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Flexible Syntheses of Tripodal Phosphine Ligands 1,1,2-Tris(diarylphosphino)ethane and Their Ruthenium η^5-C_5Me_5 Complexes

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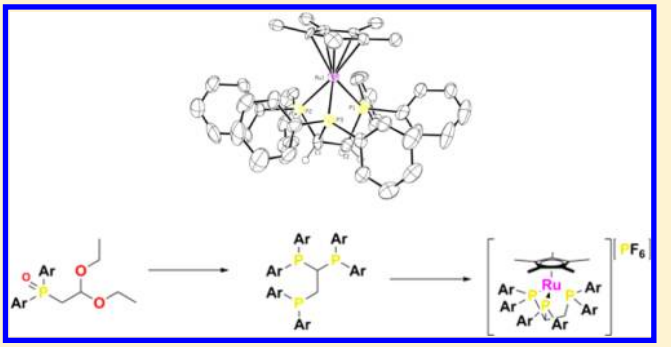
Supporting Information

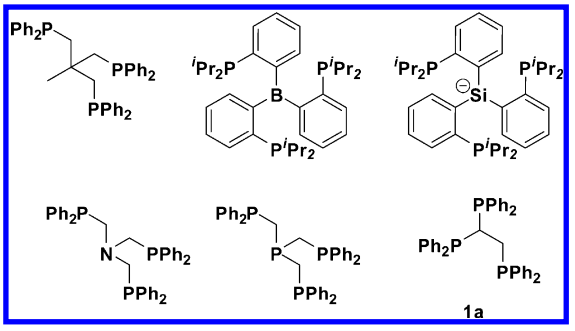
ABSTRACT: A series of four tripodal polyphosphine ligands $(PAr_2)_2CHCH_2PAr_2$ (**1a−d**) were synthesized and coordinated to ruthenium to produce the complexes $[Ru(\eta^5\text{-}C_5Me_5)((PAr_2)_2CHCH_2PAr_2)]PF_6$ (**2a−d**) (Ar = phenyl (**a**), *p*-tolyl (**b**), *o*-tolyl (**c**), *m*-xylyl (**d**)). The 1,1,2-tris(diarylphosphino)ethane compounds were generated in a novel trisubstitution reaction of diarylphosphorylacetaldehyde diethyl acetal, a useful synthetic precursor that was used previously for the synthesis of phosphonium dimers. The tridentate ligands were subsequently combined with the ruthenium(II) precursor $Ru(\eta^5\text{-}C_5Me_5)(1,5\text{-COD})Cl$, in order to probe the coordination geometry of **1a−d**. The resulting complexes **2a−d** displayed piano-stool type structures where the phosphine ligands were coordinated in a *fac* geometry. Despite the large steric bulk of the ligands, as well as the ring strain caused by the formation of a four-membered ring and two five-membered rings with the ruthenium center, complexes **2a−d** were quite stable. The ruthenium salts were air and moisture stable and did not react with CO, H_2, or $NaBH_4$, even at elevated temperatures.



INTRODUCTION

Tripodal, multidentate phosphine ligands exhibit rich and diverse coordination chemistry, and as such they have found an integral place in inorganic and organometallic chemistry (see Scheme 1 for some examples).[1−5] These chelating ligands provide a very controlled and stable coordination environment around transition-metal centers, often occupying three *cis* sites or a *fac* geometry in octahedral complexes. Such stability and predictable coordination geometry are often important for homogeneous catalytic processes and in some cases provide enhanced catalytic activity over analogous monodentate or bidentate phosphorus-containing systems.[5−19] In addition, phosphorus ligands exhibit a strong *trans* influence, which helps labilize ligands during catalysis, aiding in fast turnovers of the catalytic cycle.[20−24] Another benefit of phosphorus ligands in general is that the electronic and steric parameters of the phosphorus donors can easily be varied, the effects of which can be quantified using Tolman cone angles and electronic parameters.[25] This is an attractive feature for catalytic systems, as it allows for the systematic development of more active catalysts utilizing rational catalyst design.

