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New Superhindered Polydentate Polyphosphine Ligands $P(CH_2CH_2P^tBu_2)_3$, $PhP(CH_2CH_2P^tBu_2)_2$, $P(CH_2CH_2CH_2P^tBu_2)_3$, and their Ruthenium(II) Chloride Complexes

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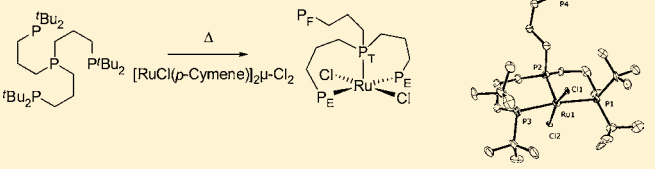
Supporting Information

ABSTRACT: The synthesis and characterization of the extremely hindered phosphine ligands, $P(CH_2CH_2P^tBu_2)_3$ ($P^2P_3^{tBu}$, **1**), $PhP(CH_2CH_2P^tBu_2)_2$ ($PhP^2P_2^{tBu}$, **2**), and $P(CH_2CH_2CH_2P^tBu_2)_3$ ($P^3P_3^{tBu}$, **3**) are reported, along with the synthesis and characterization of ruthenium chloro complexes $RuCl_2(P^2P_3^{tBu})$ (**4**), $RuCl_2(PhP^2P_2^{tBu})$ (**5**), and $RuCl_2(P^3P_3^{tBu})$ (**6**). The bulky $P^2P_3^{tBu}$ (**1**) and $P^3P_3^{tBu}$ (**3**) ligands are the most sterically encumbered PP_3-type ligands so far synthesized, and in all cases, only three phosphorus donors are able to bind to the metal center. Complexes $RuCl_2(PhP^2P_2^{tBu})$ (**5**) and $RuCl_2(P^3P_3^{tBu})$ (**6**) were characterized by crystallography. Low temperature solution and solid state $^{31}P\{^1H\}$ NMR were used to demonstrate that the structure of $RuCl_2(P^2P_3^{tBu})$ (**4**) is probably analogous to that of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) which had been structurally characterized.



INTRODUCTION

The multihapticity, strong donor ability, and lipophilicity of alkyl-substituted polydentate phosphines make them good ligands for controlling the stereochemistry of coordination complexes and solubilizing metal catalysts.[1] Ruthenium and iron complexes of PP_3-type ligands $P((CH_2)_nPR_2)_3$ (n = 2, 3 ; R = Me, Et, ^{i}Pr, Ph) have been used in a wide variety of applications including the formation of stable dinitrogen complexes (in a range of oxidation states) and in the C−H activation and the stabilization of η^2-dihydrogen complexes.[2]

The PP_3-type ligands provide a strong coordination environment, and they generally coordinate up to four points through the four strong phosphine donors. The geometry of coordination is constrained by the ligand, and when all four of the phosphines are bound, an octahedral complex must have the remaining two coordination sites geometry constrained in a cis arrangement (in adjacent coordination sites). The cis stereochemistry often results in higher catalytic activity for processes like migratory insertion or reductive elimination where a cis arrangement of the two nonphosphine ligands is essential.[3]

Additionally, bulky phosphines have been particularly good ligands to enhance the catalytic activity of transition metal systems in a range of applications e.g. tri(cyclohexyl)phosphine enhances the activity of Grubbs' catalyst,[4] and the *tertiary*-butyl groups on phosphine ligands such as tri(*tert*-butyl)phosphine have also afforded particularly active catalysts.[5]

There is now an expanding range of sterically encumbered, polydentate ligands available,[6] but to this point, the bulkiest groups employed on the terminal phosphines of PP_3-type polydentate phosphine ligands have been either isopropyl groups ($P(CH_2CH_2{}^iPr_2)_3$[2i] and $P(CH_2CH_2CH_2{}^iPr_2)_3$[2h]) or cyclohexyl groups ($P(CH_2CH_2Cy_2)_3$).[7] The work described in this paper explores the effect of increasing steric bulk on polydentate phosphines by investigating tetradentate PP_3 ligands with *tertiary*-butyl groups as substituents on the terminal phosphines. We report here the synthesis of the hindered tripodal tetradentate phosphine ligands $P(CH_2CH_2P^tBu_2)_3$ ($P^2P_3^{tBu}$, **1**) and $P(CH_2CH_2CH_2P^tBu_2)_3$ ($P^3P_3^{tBu}$, **3**) as well as the hindered tridentate phosphine ligand $PhP(CH_2CH_2P^tBu_2)_2$ ($PhP^2P_2^{tBu}$, **2**).

This work reports the synthetic routes to the hindered ligands as well as the formation and characterization of their ruthenium chlorido complexes. Characterization of the complexes allows an analysis of the binding mode of this new series of bulky ligands and the behavior of the complexes, both in solution and the solid state.

RESULTS AND DISCUSSION

Preparation and Characterization of Phosphine Ligands. *$P(CH_2CH_2P^tBu_2)_3$, $P^2P_3^{tBu}$ (1).* This was prepared by the base-induced (lithium diisopropylamide, LDA) addition of di(*tert*-butyl)phosphine to trivinylphosphine in a method modified from that of Morris et al. used in the synthesis of analogous tripodal tetradentate phosphine ligands (Scheme 1).[7] In the $^{31}P\{^1H\}$ spectrum of $P^2P_3^{tBu}$ (**1**), two resonances are observed at 34.1 and −15.3 ppm, in a ratio of 3:1 assigned to the three terminal phosphines and the central phosphine, respectively. As is typical in PP_3-type ligands with ethylene bridges, coupling between the terminal and central phosphines

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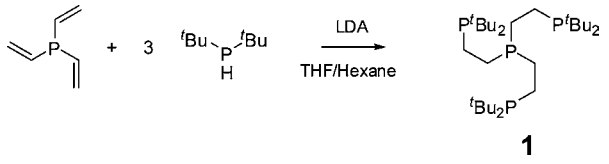
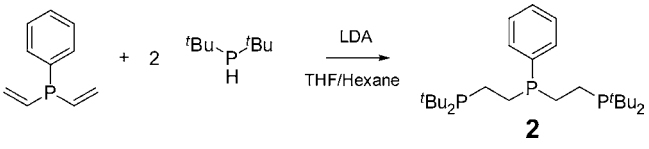
Scheme 1



($^3J_{P-P}$ = 24.9 Hz) is observed even before coordination to the metal center.

