Ruthenium Complexes of the 1,4-Bis(diphenylphosphino)-1,3-butadiene-Bridged Diphosphine 1,2,3,4-Me$_4$-NUPHOS: Solvent-Dependent Interconversion of Four- and Six-Electron Donor Coordination and Transfer Hydrogenation Activity

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Received October 16, 2002

In chloroform, [RuCl$_2$(nbd)(py)$_2$] (**1**) (nbd = norbornadiene; py = pyridine) reacts with 1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene (1,2,3,4-Me$_4$-NUPHOS) to give the dimer [Ru$_2$Cl$_3$(η^4-1,2,3,4-Me$_4$-NUPHOS)$_2$]Cl (**2a**), whereas, in THF [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(py)$_2$] (**3**) is isolated as the sole product of reaction. Compound **2** exists as a 4:1 mixture of two noninterconverting isomers, the major with C_1 symmetry and the minor with either C_s or C_2 symmetry. A single-crystal X-ray analysis of [Ru$_2$Cl$_3$(η^4-1,2,3,4-Me$_4$-NUPHOS)$_2$][SbF$_6$] (**2b**), the hexafluoroantimonate salt of **2a**, revealed that the diphosphine coordinates in an unusual manner, as a η^4-six-electron donor, bonded through both P atoms and one of the double bonds of the butadiene tether. Compounds **2a** and **3** react with 1,2-ethylenediamine (en) in THF to afford [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(en)] (**4**), which rapidly dissociates a chloride ligand in chloroform to give [RuCl(η^4-1,2,3,4-Me$_4$-NUPHOS)(en)][Cl] (**5a**). Complexes **4** and **5a** cleanly and quantitatively interconvert in a solvent-dependent equilibrium, and in THF **5a** readily adds chloride to displace the η^2-interaction and re-form **4**. A single-crystal X-ray structure determination of [RuCl(η^4-1,2,3,4-Me$_4$-NUPHOS)(en)][ClO$_4$] (**5b**) confirmed that the diphosphine coordinates in an η^4-manner as a facial six-electron donor with the η^2-coordinated double bond occupying the site trans to chloride. The η^4-bonding mode can be readily identified by the unusually high-field chemical shift associated with the phosphorus atom adjacent to the η^2-coordinated double bond. Complexes **2a**, **2b**, **4**, and **5a** form catalysts that are active for transfer hydrogenation of a range of ketones. In all cases, catalysts formed from precursors **2a** and **2b** are markedly more active than those formed from **4** and **5a**.

Introduction

Since its discovery, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) has proven to be a highly versatile chiral auxiliary for a wide range of platinum group metal catalyzed transformations[1] including ruthenium- and rhodium-catalyzed hydrogenations,[2] electrophilic alkylations,[3] ruthenium-catalyzed ring-opening polymerizations,[4] inter- and intramolecular Heck reactions,[5] palladium-catalyzed hydrocyanations,[6] and the rhodium-catalyzed enantioselective isomerization of allylic amines.[7] The success of BINAP as a supporting chiral auxiliary has prompted efforts to develop alternative structurally related conformationally flexible biaryl atropisomeric diphosphines, the majority of which are based on a 6,6′-substituted biphenyl tether such as (*R*)-MeO-BIPHEP and (*R*)-BIPHEMP[8] or a similar four-carbon sp^2-hydridized tether as in BINAPFu,[9] (*R*)-BITIANP,[10] and (+)-TMBTP (Chart 1).[11] A related conformationally flexible diphosphine 2,2′-bis(diphe-

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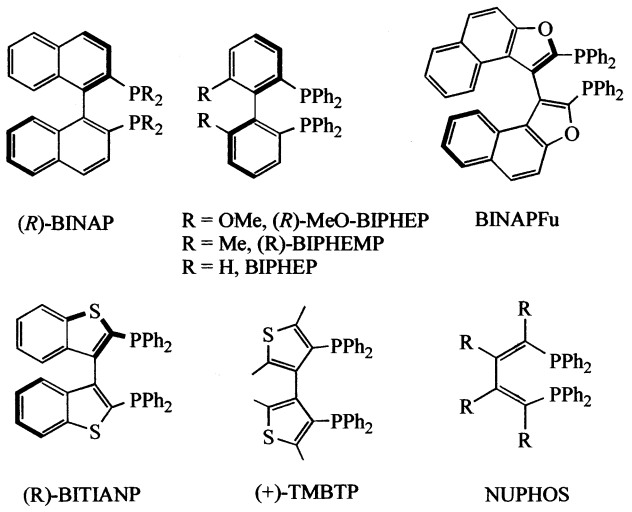
10.1021/om020861b CCC: $25.00
Publication on Web 02/26/2003

nylphosphino)-1,1′-biphenyl (BIPHEP) has recently been employed to catalyze a range of achiral transformations including the palladium-catalyzed cross coupling of sec-BuMgCl with vinyl halides, the rhodium-catalyzed Michael addition of boronic acids to enones, and the palladium-catalyzed amination of aryl bromides.[12] Given the impact of this diphosphine type in platinum-group metal catalysis we became interested in developing a new methodology for the synthesis of related diphosphines and have recently prepared an entirely new class of four-carbon-bridged diphosphine, NUPHOS, by liberating zirconacyclopentadienes with chlorodiphenylphosphine.[13] Preliminary studies have revealed that palladium complexes of NUPHOS type diphosphines are highly active for the cross coupling of *sec*-butylmagnesium bromide with bromobenzene, with activities far superior to those obtained with BINAP- and dppf-based catalysts.

