonds in iron(II) complexes (2.18–2.31 Å).[59-61] The Fe–P bonds in the present complex are longer than reported Fe–P bonds in other Fe(II) tris(*n*-butylphosphine) complexes (2.28–2.35 Å).[59,62,63] The BPh_4^- anion is tetrahedral with deviations of 3° or less from the ideal 109.5° C–B–C angles.

Preparation of Ruthenium Hydride Complexes. The chloride complexes $[RuCl(PP_3Cy)]X$ (X = Cl, BPh_4) are excellent starting materials for a range of hydride complexes stabilized by the tetradentate ligand $P(CH_2CH_2PCy_2)_3$ (PP_3Cy). The preparation reactions are summarized in Scheme II.

Preparation and Characterization of $RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)$. Treatment of $[RuCl(PP_3Cy)]Cl$ with excess $NaBH_4$ in THF produces $RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)$. In the ^1H NMR spectrum in C_6D_6 at room temperature, Ru–H is observed at −18.2 ppm as a doublet of triplets ($^2J(PH)$ = 36.6, 19.8 Hz). The hydride resonance pattern suggests that only three phosphorus atoms of the tetraphosphine ligand are coordinated to ruthenium, and the hydride is cis to the coordinated phosphorus atoms. The broad signals at −7.0 and 5.5 ppm are assigned to the bridging hydrides and terminal BH_2, respectively. The ^1H NMR parameters for the Ru–H and BH_4 groups are very similar to those of $RuH(\eta^2\text{-}BH_4)$(triphos) (triphos = $PhP(CH_2CH_2CH_2PCy_2)_2$,[64] $PhP(CH_2CH_2CH_2PPh_2)_2$[65]). The signals for the phosphine-bound BH_3 protons cannot be located, but they might be buried in the resonances of the ligand (0.8–2.8 ppm). The chemical shifts ranged from 0.24 to 1.50 ppm for several phosphine–borane complexes.[66-69] The presence of both $\eta^2\text{-}BH_4$ and $PCy_2{\cdot}BH_3$ groups is further supported by the $^{11}B\{^1H\}$ NMR spectrum, which displays two broad resonances at 12.7 and −42.9 ppm with $BF_3{\cdot}OEt_2$ as an external standard. The resonance at −42.9 ppm is assigned to the BH_3 group bound to the PCy_2 group. The chemical shift is in the range of literature values (ranging from −34.4 to −46.8 ppm with reference to $BH_3{\cdot}OEt_2$ for several $PR_3{\cdot}BH_3$ compounds).[66-73] The broad resonance at 12.7 ppm is assigned to the $\eta^2\text{-}BH_4$ group. The ^{11}B NMR signal for the $\eta^2\text{-}BH_4$ group appeared at 34.8 ppm for $Cp^*Ru(PMe_3)(BH_4)$,[74] −3.4 ppm for $Cp_2Zr(BH_4)Me$,[75] and −15.8 ppm for $Cp_2Zr(BH_4)_2$.[75] In the ^{31}P NMR spectrum of the new complex, the signal for the central phosphorus atom of the tetraphosphine appears at 123.8 ppm (dt, *J*(PP) = 32, 14 Hz), while the two PCy_2 groups mutually trans to each other appear at 78.1 ppm (d, *J*(PP) = 14 Hz). The resonance for the $PCy_2{\cdot}BH_3$ group is at 27.7 ppm (br), which is ca. 39.4 ppm downfield from that of the free ligand PP_3Cy (−16.7 ppm). Pronounced deshielding of phosphorus upon adduct formation of $BH_3{\cdot}PR_3$ compared with free PR_3 has been observed previously.[71]