Scheme 1. Selection of Tripodal Tridentate Phosphine Ligands[26,27]



One tridentate phosphine donor of note is 1,1,1-tris(diphenylphosphinomethyl)ethane (TRIPHOS), a commonly used ligand which forms three six-membered rings with a metal center and binds in a *fac* geometry (see Scheme 1).[28−31] This ligand has been employed to generate various ruthenium- and rhodium-based catalysts for the hydrogenation of alkenes,[7,32−37] alkynes,[5−7,34] ketones,[6,34,38−40] esters,[41−44] and several other substrates of interest.[34,39,45−51] A related ligand, 1,1,2-tris(diphenylphosphino)ethane (**1a**), was developed by Bookham et al. and Schmidbaur et al. in the late 1980s.[52,53] Like TRIPHOS, this ligand is a tripodal phosphine donor with an aliphatic backbone, but unlike TRIPHOS, **1a** would form two five-membered rings and one four-membered ring with a metal center when bound in a *fac* geometry. Although neither research group prepared metal complexes of **1a**, Bookham et al. did propose several different binding modes that **1a** could

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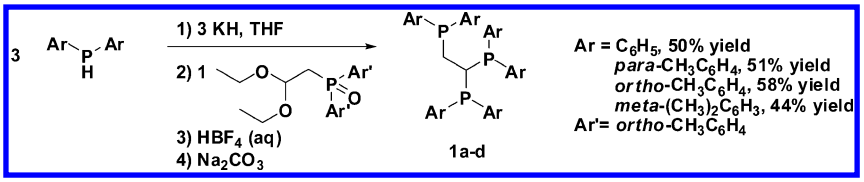
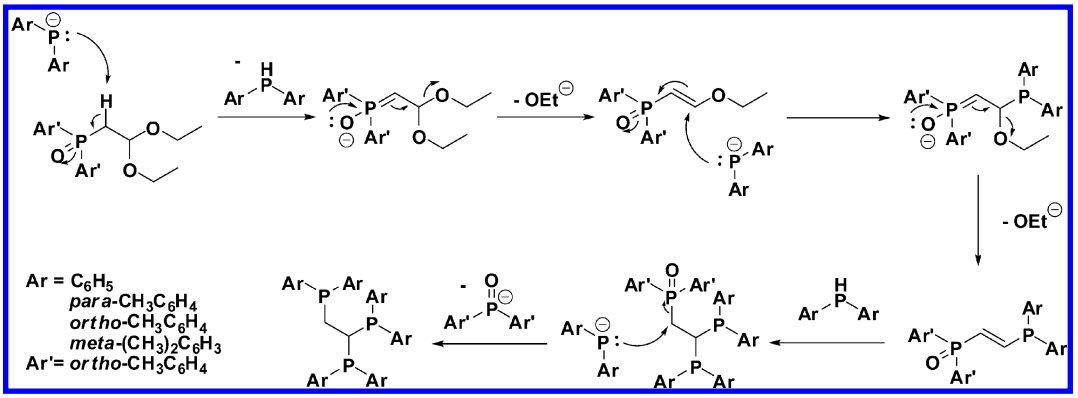
Scheme 2. Synthesis of Ligands 1a−d Starting from Diarylphosphines



Scheme 3. Proposed Mechanism for the Formation of Ligands 1a−d



adopt, including a *fac* arrangement of the ligand. They hypothesized that, although **1a** could feasibly coordinate to a single metal center, the resulting complex would have a considerable amount of strain. Despite the similarities to TRIPHOS, no other research on this unique ligand has been reported.

In this paper we report the general synthesis of 1,1,2-tris(diarylphosphino)ethane ligands, **1a−d**, as well as their characterization. We have previously outlined the syntheses of diarylphosphorylacetaldehyde diethyl acetals as convenient precursors for the production of phosphonium dimers,[54] and herein we describe their use in the synthesis of **1a−d**. Furthermore, we report the first transition-metal complexes bearing these types of ligands, ruthenium η^5-C_5Me_5 (Cp*) complexes **2a−d**, and explore their coordination geometry. With respect to nomenclature, throughout this paper, compounds will be named according to their aryl substitution pattern: **a** for phenyl, **b** for *p*-tolyl, **c** for *o*-tolyl, and **d** for *m*-xylyl.