*$PhP(CH_2CH_2P^tBu_2)_2$ ($PhP^2P_2^{tBu}$, **2**).* The literature methods[8] for the synthesis of divinylphenylphosphine from dichlorophenylphosphine by reaction with vinylmagnesium bromide are low yielding. Divinylphenylphosphine was synthesized by an alternative approach by reaction of 2 equiv of vinylmagnesium bromide with 1 equiv of diethoxyphenylphosphine in a method analogous to that of King et al. using di(*n*-butoxy)-phenylphosphine as the starting substrate.[9] $PhP^2P_2^{tBu}$ (**2**) was subsequently prepared by the base-induced (lithium diisopropylamide) addition of di(*tert*-butyl)phosphine to divinylphenylphosphine in a method similar to that used above for the synthesis of $P^2P_3^{tBu}$ (**1**) (Scheme 2). In the $^{31}P\{^1H\}$ spectrum

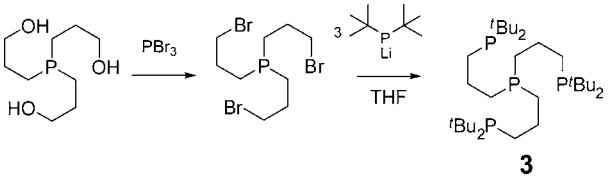
Scheme 2



of $PhP^2P_2^{tBu}$ (**2**), two resonances are observed at 34.0 and −16.9 ppm, in a ratio of 2:1, and these are assigned to the two terminal phosphines and the central phosphine, respectively. Coupling between the ^{31}P nuclei ($^3J_{P-P}$ = 27 Hz) is observed even before coordination to the metal center.

*$P(CH_2CH_2CH_2P^tBu_2)_3$, ($P^3P_3^{tBu}$, **3**).* This was prepared by the nucleophilic substitution of bromide in the reaction of lithium di(*tert*-butyl)phosphide, (LiP^tBu_2), with *tris*(3-bromopropyl)-phosphine (Scheme 3), in a method analogous that used for the

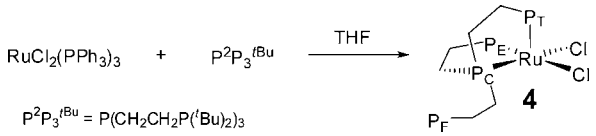
Scheme 3



synthesis of a related tripodal tetradentate phosphine ligand $P(CH_2CH_2CH_2P^iPr_2)_3$.[2h] In the $^{31}P\{^1H\}$ NMR spectrum of $P^3P_3^tBu$ (**3**), two resonances are observed at 26.2 and −35.5 ppm, in a ratio of 3:1 assigned to the terminal phosphines and the central phosphine respectively. Both resonances are singlets with no discernible coupling between the two phosphine environments, and this is consistent with data reported for other P^3P_3-type ligands incorporating propylene bridges between the apical and terminal phosphines.[2b,h]

Preparation and Characterization Ruthenium Chlorido Complexes. *$RuCl_2(P^2P_3^{tBu})$ (**4**).* Addition of $P^2P_3^{tBu}$ (**1**) to a tetrahydrofuran (THF) solution of $RuCl_2(PPh_3)_3$ afforded $RuCl_2(P^2P_3^{tBu})$ (**4**) as a tan solid which was isolated by filtration (Scheme 4).

Scheme 4



In the $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^2P_3^{tBu})$ (**4**) at room temperature, the two bound terminal phosphines P_E/P_T appear as a single very broad resonance ($W_{1/2}$ = 55 Hz at 162 MHz; CD_2Cl_2 solution) centered around 91.4 ppm. The central phosphine P_C appears as a doublet of triplets at 106.2 ppm with a $^3J_{P-P}$ coupling constant of 37 Hz to P_F, and a $^2J_{P-P}$ coupling constant of 17.5 Hz to P_E/P_T respectively. The resonance at 34.3 ppm is assigned to the pendant phosphine (not bound to the metal center) because (i) P_F displays no coupling to the other terminal phosphines P_E and P_T; and (ii) P_F has a chemical shift of 34.3 ppm, which is very close to the chemical shift observed for the terminal phosphines in the free ligand (34.1 ppm).

When the $^{31}P\{^1H\}$ NMR spectra of (**4**) were collected at lower temperatures (systematically down to about −100 °C, Figure 1), the P_E/P_T resonance broadened into the baseline

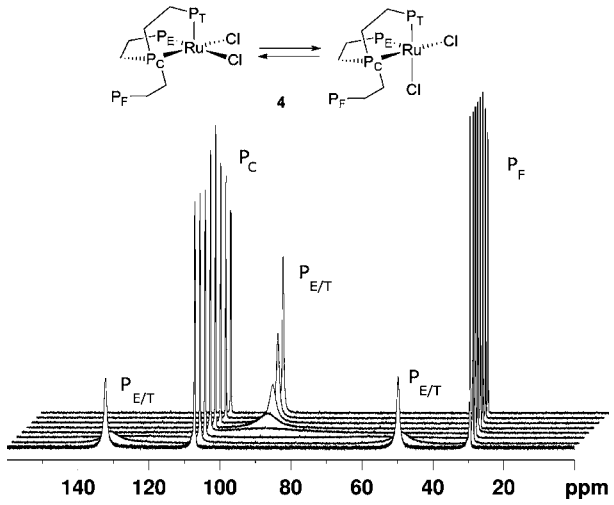
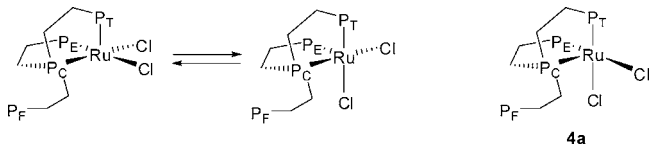


Figure 1. Variable temperature $^{31}P\{^1H\}$ NMR spectra (243 MHz, solvent: CD_2Cl_2) of $RuCl_2(P^2P_3^{tBu})$ (**4**) with spectra at (from front) 174, 188, 204, 220, 236, 252, 268, and 284 K.

before resolving and sharpening into two separate resonances at 132 and 50 ppm. This behavior can be ascribed to the two bound, terminal phosphines, P_E and P_T, being in fast exchange at room temperature—probably associated with the degenerate isomerization of Cl in the coordination sphere (Scheme 5).

Scheme 5



Simulation[10] of the exchange-broadened $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^2P_3^{tBu})$ (**4**) gives rates for the exchange process where at 174 K, $k \approx 800\ s^{-1}$ and 220 K, $k \approx 100\,000\ s^{-1}$. There is no evidence for the presence of a third steroisomer

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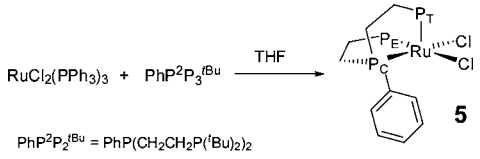
(**4a**) where the vacant coordination site is trans to P_C (the central phosphine).

*$RuCl_2(PhP^2P_2^{tBu})$ (**5**).* Addition of a THF solution of $RuCl_2(PPh_3)_3$ to a THF solution of $PhP^2P_2^{tBu}$ (**2**), followed by stirring overnight and addition of hexane, afforded $RuCl_2(PhP^2P_2^{tBu})$ (**5**) as a yellow solid (Scheme 6). Crystals

Scheme 6



suitable for structural analysis were grown by slow diffusion of pentane into a dichloromethane solution of **5** (Figure 2) and selected bond angles and lengths are given in Table 1.