Formation of the complex $RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)$ from the reaction of excess $NaBH_4$ with the complex $[RuCl(PP_3Cy)]^+$ seems related, at least partly, to the steric bulkiness of the PCy_2 groups of the ligand. Thus, one of the PCy_2 groups of the ligand PP_3Cy dissociates from the metal center during the reaction owing to the steric interactions between the PCy_2 groups. Treatment of $RuCl_2(PP_3)$ with excess $NaBH_4$ yields $RuH(\eta^1\text{-}BH_4)(PP_3)$.[8] There are a few reports concerning the dissociation of chelating phosphines. Reaction of $[CpFe(CO)(dppe)]^+$ with $LiAlH_4$ produced $CpFeH(CO)(\eta^1\text{-dppe})$ via the intermediate $CpFe(CHO)(\eta^2\text{-dppe})$.[76] Rapid exchanges of coordinated and uncoordinated PPh_2 groups have also been observed in $Rh(NO)(PP_3)$[77] and $Pt(Me)_2(ttp)$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$).[78] Ruthenium complexes of the type $RuH(\eta^2\text{-}BH_4)(P_3)$ appear to be quite stable, and many examples are known.[64,65,79-81]

Synthesis of $RuHCl(PP_3Cy)$. Treatment of $[RuCl(PP_3Cy)]Cl$ with excess NaOMe in refluxing THF for 5 h produces $RuHCl(PP_3Cy)$ as the only product. In the ^1H NMR spectrum in CD_2Cl_2, the hydride resonance is observed at −10.7 ppm (dtd, *J*(PH) = 96, 30, 22 Hz). The ^{31}P NMR spectrum in THF shows three resonances with relative intensities of 1:1:2. The highest frequency resonance at 148.8 ppm is assigned to the central phosphorus

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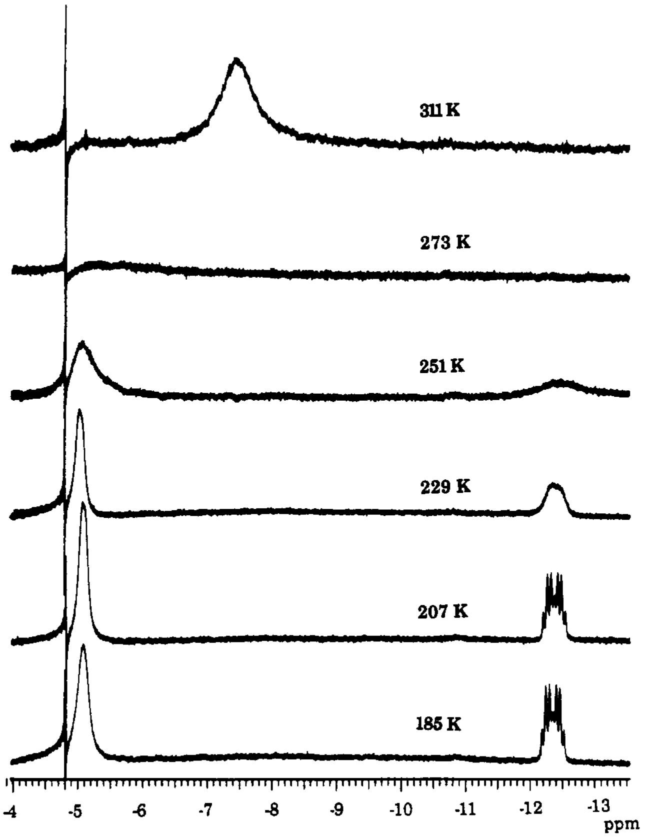

Figure 3. Variable-temperature ^{1}H NMR spectra of $[RuH(H_2)(PP_3Cy)]BPh_4$ in the hydride region (CD_2Cl_2, 400 MHz). There is a machine noise peak around −4.8 ppm.

atom of the ligand PP_3Cy (see Scheme II). The resonance for the two mutually trans PCy_2 groups appears at 54.3 ppm and that for the other PCy_2 group at 40.4 ppm. The hydride ligand is trans to the terminal PCy_2 group, as shown by a broad-band proton-coupled spectrum, in which the resonance at 40.4 ppm is split into a broad doublet. The spectroscopic parameters of the compound $RuHCl(PP_3Cy)$ are very similar to those of $RuHCl(PP_3)$.[8] The structural properties are probably similar to those of the crystallographically characterized octahedral complex $[Rh(NP_3Cy)H(Cl)]BPh_4$.[82]