RESULTS AND DISCUSSION

Synthesis and Characterization of Triphosphine Ligands 1a−d. Compounds **1a−d** were generated in a novel trisubstitution reaction of a phosphoryl-substituted protected aldehyde. Three equivalents of diarylphosphine were deprotonated with KH and then combined directly with 1 equiv of diarylphosphorylacetaldehyde diethyl acetal to yield triphosphine ligands **1a−d** as white solids in moderate yields (44−58%). In this reaction the diarylphosphoryl and ethoxide groups of the diarylphosphorylacetaldehyde diethyl acetal precursor have been replaced by diarylphosphino functionalities (see Scheme 2). Compound **1a** has previously been prepared via an alternative synthetic route employing 1,1-bis(diphenylphosphino)ethylene[52,53] but was never fully characterized. This method is less convenient than our new method for the synthesis of 1,1,2-tris(diarylphosphino)ethane compounds because the starting material used in our case is air stable. The starting material used by Schmidbaur et al. as well as Bookham et al., on the other hand, is air sensitive, expensive to purchase from commercial sources, and difficult to purify if synthesized from vinyl chlorides and diarylphosphines.[52,53]

The $^{31}P\{^1H\}$ NMR spectra of compounds **1a−d** all show characteristic peaks in the negative chemical shift region. The two equivalent phosphorus nuclei produce a doublet in the range between −27.6 and −3.8 ppm and are coupled to the remaining inequivalent phosphorus nucleus, which displays a triplet between −19.8 and −45.6 ppm. The ^1H NMR spectra of compounds **1a−d** also exhibit several diagnostic peaks. The proton α to the two equivalent phosphorus centers resonates as a doublet of triplets between 3.3 and 3.0 ppm, while the protons α to the lone phosphorus center exhibit a multiplet between 2.3 and 2.0 ppm.

This general synthetic route for the production of 1,1,2-tris(diarylphosphino)ethane compounds operates regardless of the aryl groups on the phosphoryl moiety of the starting material, but the reaction gave the cleanest products and highest yields with bis(*o*-tolylphosphoryl)acetaldehyde diethyl acetal. The latter acetal was used almost exclusively to synthesize **1a−d**, not only because it gave the highest yields and cleanest products but also because its synthesis was facile, and the bis(*o*-tolyl)phosphine oxide byproduct was easily recovered and recrystallized (up to 70% recovery).

The mechanism of formation for compounds **1a−d** is at this time poorly understood but is believed to operate in a fashion similar to the trisubstitution reaction that we described previously which yields 1,1,2-tris(diarylphosphoryl)ethane compounds.[55] We propose that a deprotonated species in solution abstracts a proton from the carbon α to the phosphoryl functionality to produce a carbanion that is stabilized by the adjoining P═O group. Subsequently, in an E_1cb fashion, an ethoxide is eliminated with concomitant carbon−carbon double bond formation. After nucleophilic attack by a diarylphosphide in solution and another E_1cb elimination reaction, a 1,2-bis(diarylphosphino)ethylene species could be produced. Protonated diarylphosphines in solution could then react with the disubstituted intermediate and hydrophosphinate the double bond, thus generating a mixed phosphine−phosphine oxide product. In the last step,

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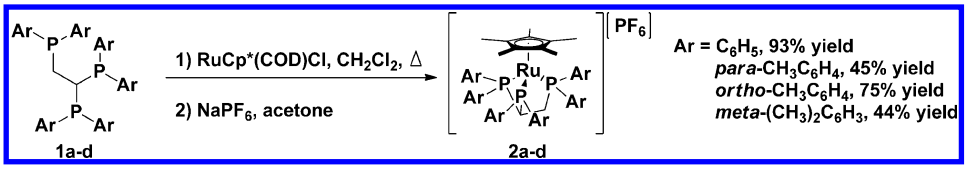
Scheme 4. Synthesis of Ruthenium Complexes 2a–d using Ligands 1a–d