Chart 1



The challenging problem of asymmetric hydrogenation of simple unfunctionalized ketones has recently been accomplished using BINAP diamine complexes of the type [RuCl$_2$(BINAP)(1,2-diamine)], the combination of *S*-XylBINAP and *S*-DAIPEN (DAIPEN = *S*-1,1-di-4-anisyl-2-methyl-1,2-ethylenediamine), resulting in quantitative hydrogenation of a range of 2′, 3′-, and 4′-substituted acetophenones to give the corresponding secondary alcohols with consistently high stereoselectivity.[14] In a particularly elegant extension of his early studies on asymmetric hydrogenation, Noyori showed that ruthenium complexes of the conformationally flexible BIPHEP, when activated by addition of a chiral diamine such as *S,S*-DPEN, catalyze the enantioselective hydrogenation of acetonaphthone to give (*R*)-1-(1-naphthyl)ethanol in 92% ee,[15] a significant improvement on the performance of the corresponding *racemic*-BINAP complex.[16] The clear similarity between the basic skeletal framework of NUPHOS and that of BINAP and BIPHEMP and its derivatives, namely, two diphenylphosphino groups connected by a four-carbon sp^2-hybridized tether, prompted us to investigate its ruthenium-based coordination chemistry with the aim of preparing potential catalyst precursors of the type [RuCl$_2$(NUPHOS)(diamine)]. Herein we report our initial studies toward this objective, which include the synthesis of [Ru$_2$Cl$_2$(η^4-1,2,3,4-Me$_4$-NUPHOS)$_2$]Cl, in which the diphosphine coordinates in an unusual η^4-manner as a six-electron donor through both P atoms and one of the double bonds of the butadiene tether, its reaction with 1,2-ethylenediamine (en) to give [RuCl$_2$-(1,2,3,4-Me$_4$-NUPHOS)(en)], which exists in a solvent-dependent dissociative equilibrium with [RuCl(η^4-1,2,3,4-Me$_4$-NUPHOS)(en)]Cl, and the results of preliminary transfer hydrogenation studies for each of the newly prepared ruthenium complexes.

Results and Discussion

Synthesis and Spectroscopic Characterization of Ruthenium(II) Complexes. Our first indication that the coordination chemistry of 1,2,3,4-Me$_4$-NUPHOS (1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene) did not parallel exactly that of BINAP arose during the attempted preparation of [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(diamine)]. Following the procedure described by Noyori for the synthesis of [RuCl$_2$(BINAP)-(diamine)],[16a] treatment of oligomeric [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(dmf)$_n$] with a slight excess of 1,2-ethylenediamine gave a mixture of several products, of which the desired compound was only a minor component. In the search for an alternative route, we noted that Bergens recently reported a versatile and convenient method for the synthesis of diphosphine−diamine complexes that involves treatment of a dichloromethane solution of [RuCl$_2$(nbd)(py)$_2$] (**1**) (nbd = norbornadiene; py = pyridine) with a variety of diphosphines to give [RuCl$_2$(diphosphine)(py)$_2$], followed by substitution of