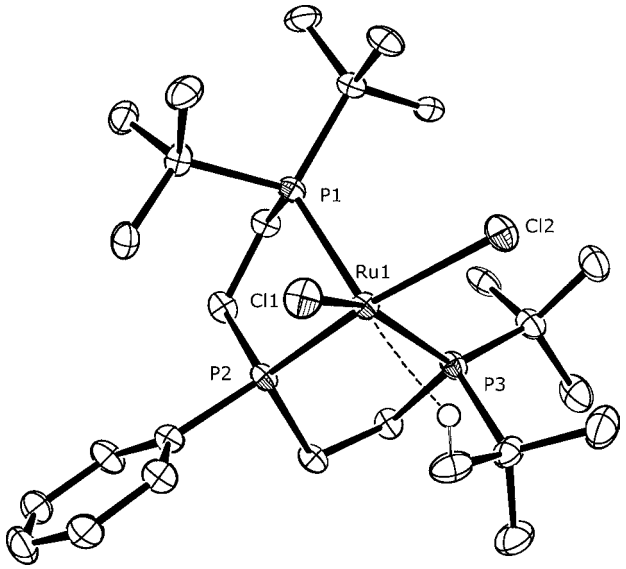


Figure 2. ORTEP plot (50% thermal ellipsoids) of $RuCl_2(PhP^2P_2^{tBu})$ (**5**), selected hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $RuCl_2(PhP^2P_2^{tBu})$ (5)

Ru1–Cl1	2.4257(10)	Ru1–Cl2	2.4628(10)
Ru1–P1	2.2748(11)	Ru1–P2	2.2652(11)
Ru1–P3	2.3849(11)		
Cl1–Ru1–Cl2	85.65(4)	P1–Ru1–Cl1	96.06(4)
P1–Ru1–Cl2	101.59(4)	P1–Ru1–P2	82.00(4)
P1–Ru1–P3	111.66(4)	P2–Ru1–P3	81.96(4)
P2–Ru1–Cl1	103.86(4)	P2–Ru1–Cl2	169.52(4)
P3–Ru1–Cl1	152.26(4)	P3–Ru1–Cl2	87.56(4)

The geometry of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) is a distorted square-based pyramid with atoms Cl1, Cl2, P2, and P3 making up the base and P1 at the apex. The structure has a τ value of 0.29, where τ is a geometric parameter indicative of 5-coordinate complex geometry where τ = 0 is perfect square pyramidal geometry and τ = 1 is perfect trigonal-bipyramidal geometry.[11] One of the *tertiary*-butyl methyl groups fills and blocks the void under the base of the pyramid, through an anagostic (pseudoagostic) interaction (d(Ru–H) 2.34(3) Å and ∠(Ru–H–C) 111(2)°).[12]

The structure of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) is comparable to that of $RuCl_2(PhP(CH_2CH_2CH_2PCy_2)_2)$[13] and $RuCl_2(PhP(CH_2CH_2PPh_2)_2)$,[14] both of which are 5-coordinate complexes with similar $PhP^nP_2^R$ ligands on ruthenium and two chloro ligands arranged in cis coordination sites. $RuCl_2(PhP(CH_2CH_2CH_2PCy_2)_2)$ (τ = 0.50) and $RuCl_2(PhP(CH_2CH_2PPh_2)_2)$ (τ = 0.37) are both more significantly distorted toward a trigonal bipyramidal character than **5** but neither to the extent that they would be classified as trigonal bipyramidal geometry. There is also a difference in the way the tridentate ligand is bound geometrically. The central phosphorus of complexes $RuCl_2(PhP(CH_2CH_2CH_2PCy_2)_2)$ and $RuCl_2(PhP(CH_2CH_2PPh_2)_2)$ is located at the apex of the square based pyramids while for complex **5** it is located within the base of the pyramid with a terminal phosphine at the apex. There is a trend toward lengthening of the Ru–P bonds as the steric bulk on the terminal phosphines increases from phenyl (Ru–P = 2.198(2), 2.260(2), 2.280(2) Å) to cyclohexyl (Ru–P = 2.211(1), 2.276(1), 2.306(1) Å) to *tert*-butyl, (Ru–P = 2.265(1), 2.275(1), 2.385(1) Å).

The $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) has the two bound terminal phosphines P_E/P_T as a very broad resonance at 92.3 ppm ($W_{1/2}$ = 75 Hz at 162 MHz; CD_2Cl_2 solution, 298 K). The central phosphine P_C appears as a triplet at 94.4 ppm, with a $^2J_{P-P}$ coupling constant of 12.6 Hz to P_E/P_T. $^{31}P\{^1H\}$ NMR spectra were also collected at decreased temperatures down to about −90 °C (Figure 3). As the

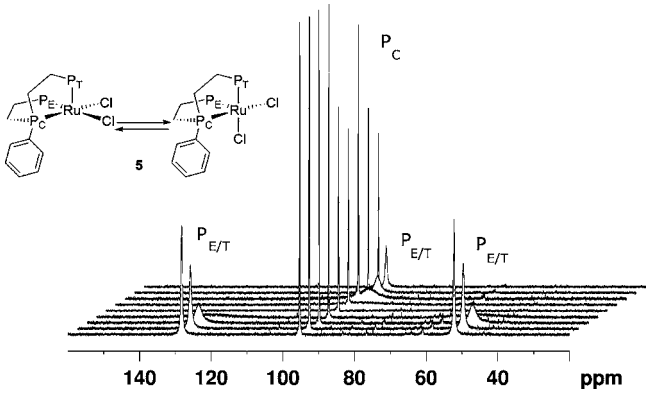


Figure 3. Variable temperature $^{31}P\{^1H\}$ NMR spectra (243 MHz, solvent: CD_2Cl_2) of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) with spectra at (from front) 179, 184, 195, 211, 226, 226, 243, 259, 275, and 300 K.

temperature descended the P_E/P_T resonance broadened into the baseline before resolving into two separate resonances at 128 and 52 ppm. As observed for $RuCl_2(P^2P_3^{tBu})$ (**4**), the resonances for P_E and P_T are in fast exchange at room temperature and the NMR data is consistent with a fluxional 5-coordinate complex with the exchange similar to that depicted in Scheme 5. This assignment is also consistent with the structural data from the X-ray crystal structure.

*$RuCl_2(P^3P_3^{tBu})$ (**6**).* While, $RuCl_2(P^3P_3^{tBu})$ (**6**) could be prepared in a similar manner to the syntheses of $RuCl_2(P^2P_3^{tBu})$ (**4**) and $RuCl_2(PhP^2P_2^{tBu})$ (**5**) (by the direct reaction of $RuCl_2(PPh_3)_3$ with $P^3P_3^{tBu}$ ligand), the separation of $RuCl_2(P^3P_3^{tBu})$ (**6**) from the triphenylphosphine byproduct was difficult. A better route to $RuCl_2(P^3P_3^{tBu})$ (**6**) was by reaction of a toluene solution of $P^3P_3^{tBu}$ (**3**) with di-μ-

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chlorobis[(*p*-cymene)chlororuthenium]. $RuCl_2(P^3P_3^{tBu})$ (**6**) was isolated cleanly as a green solid and crystals suitable for structural analysis were grown by slow evaporation of a toluene solution (Figure 4). Selected bond angles and lengths are given in Table 2.