Synthesis and Characterization of the Dihydrogen Complex $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$. The hydrido dihydrogen complex $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ is readily synthesized by the reaction of $[RuCl(PP_3Cy)]^+$ with $NaBH_4$ under a hydrogen atmosphere in THF/EtOH. The procedure is similar to that employed in synthesizing molecular dihydrogen complexes such as $[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ [9] and $[MH(\eta^2\text{-}H_2)(L_2)_2]^+$ (M = Fe, Ru, Os, L_2 = depe; M = Ru, Os, L_2 = dppe).[83] The compound is quite air sensitive both in the solid state and in solution. The dihydrogen ligand can be easily replaced by Cl^- to form $RuHCl(PP_3Cy)$. It also undergoes facile H_2/D_2 exchange at room temperature in solution. The stability with respect to loss of hydrogen under vacuum is considerably higher; no H_2 is lost if the solid complex is kept under vacuum for a few hours at room temperature. Other similar ruthenium molecular dihydrogen complexes such as $[RuH(\eta^2\text{-}H_2)(L_2)_2]^+$ (L_2 = dppe,[20] dtfpe (=1,2-bis(bis(trifluorotolyl)phosphino)ethane)[84]) and $[RuH(\eta^2\text{-}H_2)(L)_4]^+$ (L = $P(OMe)_3$, $P(OEt)_3$)[85] are known to lose H_2 readily.

Scheme III. ^{1}H and ^{31}P Site Exchange

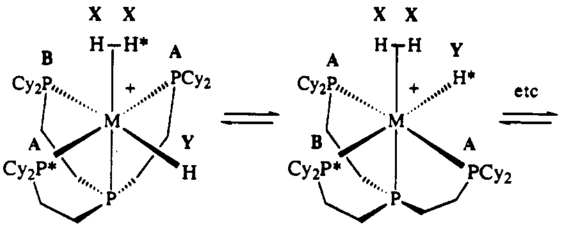

Table V. Free Energies of ^{1}H and ^{31}P Site Exchange in $[MH(H_2)L]^+$ Complexes (L = PP_3Cy, PP_3)

	M = Fe		M = Ru	
	T, K	ΔG‡, kcal/mol	T, K	ΔG‡, kcal/mol
		L = PP_3Cy		
$P^A \rightarrow P^B$	233	10.6	253	11.2
$H^X \rightarrow H^Y$	213	10.8	229	11.6
	263	11.1	273	11.5
		L = PP_3		
$P^A \rightarrow P^B$	273	12.3	269	12.5
$H^X \rightarrow H^Y$	290	12.6	303	13.1

At 35 °C, the ^{1}H NMR spectrum of $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ in the hydride region shows a broad resonance at ca. −7.45 ppm in CD_2Cl_2 (Figure 3). The broad hydride resonance separates into two signals when the temperature is lowered below −20 °C (at 400 MHz); one signal is a broad peak at ca. −5.1 ppm, and the other is a doublet of pseudoquartets at −12.35 ppm with an intensity ratio of ca. 2:1. The line shapes of the variable-temperature ^{1}H NMR spectra are typical for hydrido η^2-dihydrogen complexes with rapidly exchanging hydrogens at the metal center. The more intense signal is assigned to the dihydrogen signal. The multiplet resonance at −12.35 ppm is assigned to the terminal hydride. The doublet multiplicity results from the coupling of the hydride to a trans phosphorus atom (J(PH) = 64 Hz). The pseudoquartet pattern (J(PH) ≈ 24 Hz) is observed because the other three phosphorus atoms of the ligand all have similar coupling constants with the hydride. The hydride is trans to one of the terminal PCy_2 groups, as determined by a proton-coupled ^{31}P NMR spectrum at −60 °C in THF, where the resonance at 64.9 ppm appears as a broad doublet. Thus, the dihydrogen ligand must be located trans to the central phosphorus atom.