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Scheme 1

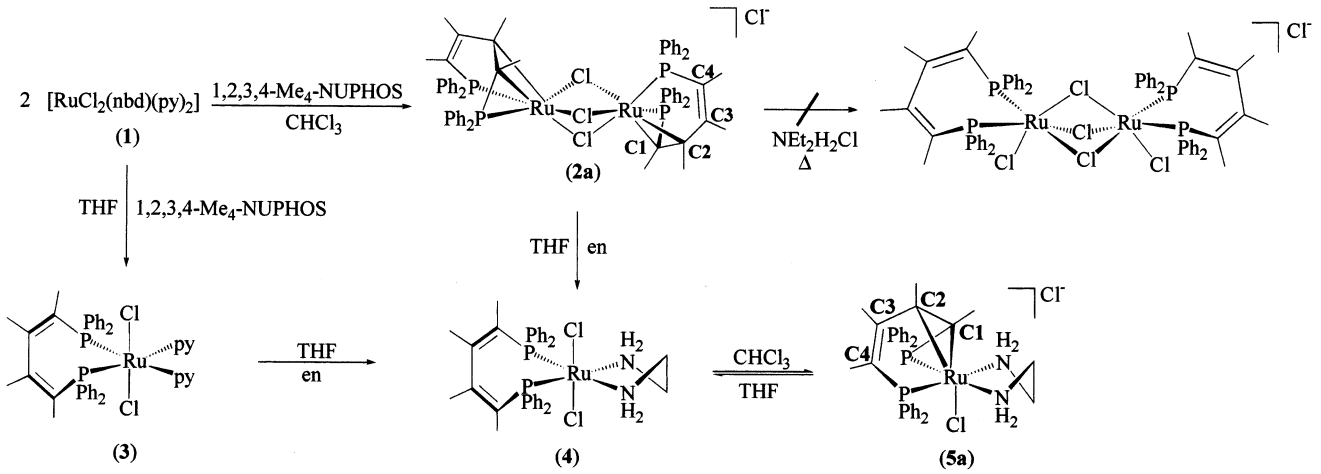
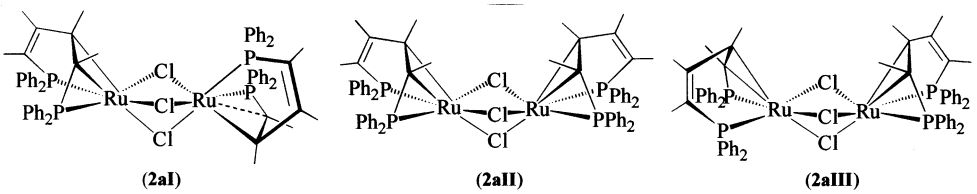


Chart 2



pyridine with a diamine at room temperature.[17] Following this protocol, addition of 1,2,3,4-Me$_4$-NUPHOS to a dichloromethane or chloroform solution of **1** resulted in rapid and quantitative formation of [Ru_2Cl_3(η^4-1,2,3,4-Me$_4$-NUPHOS)$_2$]Cl (**2a**), identified initially by a molecular ion peak at 1268 amu in the electrospray mass spectrum and subsequently by a single-crystal X-ray study of its hexafluoroantimonate salt (Scheme 1). In contrast, **1** reacts with 1,2,3,4-Me$_4$-NUPHOS at 50 °C in THF to give predominantly [$RuCl_2$(1,2,3,4-Me$_4$-NUPHOS)(py)$_2$] (**3**) together with minor amounts of **2a** (typically < 5%). The $^{31}P\{^1H\}$ NMR spectrum of **2a** (Figure 1) contains two distinct sets of resonances consistent with a mixture of two noninterconverting isomers, the minor of which appears as a single AX spin system (●, minor isomer, δ 86.8 and 10.5 ppm; $^2J_{PP}$ = 50.2 Hz) and the major of which can be treated as two independent AX spin systems (◆, major isomer, δ = 87.6 and 13.3; 83.4 and 6.4 ppm; $^2J_{PP}$ = 49.8 Hz). The methyl region of the ^1H NMR spectrum of **2a** contains a set of eight equal intensity signals for the major isomer and a set of four equal intensity signals for the minor isomer. Integration of these resonances gave an isomeric ratio close to 4:1, which is consistent with that obtained from the ^{31}P NMR spectrum. Three of the doublets in the $^{31}P\{^1H\}$ NMR spectrum of **2a** appear at unexpectedly high field, in the region associated with an uncoordinated diphosphine, which is consistent with η^4-coordination as a six-electron donor through both phosphorus atoms and one of the double bonds of the butadiene tether. Pregosin has recently identified and structurally characterized a number of related ruthenium complexes in which MeO-BIPHEP and BINAP coordinate in an η^4-manner.[18] In each case, the $^{31}P\{^1H\}$ NMR spectrum contains an unexpectedly low-frequency resonance, now

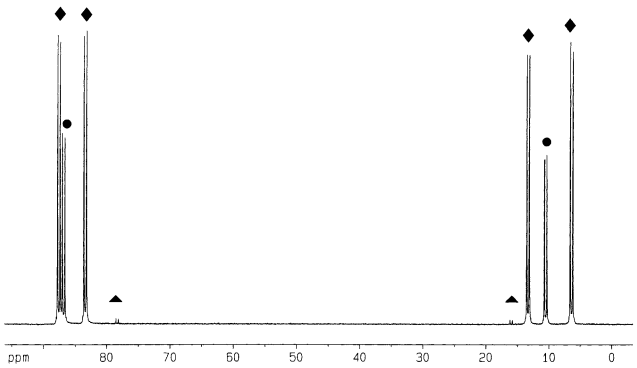


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **2a** showing the disparate chemical shifts of the two types of phosphorus atoms in the major (◆) and minor (●) isomers ($CDCl_3$, 298 K). A second set of doublets of low intensity (▲, < 1%) probably belong to the third possible isomer.