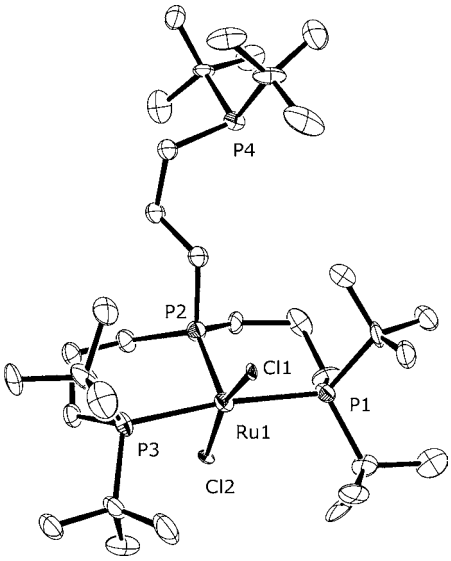

Figure 4. ORTEP plot (50% thermal ellipsoids) of $RuCl_2(P^3P_3^{tBu})$ (**6**). Hydrogen atoms have been removed for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $RuCl_2(P^3P_3^{tBu})$ (6)

Ru1−Cl1	2.416(3)	Ru1−Cl2	2.467(3)
Ru1−P1	2.411(4)	Ru1−P2	2.195(4)
Ru1−P3	2.408(4)		
Cl1−Ru1−Cl2	164.11(13)	P1−Ru1−Cl1	88.96(13)
P1−Ru1−Cl2	89.57(14)	P1−Ru1−P2	93.59(16)
P1−Ru1−P3	172.88(17)	P2−Ru1−P3	93.20(16)
P2−Ru1−Cl1	114.45(15)	P2−Ru1−Cl2	81.43(14)
P3−Ru1−Cl1	90.18(13)	P3−Ru1−Cl2	89.32(14)

The geometry of $RuCl_2(P^3P_3^{tBu})$ (**6**) is a distorted square-based pyramid with the central phosphorus P_C occupying the apical position. Only two of the three terminal phosphines P_E are bound to ruthenium and they are in mutually trans positions. The two chloride ligands are also in mutually trans positions, with the two terminal phosphines making up the base of the pyramid (τ = 0.15). There are six previously reported structures of ruthenium(II) triphosphine dichloride complexes with similar geometry with linked phosphines donors in a meridional arrangement.[15] The only other reported structure in which all three of the phosphine donors are part of the one ligand is [bis-1-(1′-diphenylphosphinoferrocenyl)-phenylphosphine]dichlororuthenium(II),[15a] which has shorter Ru−P bond distances to the terminal phosphines (2.332(1) and 2.369(2) Å) than those observed in **6** (2.416(3) and 2.467(3) Å) probably due to the larger steric bulk of the *tertiary*-butyl groups in **6**, but otherwise the structure has very similar bond lengths and angles.

The structure of $RuCl_2(P^3P_3^{tBu})$ (**6**) has a P_{222} space group indicating there are no mirror planes within the unit cell. There is only a single isomer of **6** within the crystal, that being the isomer pictured in Figure 4. A second crystal of $RuCl_2(P^3P_3^{tBu})$ (**6**) was also used for structural analysis through single crystal X-ray diffraction, and this afforded only low quality diffraction data due to the small crystal size. However, the solution was sufficient to determine that the structure was of a second isomer in which the ligand arm of the pendant phosphine P_F is bent in the opposite direction to the original isomer. This difference can be clearly observed in an overlay of the two structures (Figure 5).

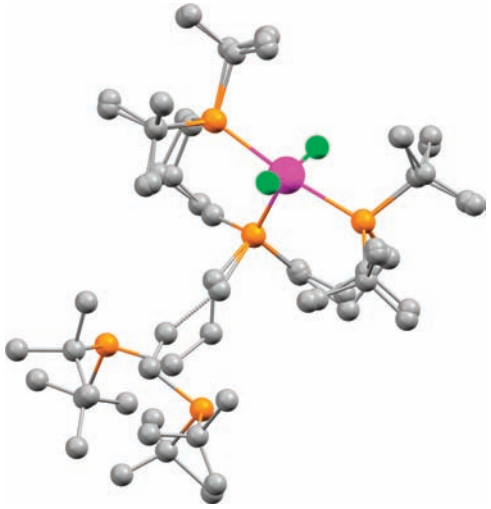

Figure 5. Overlay of structural data for the two isomers of $RuCl_2(P^3P_3^{tBu})$ (**6**) in the solid state. Hydrogen atoms have been removed for clarity.

In the $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^3P_3^{tBu})$ (**6**), the central phosphine P_C appears as a triplet at 60.8 ppm with a $^2J_{P-P}$ coupling of 35 Hz to P_E. The two bound terminal phosphines P_E appear as a doublet at 31.1 ppm, and the pendant phosphine P_F appears as a singlet at 25.5 ppm. The resonance at 25.5 ppm is assigned as a pendant phosphine not bound to the metal center for two reasons: first P_F displays no coupling to the bound phosphines and second because P_F has a chemical shift at high field in the spectrum, very close to the chemical shift observed for the terminal phosphines in the free ligand (26.2 ppm). In contrast to the fluxional behavior observed in $RuCl_2(P^2P_3^{tBu})$ (**4**), and $RuCl_2(PhP^2P_2^{tBu})$ (**5**) where there are ethylene bridges between central and terminal phosphorus atoms, the $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^3P_3^{tBu})$ (**6**), where there are propylene bridges between the phosphine donors, is sharp at room temperature and unchanged by variation in temperature. The presence of the longer arms in the $P^3P_3^{tBu}$ ligand probably results in a more stable framework with less backbone strain and a higher barrier to reorganization and isomerization of the coordination sphere of the metal.

Solid State NMR Analysis. Solid state $^{31}P\{^1H\}$ NMR spectra can be used for characterization for metal phosphine complexes in the solid state,[16] and comparison with $^{31}P\{^1H\}$ NMR spectra of complexes for which X-ray crystallographic data is available provides additional structural information.[17,18] We have, so far, been unable to grow crystals of $RuCl_2(P^2P_3^{tBu})$ (**4**) suitable for diffraction studies; however, solid state NMR provides some level of structural characterization of complex **4**, by comparison with the solid state NMR spectra of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) and $RuCl_2(P^3P_3^{tBu})$ (**6**) for which both solid-state NMR and X-ray data are available.

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The solid state $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(PhP^2P_2^{tBu})$ (**5**) shows the presence of a single species with three ^{31}P resonances at 129, 88, and 47 ppm which we assign to $P_{E/T}$, P_C, and $P_{E/T}$, respectively. These shifts correspond to those observed in solution state at low temperature (see Figure 3).

The solid state $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^3P_3^{tBu})$ (**6**) shows the presence of two species each with three resonances. Species A′ with resonances at 63, 32, and 31 ppm (masked by the P_E signals for both species) corresponding to P_C, P_E, and P_F, respectively, and species B′ with resonances at 62, 31, and 13 ppm corresponding to P_C, P_E, and P_F, respectively (Figure 6). The two species probably correspond to the 2 polymorphs of this compound identified by X-ray crystallography.