In fact, the variable-temperature ^{1}H NMR spectra in the hydride region are like those reported for the similar dihydrogen complex $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$, except that the η^2-H_2 and the hydride resonances coalesce at a lower temperature for $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]^+$ (273 K, 400 MHz) than for $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (303 K, 300 MHz).[8] The method of Shannan-Atidi and Bar-Eli[86] can be used to estimate the rates of H atom exchange for a system with site populations 2:1 and no-exchange peak separations of 2900 and 1818 Hz for the PP_3Cy and PP_3 complexes, respectively. The rates for H atoms traveling from site X to site Y as in Scheme III are 2900 and 1820 s^{-1}, respectively. The $\Delta G^{\ddagger}$ values for these rates are 11.5 and 13.1 kcal/mol, respectively (Table V).

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The presence of a η^2-H_2 ligand in the complex is confirmed by the T_1 values, which were measured by the inversion recovery method. At 38 °C and 400 MHz in CD_2Cl_2, the T_1 value for the broad hydride resonance is 46 ms. At −44 °C, the T_1 values for the dihydrogen resonance at −5.1 ppm and the hydride resonance at −12.35 ppm were measured to be 26 and 37 ms, respectively. The similarity in the T_1 values of the dihydrogen and the hydride signal is caused by the hydride site exchange of the hydride and dihydrogen ligand. Therefore, 229 K is approximately the temperature of relaxation coalescence. The rate constant of exchange ($H^X \rightarrow H^Y$) can be estimated as $1/T_1(H^Y)$,[87] and thus an activation free energy of 11.6 kcal/mol is calculated (Table V). As the temperature is further decreased, the value for the hydride resonance increases and is 135 ms at −88 °C. The minimum T_1 value for the dihydrogen signal was observed to be 24 ms at −66 °C. An H–H distance of 0.91 Å is calculated from this value, assuming that the dihydrogen ligand is rapidly spinning.[20] This value will be larger (up to 0.93 Å), depending on how many cyclohexyl protons contribute to the relaxation.[88] It should be noted that an alternative H–H distance of about 1.15 Å can be calculated from the minimum T_1 value on the assumption of no rapid internal motion of the H_2 ligand.[89] However, the large J(HD) coupling for the HD isotopomer (see below) suggests that the 0.91–0.93 Å range of distances is more appropriate.

A shorter minimum T_1 value (8 ms in THF, 6 ms in acetone at 300 MHz) is observed for the dihydrogen resonance in the similar complex $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$.[8] Thus, the H–H distance in the more basic complex $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]^+$ (approximately 0.92 Å) is longer than that in $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (approximately 0.80 Å), as one might expect.

Further evidence for the presence of a dihydrogen ligand is the observation of an H–D coupling in the isotopomer $[RuH_xD_{3-x}(PP_3Cy)]BPh_4$. Partially deuterated (ca. 50% deuterium) $[RuH_xD_{3-x}(PP_3Cy)]BPh_4$ is prepared by storing a ^{1}H NMR sample of $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ in CD_2Cl_2 under an atmosphere of HD gas for ca. 10 min. At −60 °C, the spectrum displays a broad pseudoquartet at −5.1 ppm, which is assigned to the resonance of the η^2-HD molecule. The pseudoquartet arises from the 1:1:1 triplet due to H–D coupling, which is further split into doublets due to coupling of the H–D proton to the trans central phosphorus atom of PP_3Cy. An accurate simulation of the spectrum was obtained by using ^1J(HD) and ^2J(PH) coupling constants of 28 and 32 Hz, respectively. Strong coupling of HD to the trans phosphorus has been observed in other η^2-H_2 complexes.[6,8,90] The ^1J(HD) coupling constant of 28 Hz confirms that the H–D bond is intact. The compound also exhibits a primary isotopic shift (δ(HD) − $\delta(H_2)$) of −50 ppb. A ^1J(HD) coupling constant of 29.7 Hz and a secondary isotopic shift (δ(HD) − $\delta(H_2)$) of 20 ppb were observed for $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$.[8]