recognized as typical of this coordination mode and belonging to the phosphorus donor adjacent to the coordinated double bond. Prior to this Pathak reported disparate chemical shifts for the two phosphorus nuclei in [RuCp(BINAP)][CF_3SO_3], in which the BINAP coordinates in a similar η^4-six-electron manner.[19] Although high-field carbon-13 chemical shifts provide an indication of this unusual bond type, Pregosin recommends the use of long-range correlation spectroscopy to unequivocally assign resonances associated with the carbon atoms of the coordinated double bond.[18] In the case of compound **2a**, long-range correlation spectroscopy identified three doublets of doublets at δ 89.6, 88.6, and 87.0 ppm and a further three doublets at δ 52.3, 51.4,

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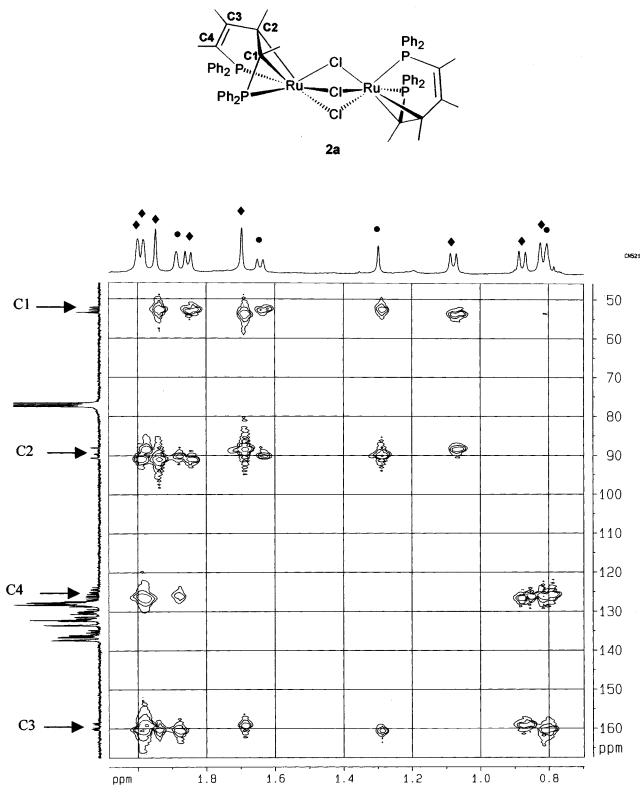

Figure 2. $^{13}C-^{1}H$ long-range correlation for **2a** showing the cross-peaks arising from $^{2}J(C-H)$ and $^{3}J(C-H)$ coupling between the η^2-coordinated sp^2-hybridized carbons and the protons attached to the neighboring methyl groups (◆, 4 doublets + 4 singlets associated with the major isomer, **2aI**; ●, 2 doublets and 2 singlets associated with the minor isomer, either **2aII** or **2aIII**).

and 51.3 ppm, which we confidently assign to the six carbon atoms associated with the three magnetically nonequivalent η^2-coordinated carbon−carbon double bonds of the two noninterconverting isomers (vide infra). Each of these carbon-13 signals has either two or three cross-peaks arising from two- and three-bond $J(C-H)$ coupling constants to the protons of neighboring methyl groups (Figure 2). The three C1 resonances appear as doublets, and each clearly correlates with two sets of methyl protons, a singlet and doublet, whereas the three doublets of doublets corresponding to C2 each correlate with three sets of methyl protons: two singlets and a doublet. Similarly, this long-range correlation study can also be used to identify the resonances associated with the carbon atoms of the uncoordinated double bond (C3 + C4). Since the η^4-six-electron donor NUPHOS is geometrically constrained to coordinate in a facial arrangement to a trichloride-bridged dimer, there are only three possible isomers, **2aI**, **2aII**, and **2aIII**, the first of which has C_1 symmetry while **2aII** and **2aIII** have C_s and C_2 symmetry, respectively (Chart 2). Considering each isomer in turn, C_1 symmetrical **2aI** is expected to give rise to two independent AX doublets of doublets in the $^{31}P\{^{1}H\}$ NMR spectrum (Figure 1, ◆), four high-field ^{13}C signals associated with two sets of C1 and C2 carbon atoms, and four doublets and four singlets in the ^{1}H NMR spectrum for the eight nonequivalent methyl groups (Figure 2, ◆). The remaining two isomers with C_s and C_2 symmetry should each give rise to an AX type $^{31}P\{^{1}H\}$ NMR spectrum (Figure 1, ●), two high-field ^{13}C signals for C1 and C2, and only two doublets and two singlets in the ^{1}H NMR spectrum for the methyl groups (Figure 2, ●). Clearly, based on the pattern of resonances in the $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of **2a**, **1** reacts with 1,2,3,4-Me$_4$-NUPHOS to give a mixture of two isomers, **2aI** and either **2aII** or **2aIII**. An additional low-intensity (<1%) AX spin system (▲, Figure 1) is consistent with the formation of a minor amount of the third possible isomer, although at this stage we cannot confidently assign the two AX spin systems to their respective isomers, **2aII** and **2aIII**.