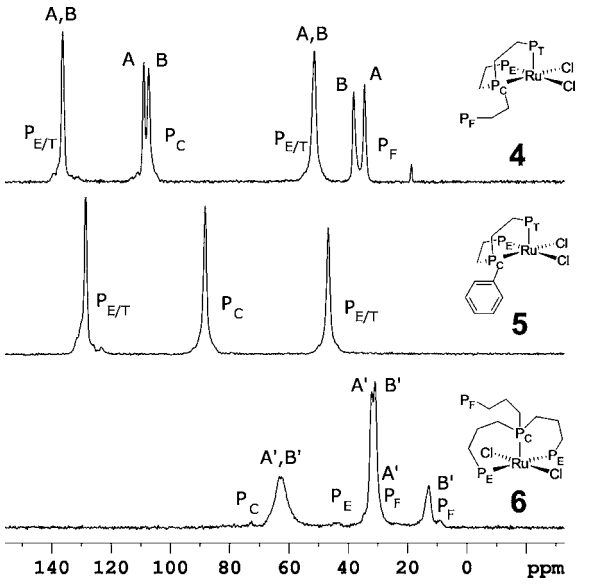

Figure 6. Solid state $^{31}P\{^1H\}$ NMR (121 MHz, 25 kHz MAS, 295 K) of $RuCl_2(P^2P_3^{tBu})$ (**4**), $RuCl_2(PhP^2P_2^{tBu})$ (**5**), and $RuCl_2(P^3P_3^{tBu})$ (**6**).

The solid state $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(P^2P_3^{tBu})$ (**4**) was initially obtained on material precipitated directly from a THF solution. These spectra displayed upward of five differing species in varying proportions, all with very similar chemical shifts, and this probably indicates why it has been difficult to obtain diffraction-quality crystals for this compound. When $RuCl_2(P^2P_3^{tBu})$ (**4**) was recrystallized from dichloromethane, the solid state $^{31}P\{^1H\}$ NMR spectrum indicated the presence of only two species present in approximately equal amounts. In the $^{31}P\{^1H\}$ NMR spectrum of (**4**), both species have four ^{31}P resonances: species A with four resonances at 136, 109, 51, and 35 ppm corresponding to $P_{E/T}$, P_C, $P_{E/T}$, and P_F, respectively, and isomer B with four resonances at 136, 107, 51, and 38 ppm corresponding to $P_{E/T}$, P_C, $P_{E/T}$, and P_F, respectively (Figure 6).

The most significant difference in chemical shifts between the isomers appears to be in the two P_F resonances, with a smaller, but still significant, difference in the P_C resonances. The difference between the two isomers is likely to be the result of the pendant phosphine of the complex being able to adopt two different positions in the unit cell, as was observed in the structure of $RuCl_2(P^3P_3^{tBu})$ (**6**).

The chemical shifts for P_C, P_E, and P_T of complex **4** and **5** are very similar, with differences in chemical shift for the two metal-bound phosphines $P_{E/T}$ of only 4 and 7 ppm. Given that the length of the straps and the substituents on the terminal phosphines are the same for complexes **4** and **5**, the fact that the observed shifts for **4** are closely aligned with **5** is indicative that the geometric arrangement of the coordinated phosphines in **4** are probably facially coordinated (as in **5**). If **4** was to be meridionally coordinated the pattern of resonances would be expected to be like that of **6** even though the strap length of the ligands would result in differences in the actual chemical shifts.[19]

CONCLUSIONS

The new sterically hindered, tridentate ligands $P(CH_2CH_2P^tBu_2)_3$ ($P^2P_3^{tBu}$, **1**), $PhP(CH_2CH_2P^tBu_2)_2$ ($PhP^2P_2^{tBu}$, **2**), and $P(CH_2CH_2CH_2P^tBu_2)_3$ ($P^3P_3^{tBu}$, **3**) were synthesized and used in the synthesis of the corresponding ruthenium dichloride compounds $RuCl_2(P^2P_3^{tBu})$ (**4**), $RuCl_2(PhP^2P_2^{tBu})$ (**5**), and $RuCl_2(P^3P_3^{tBu})$ (**6**). Complexes **4**, **5**, and **6** were all characterized by multinuclear NMR spectroscopy, with low temperature $^{31}P\{^1H\}$ NMR spectroscopy being used to explore the dynamic processes of exchange present in complex **4** and **5** in solution. Complexes **5** and **6** were both characterized crystallographically.

The bulky $P^2P_3^{tBu}$ (**1**) and $P^3P_3^{tBu}$ (**3**) ligands are the most sterically encumbered PP_3-type ligands so far synthesized. These ligands appear to be so sterically encumbered that they can only bind to ruthenium through three of the four phosphine donors leaving one of the terminal phosphines as a free pendant arm. All three ligands **1**, **2**, and **3** provide a highly sterically constrained ligand environment around the metal, and this restricts the nature of other groups that can bind to the metal center.

Solid state $^{31}P\{^1H\}$ NMR of $RuCl_2(P^2P_3^{tBu})$ (**4**), $RuCl_2(PhP^2P_2^{tBu})$ (**5**), and $RuCl_2(P^3P_3^{tBu})$ (**6**) was used to gain insights into the solid state structure of $RuCl_2(P^2P_3^{tBu})$ (**4**) which could not be characterized crystallographically. Comparative solid-state NMR analysis also indicate that the solid state structure of $RuCl_2(P^2P_3^{tBu})$ (**4**) is analogous to that determined by X-ray crystallography for $RuCl_2(PhP^2P_2^{tBu})$ (**5**).

EXPERIMENTAL SECTION

General Information. All manipulations were carried out using standard Schlenk, vacuum, and glovebox techniques under a dry atmosphere of nitrogen. Solvents were dried, distilled under nitrogen or argon using standard procedures,[20] and stored in glass ampules fitted with J. Youngs Teflon taps. Benzene was dried over sodium wire before distillation from sodium/benzophenone. THF (inhibitor free), toluene, and pentane were dried and deoxygenated using a Pure Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents THF-d_8, toluene-d_8, and benzene-d_6 were dried over, and distilled from, sodium/benzophenone and were vacuum distilled immediately prior to use. Dichlorotris(triphenylphosphine)-ruthenium(II),[21] trivinylphosphine,[22] diethoxyphenylphosphine, and di(*tert*-butyl)phosphine[23] were prepared by literature methods. Tris(3-hydroxypropyl)phosphine was purchased from Strem. Air sensitive NMR samples were prepared in an argon- or nitrogen-filled glovebox or on a high vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric Teflon valve. Solution ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker DPX300, Avance III 400, Avance III 500, or Avance III 600 NMR spectrometers operating at 300.3, 400.13, 500.13, and 600.13 MHz for ^1H, 100.61 or 150.92 MHz for $^{13}C\{^1H\}$, and 121.49, 161.98, 202.49, and 242.95 MHz for $^{31}P\{^1H\}$, respectively. All NMR spectra were recorded at 298 K, unless stated otherwise. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to

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solvent resonances. $^{31}P\{^{1}H\}$ NMR spectra were referenced to external neat trimethyl phosphite at 140.85 ppm.

Solid state NMR $^{31}P\{^{1}H\}$ were recorded on an Avance III 300 Bruker NMR spectrometer equipped with an Oxford 300 Magnet and a 2-channel 2.5 mm probehead. Samples were spun at 25 kHz MAS at the temperatures described. Solid state $^{31}P\{^{1}H\}$ NMR spectra were referenced to external ammonium dihydrogen phosphate (ADP) (δ = 1.0 ppm). Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. High resolution mass spectrometry was carried out at the Bioanalytical Mass Spectrometry Facilities within the Analytical Centre of the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA) ion trap mass spectrometer using a nanospray ionization source. Details of the X-ray analyses are given in Table 3.