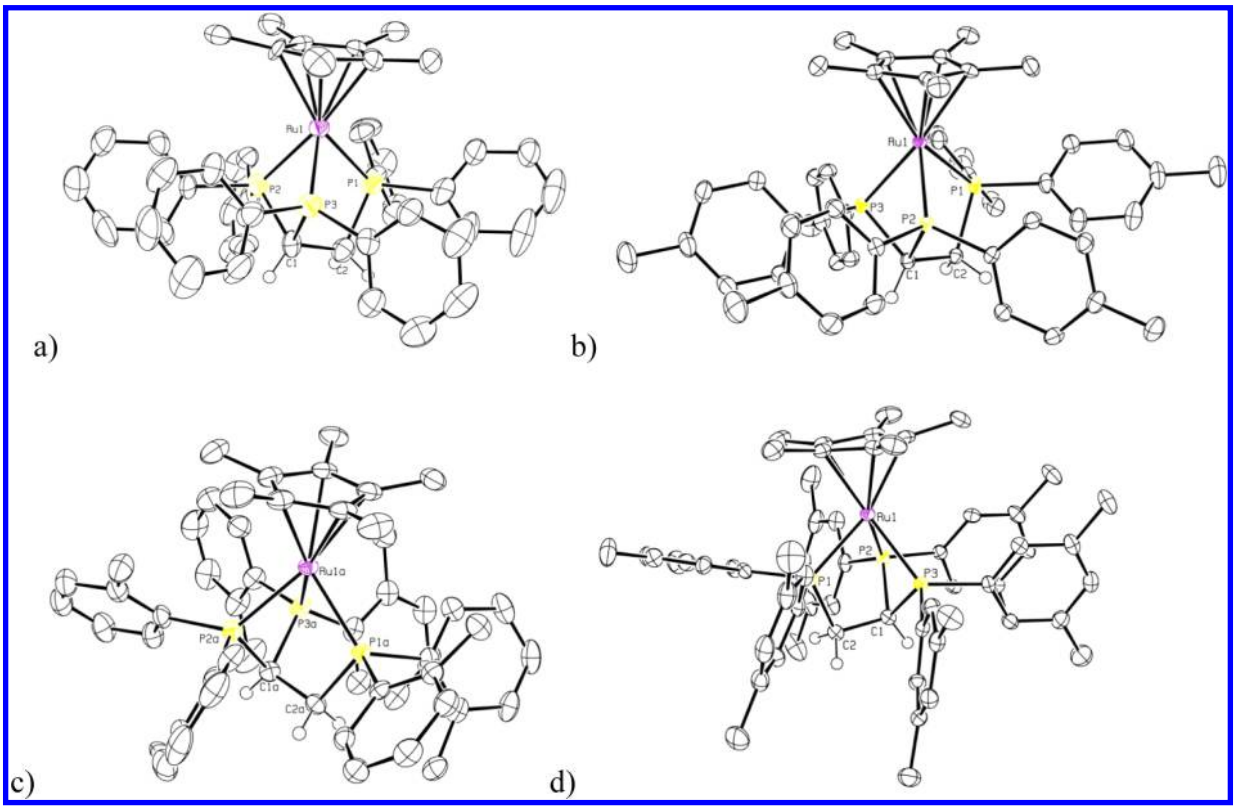


Figure 1. ORTEP3 representations (thermal ellipsoids at 50% probability) and atom numbering for (a) **2a** (the counterion, and most hydrogens are omitted for clarity), (b) **2b** (the solvent, counterion, and most hydrogens are omitted for clarity), (c) **2c** (the solvent, counterion, and most hydrogens are omitted for clarity), and (d) **2d** (the counterion and most hydrogens are omitted for clarity).

another 1 equiv of diarylphosphide in solution could displace the phosphoryl group (a better leaving group than a diarylphosphine) in an S_N2 reaction and generate the observed triphosphine product (summarized in Scheme 3).

Efforts were made to isolate some of the possible intermediates in the hypothetical mechanism, with special emphasis placed on isolating or trapping the 1,2-bis-(diarylphosphino)ethylene species, but these attempts met with little success. Despite adding only 1 equiv of deprotonated phosphine at a time at −78 °C and then warming to room temperature, thus strictly controlling the stoichiometry of the reaction, the only products isolated were the trisubstituted ligand, diarylphosphine oxide, and the starting materials. Furthermore, the addition of silane in order to trap either of the proposed unsaturated intermediates was not successful, and the only products observed were the 1,1,2-tris-(diarylphosphino)ethane species, the reactants, and some undetermined decomposition products. As in our related phosphine oxide paper,[54] several attempts were made to generate structures similar to the polyfunctional phosphines by first installing a different functional group (phosphino or amino) in place of the diarylphosphoryl moiety in the diarylphosphorylacetaldehyde diethyl acetal precursor. The differently substituted products were then subjected to an excess of deprotonated diarylphosphine in an endeavor to replace the ethoxides with phosphino functionalities. Unfortunately, every effort resulted in recovery of the monosubstituted starting material with no incorporation of the phosphine functionalities. The phosphine oxide appears to be crucial in initiating the trisubstitution process.