Under the same conditions as those used to form **2a**, *rac*-BINAP reacts with [RuCl$_2$(nbd)(py)$_2$] in chloroform to afford [RuCl$_2$(*rac*-BINAP)(py)$_2$] with no evidence for the formation of the corresponding [Ru$_2$Cl$_3$(*rac*-BINAP)$_2$]-Cl, even after heating at reflux overnight. Thus, 1,2,3,4-Me$_4$-NUPHOS demonstrates a much greater propensity to coordinate in a η^4-manner than does BINAP, possibly because of the greater conformational flexibility of the four-carbon tether in the former. The stability of **2a** in refluxing chloroform was confirmed by monitoring the thermolysis of a sample by ^{31}P NMR spectroscopy in the presence of an internal standard containing triphenylphosphine in chloroform. This experiment demonstrates that formation of an unobserved paramagnetic Ru(III) dimer is unlikely since the **2a**:PPh$_3$ ratio remained constant while the sample was heated at 55 °C for 14 h. The stability of [RuCl$_2$(*rac*-BINAP)(py)$_2$] with respect to oxidation is not surprising since the thermolysis of this compound was conducted under an inert atmosphere. For comparison, [RuCl$_2$(BINAP)(bipy)] (bipy = 2,2′-bipyridine) has recently been reported to undergo aerobic oxidation in methanol to give the monoxide [RuCl(BINAPO)(bipy)][PF$_6$].[20]

X-ray Structure of [Ru$_2$Cl$_3$(1,2,3,4-Me$_4$-NUPHOS)$_2$][SbF$_6$] (2b). In view of the unusual coordination mode of 1,2,3,4-Me$_4$-NUPHOS a single-crystal X-ray study of **2b**, prepared by exchange of the chloride in **2a** with SbF$_6$, was undertaken to provide precise details on the nature of the metal−ligand bonding. Since the crystal quality was poor, discussion of the structure has been limited to a description and comparison of the most important features. The molecular structure of **2b** is shown in Figure 3, a selection of bond lengths and angles is listed in Table 1, and crystal data are provided in Table 5. The most notable feature of this structure is the six-electron donor diphosphine, which coordinates to ruthenium through both phosphorus atoms and one of the double bonds of the butadiene tether. Three chlorides asymmetrically bridge the two ruthenium atoms to complete a distorted octahedral coordination geometry. The Ru(μ-Cl)Ru angles (average 86.0°) are similar to those in the diruthenium monoalkylidene [Ru(dcypb)(μ-Cl)$_3$(dcypb)(CHCH=CMe$_2$)][21a] and the diruthenium cation [{(*t*Bu$_2$PCH$_2$P*t*Bu$_2$CHPh)Ru}$_2$(μ-Cl)$_3$]-[Cl].[21b] The Ru−C bond lengths lie between 2.17(2) and 2.22(2) Å and are comparable to those previously

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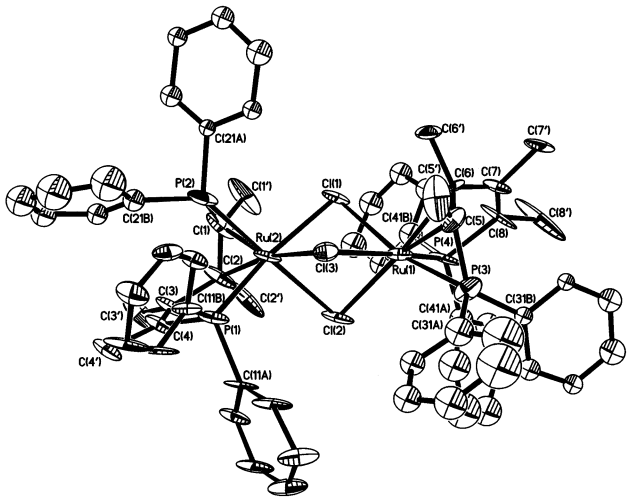

Figure 3. Molecular structure of $[Ru_2Cl_3(\eta^4\text{-}1,2,3,4\text{-}Me_4\text{-}NUPHOS)_2][SbF_6]$ (**2b**). Hydrogen atoms, solvent molecules of crystallization, and hexafluoroantimonate anion have been omitted for clarity. Ellipsoids are at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2b