Table 3. Crystal Data Refinement Details for 5 and 6

	5	6
chemical formula	$C_{26}H_{49}Cl_2P_3Ru$	$C_{33}H_{72}Cl_2P_4Ru$
formula mass	626.53	764.76
crystal system	monoclinic	orthorhombic
a/Å	11.1544(11)	12.462(2)
b/Å	16.0550(15)	14.307(3)
c/Å	16.0390(14)	21.914(4)
α/deg	90.00	90.00
β/deg	95.990(3)	90.00
γ/deg	90.00	90.00
V (Å^3)	2856.6(5)	3907.1(12)
temperature/K	150(2)	150(2)
space group	$P2(1)/c$	$P2(1)2(1)2(1)$
Z	4	4
μ(Mo Kα) (mm^{-1})	0.918	0.723
N	17217	15684
N_{ind}	5033	6760
R_{int}	0.0791	0.1778
final R_1 values ($I > 2\sigma(I)$)	0.0393	0.0840
final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0577	0.1695
final R_1 values (all data)	0.0753	0.1939
final $wR(F^2)$ values (all data)	0.0657	0.2326
goodness of fit on F^2	1.072	0.908

Synthesis of $P(CH_2CH_2P^tBu_2)_3$, $P^2P_3{}^{tBu}$ (1); $LiN(CH(CH_3)_2)_2$. Diisopropylamine (14.0 mL, 100 mmol) was added to a flask containing THF (100 mL) at 0 °C. *n*-Butyllithium (2.32 M in hexane, 43.0 mL, 99.8 mmol) was added dropwise over a 10 min period with stirring to give a yellow solution of lithium diisopropylamide. This solution was used directly in the next step without further purification.

$P^2P_3{}^{tBu}$ (1). Di(*tert*-butyl)phosphine (11.5 mL, 9.08 g, 62.1 mmol) was added to a solution of trivinylphosphine (ca. 15.7 mmol) in THF/ether (100 mL). Lithium diisopropylamide in THF/hexane (from the previous step) was added in stages with stirring over a period of 1 h. During the course of the reaction, the color of the solution turned bright orange. The reaction was monitored ($^{31}P\{^{1}H\}$ NMR) and the addition of base halted when no trivinylphosphine or reaction intermediates remained (≈70 mmol of lithium diisopropylamide). All volatiles were removed under vacuum, and the orange oil/solid residue was suspended in benzene (100 mL). Deaerated water (50 mL) was added with care to quench the excess base. The layers were separated, and the aqueous layer was discarded. The organic layer was dried over anhydrous Na_2SO_4, and the volatiles removed under reduced pressure leaving $P^2P_3{}^{tBu}$ as an orange oil (6.77 g, 12.3 mmol, 78% from trivinylphosphine). Anal. found: C 65.15, H 12.00. $C_{30}H_{66}P_4$ (MW 550.74) requires C 65.42, H 12.08. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, benzene-d_6): δ 34.1 (3P, d, $^{3}J_{P-P}$ = 24.9 Hz, $\mathbf{P_T}$); −15.3 (1P, q, $\mathbf{P_C}$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, benzene-d_6): δ 31.6 (d, $^{1}J_{C-P}$ = 23.9 Hz, P**C**$(CH_3)_3$); 30.0 (d, $^{2}J_{C-P}$ = 13.8 Hz, PC$(\mathbf{C}H_3)_3$); 28.5 (dd, $^{1}J_{C-P}$ = 25.8 Hz, $^{2}J_{C-P}$ = 16.7 Hz, $PCH_2\mathbf{C}H_2P$); 18.2 (dd, $^{1}J_{C-P}$ = 25.4 Hz, $^{2}J_{C-P}$ = 14.6 Hz, $P\mathbf{C}H_2CH_2P$). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.89 (6H, m, $C\mathbf{H}_2$); 1.71 (6H, m, $C\mathbf{H}_2$); 1.12 (54H, d, $^{3}J_{H-P}$ = 10.5 Hz, $C(C\mathbf{H}_3)_3$).

Synthesis of $PhP(CH_2CH_2P^tBu_2)_2$ $PhP^2P_2{}^tBu$ (2); $CH_2CHMgBr$. Vinyl bromide (50.6 g, 473 mmol) was condensed into THF (100 mL) cooled to 0 °C. An initial aliquot (10 mL) of the vinyl bromide solution was added to a stirred suspension of magnesium turnings (10.0 g, 411 mmol) in THF (150 mL). The reaction was initiated by addition of a crystal of iodine and application of heat, and after the reaction had commenced, the remainder of the solution was added dropwise at a rate which maintained a moderately vigorous reflux. On completion of the reaction, the magnesium turnings were consumed leaving a brown solution of vinylmagnesium bromide in THF. This solution was refluxed for 30 min with a needle vent above the condenser to remove any excess vinyl bromide. This solution was used directly in the preparation of divinylphenylphosphine without further purification (≈1.6 M, 250 mL).

$PhP(CH{=}CH_2)_2$. The solution of vinylmagnesium bromide from the previous step was chilled to 0 °C, resulting in the formation of a light brown precipitate. Diethoxyphenylphosphine (31.4 g, 158 mmol) was then added dropwise over a period of 30 min to the chilled solution. The solution was allowed to warm to room temperature at which point the precipitate disappeared, it was stirred for a further hour then heated under reflux for 30 min. The solution was cooled to room temperature and dioxane (35 mL, 410 mmol) was added, resulting in a large amount of precipitation. The solution was then briefly refluxed, and THF (150 mL) was added before the solution was filtered. THF was then distilled off at 66−68 °C leaving a red/orange solid which was extracted with ether (100 mL) to give an ether solution of divinylphenylphosphine (18.2 mmol by quantitative NMR). Divinylphenylphosphine was not isolated from the ether solution (to prevent polymerization), and the solution was used directly in the preparation of bis(3-di(*tert*-butyl)phosphinoethyl)-phenylphosphine without further purification. $^{31}P\{^{1}H\}$ NMR (162 MHz, 25% benzene-d_6/75% ether): δ −16.1 (1P, s, $Ph\mathbf{P}(CH{=}CH_2)_2$)