A THF solution of the dihydrogen complex $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]^+$ displays interesting variable-temperature ^{31}P NMR spectra, as shown in Figure 4. At room temperature the spectrum consists of an AM_3 splitting pattern, which indicates that all the terminal PCy_2 groups are made equivalent by rapid site-exchange processes. The signal for the bridgehead phosphorus atom appears at 144.4 ppm (q, J(PP) = 13.7 Hz) and that for the terminal PCy_2 groups at 73.0 ppm (br). When the temperature is lowered, the resonance at 144.4 ppm does not undergo appreciable change except that the line becomes more broad because of the decrease in T_2. However, dramatic changes occur for the signal at 73.0 ppm. As the temperature is lowered, the signal is separated into two broad peaks at 213 K, one at 76.6 ppm and the other one at 64.9 ppm, with an intensity ratio of 2:1. The coalescence temperature is 253 K for this process of exchanging nuclei with a frequency separation of 948 Hz, and the ΔG^* value calculated is 11.2 kcal/mol for the site-exchange process $p^A \rightarrow P^B$ (Scheme III). The similarity to the activation energies from the ^{1}H NMR spectra suggests that H atom and terminal P group exchange processes are concurrent. We have estimated a ΔG^* value of 12.5 kcal/mol from the ^{31}P NMR data reported for the complex $[Ru(\eta^2\text{-}H_2)(H)(PP_3)]^+$. The coalescence temperature for this complex is 269 K with a peak separation of 330 Hz. Again, the ΔG^* values from the H atom and P group exchange process are similar for this PP_3 complex. Bianchini et al.[8] report a ΔG^* value at this temperature of 12 ± 1 kcal mol^{-1} for the P group exchange. Therefore, the bulkier PCy_2 groups of the electron-donating PP_3Cy favor the H and P site exchange processes compared to the PPh_2 groups of the PP_3 ligand,

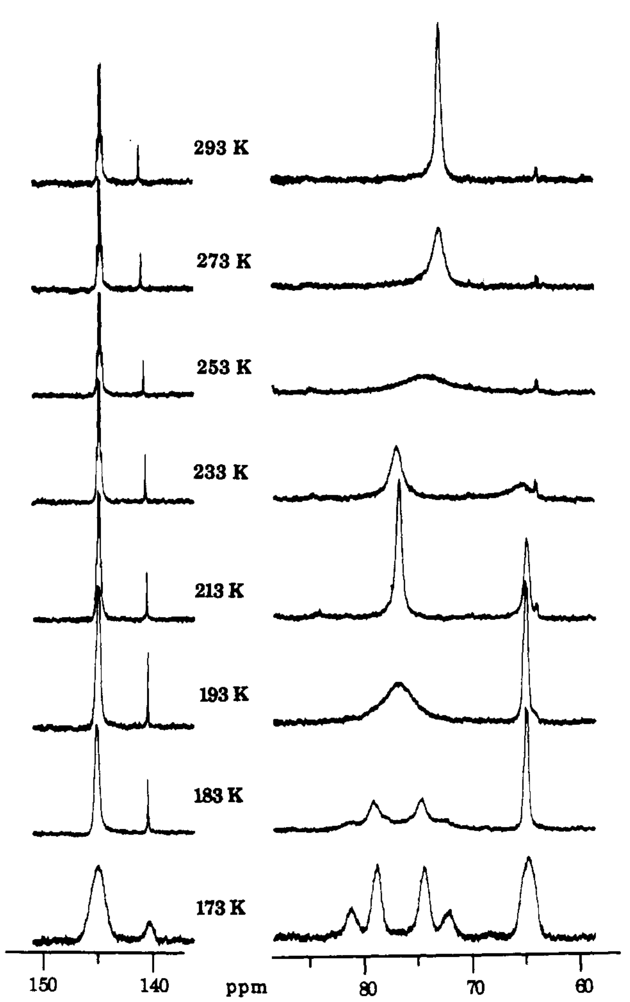

Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[RuH(H_2)(PP_3Cy)]BPh_4$ in THF (80.98 MHz). The chemical shift scale is referenced to $P(OMe)_3$ (singlet at 140.4 ppm).