Variable-temperature NMR studies of the reaction mixture were able to provide a little more insight into the mechanism of formation for these tripodal ligands. We were able to completely freeze the reaction at −40 °C, and in a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture we were able to observe several species in solution. Diphenylphosphide, diarylphosphorylacetaldehyde diethyl acetal, deprotonated diarylphosphine oxide, and the trisubstituted product could all be readily identified in solution, but an unidentified phosphorus-containing compound that displayed a singlet at −0.40 ppm in the $^{31}P\{^1H\}$ NMR was also present. In addition, a ^1H NMR spectrum of the reaction mixture displayed a peak between 6.4 and 6.3 ppm that corresponds to a vinylic proton. As the solution was warmed to −30 °C, the reaction began to proceed and was monitored via $^{31}P\{^1H\}$ NMR. The diphenylphosphide, diarylphosphorylacetaldehyde diethyl acetal, and the intermediate at −0.40 ppm all diminished in intensity with a corresponding increase in intensity for the tripodal ligand and

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deprotonated diarylphosphine oxide. However, when all of the diarylphosphorylacetaldehyde diethyl acetal starting material had disappeared, there were still residual amounts of the species at −0.40 ppm and diphenylphosphide. These two species, upon sitting, further decreased in intensity and disappeared, while the trisubstituted product and deprotonated diarylphosphine oxide grew in intensity. We believe that the species at −0.40 ppm is the (2-ethoxyvinyl)phosphine oxide intermediate that we had postulated in the mechanism, which, upon reaction with diphenylphosphide, releases deprotonated diarylphosphine oxide.

Synthesis and Characterization of Ruthenium Complexes 2a−d. In order to probe the binding mode of compounds **1a−d**, the tripodal polyphosphine ligands were bound to ruthenium and the resulting complexes were characterized. One equivalent of **1a−d** was dissolved in dichloromethane and added to a solution of Ru(Cp*)(COD)Cl in dichloromethane. After heating overnight, the solvent was removed and the residue was dried to remove residual 1,5-cyclooctadiene. $^{31}P\{^{1}H\}$ NMR spectra of the crude residues revealed that multiple ruthenium complexes had formed, many with pendant phosphorus functionalities. This indicated that the tridentate ligands were not capable of displacing the chloride ligand from ruthenium and, therefore, an abstracting agent was necessary. To remove the chloride, the crude residues were dissolved in acetone and an excess of $NaPF_6$ was added (see Scheme 4). After workup, air-stable pale yellow powders of **2a−d** as PF_6^- salts were isolated in moderate to exceptional yields (44−93%). The poor yields of **2b,d**, 45% and 44%, respectively, can be attributed to their higher solubility in organic solvents, because their conversions were nearly quantitative as determined by NMR.

The $^{31}P\{^{1}H\}$ NMR spectra of compounds **2a,b,d** all show characteristic peaks significantly downfield from those of the free ligand forms. The two equivalent phosphorus nuclei display a doublet around 30 ppm and are coupled to the remaining inequivalent phosphorus nucleus, which displays a triplet around 60 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum of **1c**, on the other hand, displays a triplet around 54 ppm, similar to the other complexes, but the doublet for the two equivalent phosphorus nuclei is split into four sets of doublets between 32 and 36 ppm. This arises from different orientations of the methyl groups about the phosphorus centers, which give rise to several rotamers in solution that do not interconvert because the binding of the phosphine donors to the ruthenium center locks the conformation of the methyl groups. This type of behavior has been seen previously with bulky *o*-tolyl substituents,[54,55] which are known to have barriers of rotation about the carbon−phosphorus bond.[56] The ^{1}H NMR spectra of compounds **2a−d** also exhibit several diagnostic peaks. The proton α to the two equivalent phosphorus centers displays a unique multiplet between 5.7 and 5.3 ppm, as do the protons α to the lone phosphorus center, between 3.7 and 3.0 ppm.