$PhP^2P_2{}^tBu$ (2). A solution of divinylphenylphosphine (2.95 g, 18.2 mmol) in ether (100 mL) from the previous step was added to a solution of di(*tert*-butyl)phosphine (9.0 mL, 49 mmol) in THF (100 mL). Lithium diisopropylamide (ca. 150 mmol) in THF/hexane (200 mL) was added in stages with stirring over an hour period. During the course of the reaction, the color of the solution turned to dark red. The reaction was monitored ($^{31}P\{^{1}H\}$ NMR), and the addition of base was halted when no divinylphenylphosphine or reaction intermediates remained. All solvent was removed under reduced pressure, and the remaining red/brown oil/solid residue was suspended in benzene (150 mL). Deaerated water (50 mL) was added, with care, to quench any residual base. The aqueous layer was discarded and the organic layer dried over anhydrous Na_2SO_4. The benzene was removed under reduced pressure leaving $PhP^2P_2{}^tBu$ (**2**) as an orange oil (6.17 g, 13.6 mmol, 75% yield from divinylphenylphosphine). $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6): δ 34.0 (2P, d, $^{3}J_{P-P}$ = 27 Hz, $\mathbf{P_{E/T}}$); −16.9 (1P, t, $\mathbf{P_C}$). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.58 (2H, m, Ar-**H**); 7.18 (3H, m, Ar-**H**); 2.06 (2H, m, $C\mathbf{H}_2$); 1.55 (2H, m, $C\mathbf{H}_2$); 1.43 (2H, m, $C\mathbf{H}_2$); 1.19 (2H, m, $C\mathbf{H}_2$); 1.03 (36H, m, $C\mathbf{H}_3$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, benzene-d_6): δ 139.0 (d, J_{C-P} = 18 Hz, $\mathbf{C}^{Ar}$); 133.2 (d, J_{C-P} = 19 Hz, $\mathbf{C}^{Ar}$); 129.9 (d, J_{C-P} = 44 Hz, $\mathbf{C}^{Ar}$); 128.6 (s, $\mathbf{C}^{Ar}$); 31.8 (d, J_{C-P} = 24 Hz, $\mathbf{C}(CH_3)_3$); 29.9 (d, J_{C-P} = 14 Hz, $C(\mathbf{C}H_3)_3$); 29.8 (d, J_{C-P} = 14 Hz, $C(\mathbf{C}H_3)_3$); 29.6 (dd, J_{C-P} = 27 Hz, J_{C-P} = 15 Hz, $\mathbf{C}H_2$); 17.7 (dd, J_{C-P} = 25 Hz, J_{C-P} = 14 Hz, $\mathbf{C}H_2$). HRMS (ES) m/z: $[M + H]^+$ 455.3092 (calcd 455.3125)

Synthesis of $P(CH_2CH_2CH_2P^tBu_2)_3$, $P^3P_3{}^tBu$; Tris(3-bromopropyl)phosphine. Phosphorus tribromide (4.3 mL, 46 mmol) was added dropwise to a stirred suspension of tris(3-hydroxypropyl)phosphine (7.7 g, 37 mmol) in dichloromethane (80 mL). Initial portions of phosphorus tribromide caused the solution to become viscous and made stirring difficult, but continued addition of phosphorus tribromide dropwise resulted in the suspension returning to a less viscous solution which could be stirred. The reaction mixture was stirred at room temperature for 18 h. Saturated aqueous sodium carbonate solution (approximately 40 mL) was added to the reaction

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mixture until all effervescence ceased. The organic layer was separated and dried over anhydrous sodium sulfate. The solution was filtered and the solvent was removed under reduced pressure to give tris(3-bromopropyl)phosphine as a clear liquid (4.2 g, 11 mmol, 29%). This product was used immediately in the next step without further purification.

LiP(C(CH$_3$)$_3$))$_2$. *n*-Butyllithium (2.5 M in hexane, 16 mL, 40 mmol) was added to a solution of di(*tert*-butyl)phosphine (5.3 g, 36 mmol) in THF (50 mL) at 0 °C with stirring. The solution remained colorless during the addition, until the reaction was complete when a pale yellow color persisted. The reaction mixture was allowed to warm to room temperature and THF (40 mL) was added, resulting in a bright yellow solution which was used directly in the next step.

P^{3}P$_3^{tBu}$ (3). The lithium di(*tert*-butyl)phosphide solution from the previous step was added to a stirring solution of tris(3-bromopropyl)-phosphine (4.20 g, 10.6 mmol) in THF (approximately 40 mL) at 0 °C. During the addition, a pink/orange color formed before the color returned to yellow once addition was complete. The reaction mixture was left to stir at room temperature for 18 h. The solvent was removed under reduced pressure and deaerated water (approximately 30 mL) added, with care, until all excess lithium phosphide had been destroyed. Benzene (approximately 40 mL) was added and the mixture was stirred for 1 h. The organic layer was decanted, dried over anhydrous sodium sulfate, and filtered to give a clear solution. The solvents were removed under reduced pressure and the resulting oil was heated under reduced pressure (0.4 mbar) to remove volatile impurities, leaving tris(3-di(*tert*-butyl)phosphinopropyl)phosphine as a clear wax (3.82 g, 6.44 mmol, 61% from tris(3-bromopropyl)-phosphine). ^{31}P{^{1}H} NMR (121.5 MHz, benzene-d_6): δ 26.2 (3P, s, **P**$_T$); −35.5 (1P, s, **P**$_C$). ^{1}H{^{31}P} NMR (300 MHz, benzene-d_6): δ 1.87 (6H, m, CH$_2$C**H$_2$**CH$_2$); 1.63 (6H, t, $^3J_{H-H}$ = 7.1 Hz, C**H$_2$**P); 1.49 (6H, t, $^3J_{H-H}$ = 7.4, C**H$_2$**P); 1.12 (54H, d, $^3J_{H-P}$ = 10.6 Hz, C**H$_3$**). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 31.3 (d, $^1J_{C-P}$ = 30 Hz, **C**(CH$_3$)$_3$); 29.9 (d, $^1J_{C-P}$ = 14 Hz, C(**C**H$_3$)$_3$); 29.7 (dd, J_{C-P} = 26 Hz, J_{C-P} = 14 Hz, **C**H$_2$); 27.3 (dd, J_{C-P} = 28 Hz, J_{C-P} = 14 Hz, **C**H$_2$); 23.6 (dd, J_{C-P} = 23 Hz, J_{C-P} = 11 Hz, **C**H$_2$). HRMS (ES) *m*/*z* [M + H]$^+$ 593.4647 (calcd 593.4663).