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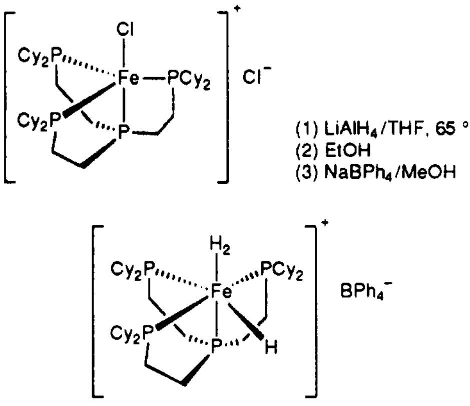
assuming that the $\Delta G^{\ddagger}$ values are not very temperature dependent. This is consistent with the trihydrogen transition state of Scheme I. The bulkier PCy_2 would force the C_{3v} structure, as discussed earlier. However, an equally valid intermediate could be the seven-coordinate trihydride $[M(H)_3(L)]^+$ (L = PP_3, PP_3Cy). The more basic PCy_2 groups would facilitate the oxidative addition of the dihydrogen ligand.

While the signal at 64.9 ppm becomes sharper when the temperature is lowered to 173 K, the signal at 76.6 ppm is separated into two resonances with an AB splitting pattern at 80.0 and 73.2 ppm and coupling constants of ca. 190 Hz. The magnitude of the J(PP) coupling constant indicates that the two phosphorus atoms are trans to each other.[91] The $\Delta G^{\ddagger}$ value is 8 kcal/mol for this site exchange with a coalescence temperature of approximately 190 K. It is assumed that restricted rotation of the cyclohexyl groups renders the trans PCy_2 groups (P^A in Scheme III) inequivalent. The less bulky PPh_2 groups of the PP_3 ligand in $[Ru(\eta^2\text{-}H_2)(H)(PP_3)]^+$ do not become inequivalent at low temperature. Similar inequivalence of two mutually trans PCy_2 groups at low temperature has previously been observed in the six-coordinate complexes $[MX(L)(dcpe)_2]^+$ (M = Ru, Os; dcpe = $Cy_2PCH_2CH_2PCy_2$).[57,92]

Attempts To Synthesize $RuH_2(PP_3Cy)$. We have attempted to synthesize and characterize the dihydride complex $RuH_2(PP_3Cy)$. It appears that the dihydride complex is unstable and decomposes to give some polymeric materials. Thus, treatment of $[RuCl(PP_3Cy)]Cl$ in THF with excess $LiAlH_4$ or $LiBHEt_3$ produces a colorless solution. A ^{31}P NMR spectrum of the solution indicates that the predominant product displays a doublet at −59.5 ppm for the terminal PCy_2 groups and a quartet at 12.1 ppm for the central phosphorus atom. The same compound could also be obtained by the reaction of $[RuCl(PP_3Cy)]Cl$ in benzene, ether, or hexane with excess $LiBHEt_3$. The compound is soluble in solvents such as benzene, Et_2O, and hexane and reacts with MeOH to form $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]^+$. Thus, the compound is likely to be $Ru(H)_2(PP_3Cy)$. However, the compound is unstable, especially under vacuum. An insoluble white solid is obtained when the solvent of the reaction mixture is removed completely under vacuum after the synthesis. Thus, we were unable to fully characterize the compound.

Preparation and Characterization of $[FeH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$. Reaction of the purple complex $[FeCl(PP_3Cy)]Cl$ with $LiAlH_4$ in hot THF under dinitrogen, followed by addition of ethanol and then $NaBPh_4$ in methanol, gives the dihydrogen complex $[FeH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ as a pale yellow powder in poor yield (eq 4). The reaction intermediates and product must be stable with respect to substitution by dinitrogen. The complex $[Fe(\eta^2\text{-}H_2)H(PP_3)]^+$ is known to react extremely slowly with dinitrogen.[10] The parent ion of the FAB mass spectrum of the product corresponds to $FeH_2(PP_3Cy)^+$. We have found that the loss of metal-bonded H atoms in FAB mass spectral determinations is quite common. However, the NMR properties of the complexes are very similar to those of the Ru congener. The minimum T_1 of approximately 29 ms for the dihydrogen resonance occurs at −66 °C compared to 24 ms at −66 °C for the Ru complex at 400 MHz (Table I). The calculated H–H distance for the complex is 0.96 Å, with the assumption of rapid spinning and some contribution to the relaxation from other ligands; the less likely alternative distance for a nonspinning H_2 ligand would be 1.21 Å.