In addition to NMR experiments, compounds **2a−d** were characterized in the solid state utilizing single-crystal X-ray diffraction (see Figure 1). The ruthenium complexes display a distorted-piano-stool geometry with a Cp* ligand occupying half of the coordination sphere and the more sterically demanding tripodal phosphine ligands occupying the other three coordination sites. These crystal structures support the predictions made by Bookham et al. that ligands **1a−d** can occupy a *fac* geometry despite the considerable amount of strain involved in forming a four-membered ring and two five-membered rings with a metal center (although it is important to note that this may not be the case with other metal complexes generated from ruthenium precursors containing only monodentate ligands).[52] This ring strain is reflected in the P−Ru−P angles, all of which are compressed below the optimal octahedral angles of 90°. For the two P−Ru−P angles that represent the five-membered rings, P(1)−Ru(1)−P(2) and P(1)−Ru(1)−P(3), the values lie between 78.13(9) and 83.75(9)°, while the angle that represents the four-membered ring, P(2)−Ru(1)−P(3), is considerably smaller and more constrained, between 68.01(6) and 69.59(6)°. In addition, the P(1)−C(2)−C(1) bond angle has been compressed upon coordination to the metal center, between 106(2) and 108.6(6)°, which is smaller than the optimal 109.5° angle for a perfect tetrahedron. For comparison, the complex [Ru(indenyl)(TRIPHOS)]PF_6 has P−Ru−P angles that are between 86 and 89°.[57] With respect to bond lengths, **1a,b,d** have typical Ru−P bond lengths, around 2.30 and 2.31 Å, except for one longer Ru−P bond around 3.33 Å (Ru(1)−P(2) for **2a,d**, Ru(1)−P(3) for **2b**).[33,38,58] For **2c**, however, all the Ru−P bond lengths are elongated: 2.356(2), 2.331(2), and 2.381(3) Å for Ru(1)−P(1), Ru(1)−P(2), and Ru(1)−P(3), respectively. This is most likely due to the increased bulk of the *o*-tolyl substituents (for further notable bond lengths and angles, see Table 1). Another feature of note is the stacking of the aryl groups of the phosphine donors that is evident in the solid-state structures. The aryl rings align themselves parallel to each other, and for **2c** the methyl substituents are oriented in opposite directions to minimize unfavorable steric interactions.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a−d

	2a	**2b**·$2CH_2Cl_2$	**2c**·$0.5CH_2Cl_2$	**2d**
	Bond Lengths (Å)			
Ru(1)−P(1)	2.309(5)	2.316(2)	2.356(2)	2.303(2)
Ru(1)−P(2)	2.333(6)	2.310(2)	2.331(2)	2.313(2)
Ru(1)−P(3)	2.307(6)	2.336(2)	2.381(3)	2.357(2)
P(1)−C(2)	1.87(2)	1.871(6)	1.857(9)	1.871(9)
P(2)−C(1)	1.86(2)	1.861(6)	1.861(9)	1.852(9)
P(3)−C(1)	1.84(2)	1.867(6)	1.877(9)	1.884(6)
C(1)−C(2)	1.56(4)	1.539(9)	1.53(1)	1.54(1)
	Bond Angles (deg)			
P(1)−Ru(1)−P(2)	79.0(2)	81.79(3)	81.84(9)	83.75(9)
P(1)−Ru(1)−P(3)	80.8(2)	79.67(3)	78.13(9)	77.82(9)
P(2)−Ru(1)−P(3)	69.4(2)	68.59(6)	69.36(9)	68.01(6)
P(2)−C(1)−P(3)	90.9(9)	89.2(3)	91.7(4)	88.7(3)
P(1)−C(1)−C(2)	106(2)	107.4(4)	108.6(6)	106.6(5)

Preliminary reactivity studies performed on ruthenium complexes **2a−d** have led to the interesting finding that they are quite stable and are inert to ligand substitution reactions. The PF_6^- salts are completely air and moisture stable and do not react with either CO or H_2 gas, even at elevated temperatures. Furthermore, it was thought that reactions with $NaBH_4$ would yield ruthenium hydride complexes with phosphorus−borane adducts, but this was not the case. Not even **2c**, which exhibited elongated Ru−P bonds in the crystal structure, showed any reactivity; instead, the starting materials were recovered unchanged. The Cp* ligand and the bulky tripodal phosphine ligand shroud the ruthenium center and prevent associative substitution reactions. Moreover, the Ru−P

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bonds do not readily dissociate to open up a vacant coordination site.