Ru(1)−P(3)	2.251 (8)	Ru(2)−C(1)	2.17(3)
Ru(1)−P(4)	2.259(6)	Ru(2)−C(2)	2.22(2)
Ru(2)−P(1)	2.269(6)	Ru(1)−C(5)	2.17(2)
Ru(2)−P(2)	2.240(8)	Ru(1)−C(6)	2.22(2)
Ru(1)−Cl(1)	2.452(6)	C(1)−C(2)	1.37(3)
Ru(1)−Cl(2)	2.454(6)	C(2)−C(3)	1.54(3)
Ru(1)−Cl(3)	2.536(6)	C(3)−C(4)	1.30(3)
Ru(2)−Cl(1)	2.489(6)	C(5)−C(6)	1.49(3)
Ru(2)−Cl(2)	2.499(7)	C(6)−C(7)	1.47(3)
Ru(2)−Cl(3)	2.459(6)	C(7)−C(8)	1.30(3)
Ru(1)−Cl(1)−Ru(2)	86.5(2)	Cl(3)−Ru(2)−P(1)	92.1(2)
Ru(1)−Cl(2)−Ru(2)	86.2(2)	Cl(3)−Ru(2)−P(2)	114.3(2)
Ru(1)−Cl(3)−Ru(2)	85.3(2)	Cl(2)−Ru(2)−P(1)	95.7(2)
P(1)−Ru(2)−P(2)	91.1(2)	Cl(2)−Ru(2)−P(2)	165.6(3)
P(3)−Ru(1)−P(4)	90.6(3)	Ru(1)−C(5)−C(5′)	124.3(17)
Cl(1)−Ru(1−Cl(2)	80.2(2)	Ru(1)−C(5)−C(6)	71.9(12)
Cl(1)−Ru(1)−Cl(3)	78.0(3)	Ru(1)−C(5)−P(3)	68.4(9)
Cl(2)−Ru(1)−Cl(3)	77.6(2)	Ru(1)−C(6)−C(6′)	117.1(15)
Cl(1)−Ru(1)−P(3)	165.0(3)	Ru(1)−C(6)−C(7)	116.0(13)
Cl(1)−Ru(1)−P(4)	92.7(2)	Ru(1)−C(6)−C(5)	68.4(13)
Cl(3)−Ru(1)−P(4)	167.0(2)	Ru(2)−C(1)−C(1′)	121.7(18)
Cl(3)−Ru(1)−P(3)	100.8(2)	Ru(2)−C(1)−C(2)	73.7(16)
Cl(2)−Ru(1)−P(3)	114.3(3)	Ru(2)−C(1)−P(2)	64.6(10)
Cl(2)−Ru(1)−P(4)	91.9(2)	Ru(2)−C(2)−C(2′)	116(2)
Cl(1)−Ru(2)−P(1)	170.0(2)	Ru(2)−C(2)−C(3)	113.87(14)
Cl(1)−Ru(2)−P(2)	96.3(2)	Ru(2)−C(2)−C(1)	69.8(15)
Cl(3−Ru(1)−Cl(1)	78.8(2)		

reported for cationic ruthenium olefin complexes.[22,23] However, they are significantly shorter than the corresponding distances of 2.299(1) and 2.366(5) Å in the analogous MeO-BIPHEP complex $[Ru(\eta^5\text{-}C_8H_{11})(MeO\text{-}BIPHEP)][CF_3CO_2]$,[18b] which is presumably due to η^2-interaction of the isolated π-bond in **2b** compared to the delocalized π-system of the biphenyl tether in MeO-BIPHEP. The C(1)−C(2) and C(5)−C(6) bond lengths of 1.37(3) and 1.49(3) Å, respectively, are significantly longer than C(3)−C(4) and C(7)−C(8) and are typical of an η^2-coordinated olefin.[24] The Ru−P bond lengths are similar to those reported for the binuclear ruthenium(II) complex [{RuCl{(*R*)-2,2′-bis(bis(*p*-methoxyphenyl)phosphino)-1,1′-binaphthyl}$_2$(μ-Cl)$_3$][NEt_2H_2].[25] The natural bite angles of 90.1(2)° and 90.6(3)° for P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4), respectively, are similar to that of 91.0(3)° reported for $[Ru(\eta^6\text{-indole})(MeO\text{-}BIPHEP)][BF_4]$.[18a] The separation of 3.385 Å between Ru(1) and Ru(2) is similar to that in other trichloride-bridged dimers[27,28] and is outside of the range for a Ru−Ru bond. The twist of the butadiene tether away from the expected δ/λ conformation is required to orientate the π-system of the double bond toward the metal for complexation. The gross structural features of **2b** are similar to those of the anionic binuclear hydrogenation catalyst [{RuCl{(*R*)-TolBINAP)}$_2$(μ-Cl)$_3$][NEt_2H_2][26] in that both are based on trichloride face-sharing octahedra with two P-donors in the coordination sphere. Despite this similarity, we have been unable to convert **2a** into the analogous binuclear anion [{RuCl(1,2,3,4-Me_4-NUPHOS)}$_2$(μ-Cl)$_3$][NEt_2H_2] by substitution of the η^2-coordinated double bonds with chloride, even using conditions similar to those reported for the synthesis of its BINAP counterpart (Scheme 1).