(4)

The ^1H and ^{31}P NMR spectra of the iron complex change with temperature in a fashion very similar to that for the ruthenium complex. The 400-MHz ^1H NMR spectrum at 193 K consists of a broad peak at −9.35 ppm (η^2-H_2) and a pseudoquartet at −15.96 ppm (hydride). The latter pattern is slightly different from the doublet of quartets observed for the Ru analogue because iron has, as a rule, $|J(PH)_{trans}| < |J(PH)_{cis}|$ whereas Ru has the reverse with $|J(PH)_{cis}| < |J(PH)_{trans}|$; this trend has been noted before[18,93] and is true in isostructural complexes of the type *cis*-$MH_2(dmpe)_2$[93] (dmpe = 1,2-bis(dimethylphosphino)ethane), *cis*-$MH_2(dppe)_2$,[20] *cis*-$MH(R)(dmpe)_2$,[93,94] and $[M(H_2)H(PP_3)]^+$ (M = Fe, Ru).[8,9] At −60 °C the T_1 values of the H_2 and H ligands are nearly equal (relaxation coalescence). An exchange rate constant ($H^X \rightarrow H^Y$) of 30 s^{-1} and a $\Delta G^{\ddagger}$ value of 10.8 kcal/mol is calculated on the basis of this information (Table V). The line shape coalescence temperature is approximately −10 °C, and a $\Delta G^{\ddagger}$ value of 11.1 kcal/mol is estimated for the exchange at this temperature. At 20 °C the near fast exchange spectrum is a broad singlet at −11.4 ppm, which is close to the weighted average (−11.5 ppm) of the no-exchange chemical shifts.

At −66 °C the ^{31}P NMR spectrum of the iron complex is very similar to that of the Ru complex and consistent with a structure where the PP_3Cy ligand occupies four sites on an octahedral complex. The central P atom has a chemical shift of 171.9 ppm (acetone-d_6 solvent) and gives a quartet pattern. Two trans PCy_2 groups (atoms P^A in Scheme III) produce a broad singlet (intensity approximately 2) at 97.4 ppm, and the unique PCy_2 terminal group (P^B) gives a broad peak at 90.9 ppm. Line shape coalescence of the signals corresponding to P^A and P^B is observed at 233 K. A $\Delta G^{\ddagger}$ value of 10.6 kcal/mol is calculated. This agrees well with the $\Delta G^{\ddagger}$ values from the ^1H spectra and suggests that the $2H^X \rightleftharpoons H^Y$ and $2P^A \rightleftharpoons P^B$ processes are linked to each other as indicated in Scheme III. We have calculated corresponding energies $\Delta G^{\ddagger}$ for the complex $[Fe(\eta^2\text{-}H_2)(H)(PP_3)]^+$ from the literature data[9,10] and include them also in Table V for comparison. Recently Bianchini et al. have reported a detailed line shape analysis of the $^{31}P\{^1H\}$ spectra of $[Fe(\eta^2\text{-}H_2)(H)(PP_3)]^+$ and obtained activation parameters:

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[92] Mezzetti, A.; Zotto, A. D.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1990**, 251.

[93] Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080.

[94] Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

$\Delta G^\ddagger$(263 K) = 12 ± 1, $\Delta H^\ddagger$ = 9.7 ± 0.5 kcal mol^{-1}, $\Delta S^\ddagger$ = −9 ± 2 cal K^{-1}.[10] These parameters are consistent with the $\Delta G^\ddagger$ values reported in Table V, and they can be used to calculate $\Delta G^\ddagger$(233 K) = 11.8 kcal mol^{-1} for the PP$_3$ complex for comparison with $\Delta G^\ddagger$(233 K) = 10.6 kcal mol^{-1} for the PP$_3$Cy complex. Clearly the PP$_3$Cy ligand promotes faster exchange of terminal PR$_2$ groups than the PP$_3$ ligand.