CONCLUSION

The 1,1,2-tris(diarylphosphino)ethane compounds **1a−d** were generated in an unprecedented trisubstitution reaction of diarylphosphorylacetaldehyde diethyl acetal, a synthetic route which was found to be a general method for producing new tripodal phosphine ligands. Although the mechanism of this process is currently unknown, it is suspected that the products are generated through a series of E_1cb reactions and unsaturated intermediates, followed by a final substitution reaction, all of which depend on the presence of the crucial phosphoryl functionality. In order to test the predictions made by Bookham et al. that ligands **1a−d** can occupy a *fac* geometry despite the considerable amount of strain involved, the tridentate ligands were combined with a suitable ruthenium(II) precursor to produce the complexes $[Ru(Cp^*)(L)]PF_6$.[52] The crystal structures of the ruthenium complexes revealed distorted-piano-stool type structures where the phosphine ligands are *fac* tripodal ligands. At the moment, however, this coordination geometry is limited to the complexes we have generated and the ruthenium precursor we have employed; further studies utilizing ruthenium starting materials with only monodentate ligands are needed. Despite the large steric bulk of the ligands, as well as the ring strain caused by the formation of a four-membered ring and two five-membered rings with the ruthenium center, complexes **2a−d** were quite stable with respect to ligand exchange reactions. Further studies on these interesting ruthenium systems are currently underway.

EXPERIMENTAL SECTION

General Considerations. All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk line and glovebox techniques unless stated otherwise. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Acetone was dried and distilled over P_2O_5 under an argon atmosphere. THF, pentane, hexanes, and diethyl ether were dried and distilled over sodium and benzophenone under an argon atmosphere. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under an argon atmosphere. Dichloromethane was dried and distilled over CaH_2 under an argon atmosphere. The synthesis of bis(*o*-tolyl)phosphineoxoacetaldehyde diethyl acetal was described previously. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. The ESI-MS data were collected on an AB/Sciex QStar mass spectrometer with an ESI source, the EI-MS data were collected on a Waters GC ToF mass spectrometer with an EI/CI source, and the DART-MS data were collected on a JEOL AccuTOF-DART mass spectrometer with a DART-ion source (no solvent is required). NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F, and 161 MHz for ^{31}P) unless stated otherwise. The ^{1}H and ^{13}C NMR spectra were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. The elemental analyses were performed at the Department of Chemistry, University of Toronto, on a Perkin-Elmer 2400 CHN elemental analyzer. Some complexes gave inconsistent carbon analyses but acceptable hydrogen and nitrogen contents; we attribute this to a combustion problem caused by the hexafluorophosphate counterion.[59] Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD or Bruker Kappa APEX DUO diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The CCD data were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using SHELXTL V6.1. Refinement was by full-matrix least squares on F^2 using all data.

Synthesis of $(C_6H_5)_2PCH_2CH(P(C_6H_5)_2)_2$ (1a). Diphenylphosphine (0.500 g, 2.69 mmol) was dissolved in 2 mL of THF and added to a suspension of KH (0.108 g, 2.69 mmol) in 5 mL of THF. Gas evolved, and the solution turned bright red. After 30 min the gas evolution ceased; then bis(*o*-tolyl)phosphineoxoacetaldehyde diethyl acetal (0.310 g, 0.895 mmol) in 3 mL of THF was added. The solution slowly turned yellow-orange in color and became cloudy. The solution was left overnight. An excess of degassed 48% HBF_4 (aq) (0.24 mL) was added, and the solution turned colorless with a white precipitate. The solvent was removed under reduced pressure, and the white residue was redissolved in THF. An excess of Na_2CO_3 (approximately 0.100 g) was added and gas evolved. The solution was stirred overnight and then filtered. The solvent was removed under reduced pressure. The residue was washed with approximately 5 mL of hexanes. Methanol was added to the colorless residue, and a white precipitate formed. The precipitate was filtered to give a white solid. Yield: 49.5% (0.258 g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.31−7.09 (m, 27H, Ar H), 6.93−6.88 (m, 3H, Ar H), 3.00 (dt, 1H, CH, J = 10.9, 7.4 Hz), and 2.09−2.00 (m, 2H, CH_2) ppm. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2): δ −3.82 (d, J = 24.8 Hz) and −19.77 (t, J = 24.8 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 138.60 (d, P−C, J = 16.6 Hz), 136.99 (t, C−P, J = 5.1 Hz), 136.52 (t, C−P, J = 5.2 Hz), 134.57 (td, Ar CH, J = 10.8, 1.5 Hz), 133.87 (td, Ar CH, J = 10.7, 1.3 Hz), 133.09 (d, Ar CH, J = 19.0 Hz), 129.02 (s, Ar CH), 128.78 (s, Ar CH), 128.68 (s, Ar CH), 128.50 (d, Ar CH, J = 6.5 Hz), 128.38−128.24 (m, Ar CH), 29.81 (dt, CH_2, J = 17.5, 10.2 Hz), and 28.94 (td, CH, J = 29.7, 11.3 Hz) ppm. Anal. Calcd for $[C_{38}H_{35}P_3]0.5[C_4H_{10}O]$: C, 76.81; H, 6.60. Found: C, 77.14; H, 6.34. MS (DART; m/z^+): 583.2 $[C_{38}H_{36}P_3]^+$.