Synthesis and Spectroscopic Characterization of [$RuCl_2$(1,2,3,4-Me_4-NUPHOS)(en)] (4) and [RuCl(1,2,3,4-Me_4-NUPHOS)(en)][Cl] (5a). Although compound **2a** is inert with respect to addition of chloride, tetrahydrofuran solutions of **2a** react with 1,2-ethylenediamine to afford [$RuCl_2$(1,2,3,4-Me_4-NUPHOS)(en)] (**4**). Alternatively, **4** can be prepared in near quantitative yield by addition of 1,2-ethylenediamine to a THF solution of [$RuCl_2$(1,2,3,4-Me_4-NUPHOS)(py)$_2$] (**3**), prepared in situ by addition of 1,2,3,4-Me_4-NUPHOS to a THF solution of **1** at room temperature (Scheme 1). Compound **4** is unstable in common halogenated solvents (vide infra), which limits the range of solvents available for purification and characterization. Fortunately, a spectroscopically and analytically pure sample was obtained by crystallization from a concentrated toluene solution at room temperature overnight. The singlet at δ 49.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **4** is close to that at δ 46.87 reported for [$RuCl_2${(*R*)-BINAP}{(*R*,*R*)-DPEN}]. Surprisingly, upon standing under an inert atmosphere, chloroform solutions of **4** slowly lose chloride overnight to afford [RuCl(η^4-1,2,3,4-Me_4-NUPHOS)(en)][Cl] (**5a**), a transformation that occurs quantitatively and more rapidly at elevated temperatures (Scheme 1). The most distinctive feature in the $^{31}P\{^1H\}$ NMR spectrum of **5a** is the presence of a high-field doublet at δ 5.1 ppm, a clear indication that the 1,2,3,4-Me_4-NUPHOS coordinates as a η^4-six-electron donor. A long-range $^{13}C-^1H$ correlation study clearly showed a connectivity between two high-field doublets at δ 87.1 and 51.5 ppm, associated with nonprotonated carbons, and the protons of neighboring methyl groups. The former signal correlates with pro-

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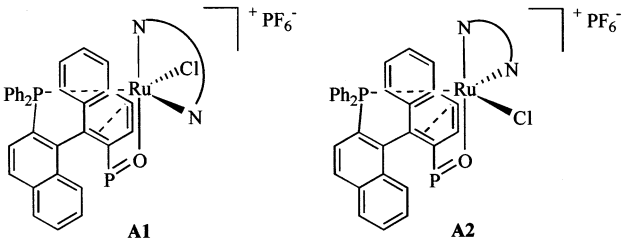
Chart 3



tons of two methyl groups and the latter with protons of three, conclusive evidence for their assignment as the C1 and C2 carbon atoms, respectively (Scheme 1). These two signals are shifted markedly to high field, consistent with coordination of the carbon−carbon double bond.[29] Pregosin has reported similar shifts for the coordinated biaryl double bond in a range of ruthenium complexes including [RuCp(BINAP)][BF_4],[18a] [Ru(η^5-C_8H_{11})(MeO-BIPHEP)][BF_4],[18b] and [Ru(η^6-indole)(MeO-BIPHEP)]-[BF_4]$_2$.[18a] Compounds **4** and **5a** can be cleanly and quantitatively interconverted in a solvent-dependent equilibrium. In tetrahydrofuran, the chloride counterion of **5a** rapidly displaces the η^2-interaction to afford **4**, within 2−3 h, while dichloromethane, chloroform, carbon tetrachloride, and 1,2-dichloroethane solutions of **4** lose chloride at room temperature overnight to re-form **5a**. This is the first example of a facile interconversion between a diphosphine that coordinates in a bidentate manner, as a four-electron donor, and as an η^4-six-electron donor via reversible coordination of a carbon−carbon double bond. Not surprisingly, the perchlorate salt [RuCl(1,2,3,4-Me$_4$-NUPHOS)(en)][ClO_4] (**5b**) is indefinitely stable in all common halogenated and non-halogenated solvents since the counterion is noncoordinating.