At 20 °C the ^{31}P NMR spectrum of the iron complex is at the fast exchange limit. The terminal PCy$_2$ groups give one resonance at 98.8 ppm. This is not the weighted average of the no-exchange chemical shifts measured at −66 °C because these shifts are quite temperature dependent.

Below −66 °C the resonance due to P^A broadens and then decoalesces into two broad singlets of equal intensity at 104.4 and 89.4 ppm. The coalescence temperature for this process is 190 K, and $\Delta G^\ddagger$ is 8.0 kcal/mol. The trans P^A nuclei become inequivalent because of restricted rotation of the PCy$_2$ groups. This behavior is not observed for the corresponding PP$_3$ complex.

Comparison of Energy Barriers to Exchange. The data in Table V indicate that the movement of ligand groups as suggested by Scheme III is slightly easier for iron than for ruthenium. This is a common trend for H$_2$/H exchange for both cis and trans complexes of the type [M(η^2-H$_2$)(H)L$_4$]$^+$.[87] Exchange is also easier for the more electron donating and bulky PP$_3$Cy ligand (L$_4$) when compared to the PP$_3$ ligand. Again, this trend is observed for other [M(η^2-H$_2$)(H)L$_4$]$^+$ complexes. The trihydride intermediate [M(H)$_3$(PP$_3$Cy)]$^+$ would be as consistent with the observations as the trihydrogen intermediate of Scheme I. Trihydride complexes [M(H)$_3$(L$_2$)$_2$]$^+$ have been proposed as intermediates for H$_2$–H exchange in the past.[20]

Conclusion. We have developed a simple method for the synthesis of the very bulky and electron-rich tetradentate phosphine P(CH$_2$CH$_2$PCy$_2$)$_3$. The ^{31}P NMR data strongly suggest that the tetraphosphine reacts with RuCl$_2$(PPh$_3$)$_3$ to form the square-pyramidal five-coordinate complex [RuCl(PP$_3$)]$^+$, possibly distorted toward a trigonal-bipyramidal geometry because of the steric interaction of the bulky PCy$_2$ groups. The corresponding iron complex has an undistorted-trigonal-bipyramidal geometry. Reaction of [RuCl(PP$_3$Cy)]$^+$ with NaBH$_4$ results in the formation of *mer*-RuH(η^2-BH$_4$)(η^3-PP$_3$Cy·BH$_3$); i.e., one of the PCy$_2$ groups dissociates from the metal center during the reaction. Treatment of [RuCl(PP$_3$Cy)]$^+$ with NaOMe in THF produced RuHCl(PP$_3$Cy). The molecular dihydrogen complexes [MH(η^2-H$_2$)(PP$_3$Cy)]$^+$ are also prepared from [MCl(PP$_3$Cy)]$^+$. Spectroscopic data suggest that there is no exchange or interaction between the H$_2$ ligand and the terminal hydride at low temperature, while T_1 averaging (relaxation coalescence) is observed at −44 °C for the ruthenium complex and −60 °C for the iron complex at 400 MHz due to slow intramolecular exchange between the H and H$_2$ ligands. It remains to be seen whether or not a stable η^3-H$_3$ complex can be synthesized.

Acknowledgment. This research was supported by grants to R.H.M. from the Natural Science and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a loan of ruthenium chloride from Johnson Matthey Co. We thank Ms. Diana Xu and Judith Jebanathirajah for help in preparing the manuscript.

Supplementary Material Available: Figures giving ^{31}P{^{1}H} NMR spectra for [Fe(H$_2$)(H)(PP$_3$Cy)]$^+$ and an ORTEP view of the BPh$_4^-$ anion and a packing diagram of the unit cell of [FeCl(PP$_3$Cy)]BPh$_4$ and tables of calculated hydrogen coordinates, thermal parameters, and bond distances and angles for [FeCl(PP$_3$Cy)]BPh$_4$ (10 pages). Ordering information is given on any current masthead page.

OM920534B