Synthesis of $(p\text{-}C_7H_7)_2PCH_2CH(P(p\text{-}C_7H_7)_2)_2$ (1b). Similar to the synthesis of **1a**; see the Supporting Information.

Synthesis of $(o\text{-}C_7H_7)_2PCH_2CH(P(o\text{-}C_7H_7)_2)_2$ (1c). Similar to the synthesis of **1a**; see the Supporting Information.

Synthesis of $(m\text{-}C_8H_9)_2PCH_2CH(P(m\text{-}C_8H_9)_2)_2$ (1d). Similar to the synthesis of **1a**; see the Supporting Information.

Synthesis of $[RuCp^*(1a)]PF_6$ (2a). **1a** (0.111 g, 0.190 mmol) and $RuCp^*(COD)Cl$ (0.072 g, 0.190 mmol) were dissolved in dichloromethane (6 mL). The red-orange solution was stirred at 36 °C overnight. The solution turned darker red-orange. The solvent was removed under reduced pressure, and the residue was dissolved in acetone (6 mL). An excess of $NaPF_6$ (approximately 0.100 g) was added, and the solution was stirred overnight. The solution turned yellow-orange with a white precipitate. The solvent was removed under reduced pressure, and the yellow-orange residue was dissolved in dichloromethane. This solution was filtered, and the solvent was removed under reduced pressure. Methanol (5 mL) was added to the residue, and the slurry was stirred for 15 min. The yellow solid was isolated and washed with ether (5 mL). Yield: 93.4% (0.145 g). Crystals suitable for X-ray diffraction studies were grown from a dichloromethane solution by diffusion of pentane vapor. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.33−7.21 (m, 14H, Ar H), 7.16 (t, 2H, Ar H, J = 7.4 Hz), 7.10 (t, 2H, J = 7.3 Hz), 7.00 (t, 8H, Ar H, J = 7.5 Hz), 6.75−6.67 (m, 4H, Ar H), 5.74−5.57 (m, 1H, CH), 3.38−3.19 (m, 2H, CH_2), and 2.08 (s, 15H, Cp* CH_3) ppm. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2) δ: 60.82 (t, J = 30.6 Hz) and 30.81 (d, J = 30.6 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ: 134.69−133.88 (m, Cp* C), 132.77 (s, Ar CH), 132.66 (s, Ar CH), 132.06 (t, Ar CH, J = 5.9 Hz), 131.52−130.86 (m, Ar CH), 130.61 (s, Ar CH), 130.25 (s, Ar CH), 129.99 (d, C−P, J = 2.4 Hz), 129.58 (t, C−P, J = 5.1 Hz), 128.28 (t, Ar CH, J = 5.4 Hz), 128.09 (s, Ar CH), 127.99 (s, Ar CH), 95.39 (d, CH, J = 1.5 Hz), 30.87 (d, CH_2, J = 30.9 Hz), and 12.22 (s, Cp* CH_3) ppm. Anal. Calcd for $[C_{48}H_{48}P_3Ru][PF_6]0.66[CH_2Cl_2]$: C, 57.28; H, 4.87. Found: C, 57.37; H, 4.97. MS (ESI$^+$, dichloromethane; m/z^+): 819.2 $[C_{48}H_{48}P_3Ru]^+$.

Synthesis of $[RuCp^*(1b)]PF_6$ (2b). Similar to the synthesis of **2a**; see the Supporting Information.

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Synthesis of [RuCp*(1c)]PF_6 (2c). Similar to the synthesis of **2a**; see the Supporting Information.

Synthesis of [RuCp*(1d)]PF_6 (2d). Similar to the synthesis of **2a**; see the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Text, a table, and CIF files giving an extended experimental section and crystallographic data for **2a–d**. 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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