Synthesis of RuCl$_2$(P^{2}P$_3^{tBu}$), (4). A solution of dichlorotris-(triphenylphosphine)ruthenium(II) (1.18 g, 1.23 mmol) in THF (50 mL) was added to a solution of tris(2-di(*tert*-butyl)phosphinoethyl)-phosphine, P^{2}P$_3^{tBu}$ (**1**), (5.0 mL, 245 mM, 1.23 mmol) in THF under nitrogen. The brown solution was to stirred overnight and a tan solid precipitated. The solid was collected by filtration and washed with THF (5 mL) to afford dichloro(tris(2-di(*tert*-butyl)phosphinoethyl)-phosphine-κ^3P)ruthenium(II) (0.40 g, 0.55 mmol 45%). Anal. found: C 49.88, H 9.05 C$_{30}$H$_{66}$Cl$_2$RuP$_4$ (MW 722.72) requires C 49.86, H 9.20. ^{31}P{^{1}H} NMR (162 MHz, dichloromethane-d_2): δ 106.2 (1P, dt, $^3J_{P-P}$ = 37 Hz, $^3J_{P-P}$ = 17.5 Hz, **P**$_C$); 91.4 (2P, br s, **P**$_E$); 34.3 (1P, d, $^3J_{P-P}$ = 37 Hz, **P**$_F$). ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 2.45 (2H, m, C**H$_2$**); 2.28−1.92 (6H, m, C**H$_2$**); 1.83 (2H, m, C**H$_2$**); 1.35 (18H, d, $^3J_{H-P}$ = 12.5 Hz, C**H$_3$**); 1.24 (18H, d, $^3J_{H-P}$ = 12.5 Hz, C**H$_3$**); 1.14 (18H, d, $^3J_{H-P}$ = 10.8 Hz, C**H$_3$**); 1.07 (2H, m, C**H$_2$**). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): δ 39.9 (d, $^1J_{C-P}$ = 18 Hz, P**C**(CH$_3$)$_3$); 36.2 (d, $^1J_{C-P}$ = 10.5 Hz, P**C**(CH$_3$)$_3$); 32.1 (d, $^1J_{C-P}$ = 22.4 Hz, P**C**(CH$_3$)$_3$) 31.9 (d, $^2J_{C-P}$ = 2.9 Hz, PC(**C**H$_3$)$_3$); 30.8 (dd, J_{C-P} = 28.3 Hz, J_{C-P} = 22.2 Hz, **C**H$_2$ (pendant arm)) 30.0 (d, $^2J_{C-P}$ = 13.6 Hz, PC(**C**H$_3$)$_3$); 28.8 (s, PC(**C**H$_3$)$_3$); 27.2 (dd, J_{C-P} = 28.0 Hz, J_{C-P} = 6.5 Hz, **C**H$_2$ (bound arm)); 24.9 (dd, J_{C-P} = 21.1 Hz, J_{C-P} = 12.6 Hz, **C**H$_2$ (bound arm)); 16.3 (dd, J_{C-P} = 25.6 Hz, J_{C-P} = 5.7 Hz, **C**H$_2$ (pendant arm)).

Synthesis of RuCl$_2$(PhP^{2}P$_2^{tBu}$) (5). A solution of dichlorotris-(triphenylphosphine)ruthenium(II) (1.06 g, 1.11 mmol) in THF (30 mL) was added to a solution of bis(2-di(*tert*-butyl)phosphinoethyl)-phenylphosphine, PhP^{2}P$_2^{tBu}$, (0.520 g, 1.14 mmol) in THF (10 mL) under nitrogen. The brown solution was stirred overnight, and a yellow solid precipitated. Hexane (50 mL) was added to assist precipitation of the solid. The cloudy suspension was stirred for 1 h, then the solid was isolated by filtration to give dichloro(bis(2-di(*tert*-butyl)phosphinoethyl)phenylphosphine-κ^3P)ruthenium(II) (0.255 g, 0.407 mmol, 37%) as a yellow solid. Anal. found C 49.52, H 7.60 C$_{26}$H$_{49}$Cl$_2$RuP$_3$ (MW 626.57) requires C 49.84, H 7.88. ^{31}P{^{1}H} NMR (162 MHz, dichloromethane-d_2): δ 94.4 (1P, t, $^2J_{P-P}$ = 12.6 Hz, Ph**P**(CH$_2$)$_2$); δ 92.3 (2P, br s, **P**C(CH$_3$)$_3$). ^{1}H NMR (300 MHz, dichloromethane-d_2): δ 8.16 (2H, m, ArH); 7.45 (3H, m, ArH); 2.4−2.1 (6H, m, C**H$_2$**); 1.44 (18H, d, $^3J_{H-P}$ = 12.7 Hz, C(C**H$_3$**)$_3$); 1.19 (18H, d, $^3J_{H-P}$ = 12.7 Hz, C(C**H$_3$**)$_3$); 1.15−1.05 (2H, m, C**H$_2$**). ^{31}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): δ 137.7 (d, $^1J_{C-P}$ = 36.3 Hz, **C**^{Ar}); 132.4 (d, J_{C-P} = 8.7 Hz, **C**^{Ar}); 130.4 (d, J_{C-P} = 2.4 Hz, **C**^{Ar}); 128.8 (d, J_{C-P} = 9.3 Hz, **C**^{Ar}); 40.7 (d, $^1J_{C-P}$ = 17.9 Hz, P**C**(CH$_3$)$_3$); 36.9 (d, $^1J_{C-P}$ = 11.4 Hz, P**C**(CH$_3$)$_3$); 31.9 (dd, J_{C-P} = 31.0 Hz, J_{C-P} = 6.3 Hz, **C**H$_2$); 31.8 (d, $^2J_{C-P}$ = 2.9 Hz, PC(**C**H$_3$)$_3$); 29.2 (s, PC(**C**H$_3$)$_3$); 25.3 (dd, J_{C-P} = 22.7 Hz, J_{C-P} = 13 Hz, **C**H$_2$).

Synthesis of RuCl$_2$(P^{3}P$_3^{tBu}$) (6). Solid di-μ-chlorobis[(*p*-cymene)-chlororuthenium] (100 mg, 0.163 mmol) was added to a solution of P^{3}P$_3^{tBu}$ (**6**), (185 mg, 0.312 mmol) in toluene (50 mL) under nitrogen. The solution was stirred and refluxed overnight to afford an extremely dark green solution with a suspended brown solid. The solution was filtered, the residue was discarded, and the volatiles of the filtrate removed under vacuum. The resulting green solid residue was dried under vacuum for 3 h to afford dichloro(tris(2-di(*tert*-butyl)phosphinopropyl)phosphine-κ^3P)ruthenium(II) (132 mg, 0.173 mmol, 55% by P^{3}P$_3^{tBu}$ (**6**)). Anal. found C 51.54, H 9.28 C$_{33}$H$_{72}$Cl$_2$RuP$_4$ (MW 764.81) requires C 51.83, H 9.49. ^{31}P{^{1}H} NMR (121 MHz, THF-d_8): δ 60.8 (1P, t, $^2J_{P-P}$ = 35 Hz, **P**$_C$); 31.1 (2P, d, $^2J_{P-P}$ = 35 Hz, **P**$_E$); 25.5 (1P, s, **P**$_F$). ^{1}H NMR (300 MHz, acetone-d_6): δ 1.89 (2H, m, C**H$_2$**); 1.79 (4H, m, C**H$_2$**); 1.62 (8H, m, C**H$_2$**); 1.48−1.62 (18H, m, C**H$_3$**); 1.62 (4H, m, C**H$_2$**); 1.12 (36H, m, C**H$_3$**).

X-ray Structure Determinations. Single crystals of **5** and **6** were attached, with Exxon Paratone N, to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A Bruker kappa APEXII area detector diffractometer employing graphite monochromated Mo Kα radiation generated from a fine focus sealed tube was used for the data collection. The data integration and reduction were undertaken with APEX2, and subsequent computations were carried out with the X-Seed graphical user interface. The structures were solved by direct methods with SHELXS-97 and extended and refined with SHELXL-97. The non-hydrogen atoms in the asymmetric unit were modeled with anisotropic displacement parameters. A riding atom model with group displacement parameters was used for the hydrogen atoms.

All calculations were performed using the crystallographic and structure refinement data summarized in Table 3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF with crystallographic data for compounds [RuCl$_2$(P^{2}P$_2^{tBu}$)] (**5**) and [RuCl$_2$(P^{3}P$_3^{tBu}$)] (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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