During a study of the solution chemistry of *cis*-[$RuCl_2$-(P−P)L_2] complexes (P−P = 1,4-bis(diphenylphosphino)-butane or *R*-BINAP; L_2 = bidentate N-donor) and their applications in the catalytic hydrogenation of imines, James and co-workers discovered that alcohol solutions of these complexes readily dissociate chloride and that methanol solutions of *cis*-[$RuCl_2$(P−P)L_2] and the cation *cis*-[RuCl(P−P)L_2(MeOH)][Cl] are not stable.[20] Slow oxidation occurs to give two isomers of [RuCl(BINAPO)-L_2][PF_6] (A1 and A2, Chart 3), with the BINAPO coordinated in a P,O-η^2-naphthyl manner as a six-electron donor through both phosphorus atoms and the two carbon atoms of the naphthyl ring proximate to the P=O group. Interestingly, [RuCl(BINAPO)L_2][PF_6] can also be prepared by aerobic oxidation of [RuCl{(*R*)-BINAP}L_2][PF_6], generated in situ by treatment of *cis*-[$RuCl_2${(*R*)-BINAP}L_2] with $AgPF_6$. The presence of two distinct well-separated resonances in the ^{31}P NMR spectrum of [RuCl{(*R*)-BINAP}L_2][PF_6], one shifted to low frequency, is characteristic of η^2-coordination of one of the binaphthyl double bonds. The η^2-naphthyl coordination in [RuCl{(*R*)-BINAP}L_2]$^+$ is stable only in non/weakly coordinating solvents and readily forms [RuCl-{(*R*)-BINAP}L_2(solvent)]$^+$ in methanol and acetonitrile. In contrast, complexes **2a** and **5a** are stable in methanol and propan-2-ol and show no sign of forming the corresponding solvento complexes [Ru_2Cl_3(1,2,3,4-Me$_4$-NUPHOS)$_2$(solvent)$_2$][SbF_6] and [RuCl(1,2,3,4-Me$_4$-NUPHOS)(en)(solvent)][ClO_4], even after standing for several days.

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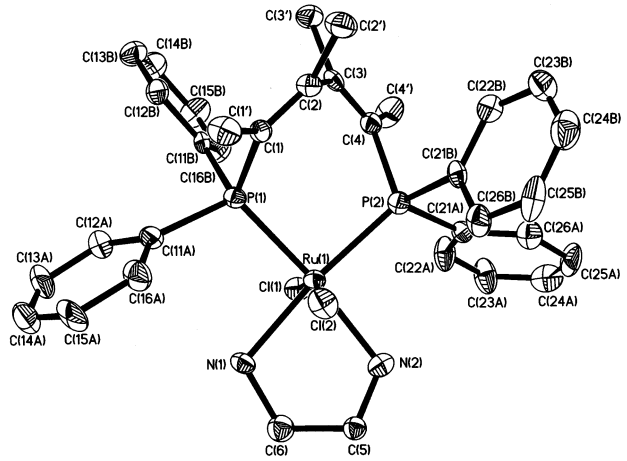


Figure 4. Molecular structure of [$RuCl_2$(1,2,3,4-Me$_4$-NUPHOS)(1,2-ethylenediamine)] (**4**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 30% probability level.

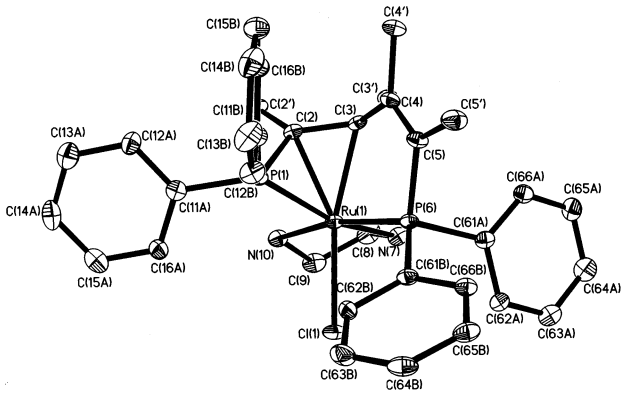


Figure 5. Molecular structure of [RuCl(η^4-1,2,3,4-Me$_4$-NUPHOS)(1,2-ethylenediamine)][ClO_4] (**5b**). Hydrogen atoms, solvent molecules of crystallization, and perchlorate anion have been omitted for clarity. Ellipsoids are at the 30% probability level.

X-ray Structures of [$RuCl_2$(1,2,3,4-Me$_4$-NUPHOS)-(en)] (4) and [RuCl(η^4-1,2,3,4-Me$_4$-NUPHOS)(en)]-[ClO_4] (5b). Single-crystal X-ray analyses of compounds **4** and **5b** have been undertaken in order to examine the influence of η^4-cordination on the metal−diphosphine bonding and the coordination geometry at the metal. Perspective views of the molecular structures of **4** and **5b** are shown in Figures 4 and 5, respectively, and selected bond lengths and angles for both molecules are listed in Table 2. The ruthenium atom in **4** has a slightly distorted octahedral geometry with near C_2 symmetry and a trans arrangement of chlorides, which show a marked distortion from linearity with a Cl(1)−Ru(1)−Cl(2) angle [164.55(7)°] very close to that in the BINAP-diamine complexes [$RuCl_2${(*R*)-TolBINAP}{(*R*,*R*)-dpen}] and [$RuCl_2${(*R*)-TolBINAP}{(*S*,*S*)-dpen}].[16a] The P-phenyl rings adopt the alternating edge−face arrangement expected for atropisomeric diphosphines, and the four-carbon sp^2-hybridized tether has a λ conformation with a dihedral angle of 67.2° between the least squares plane containing the two sp^2 carbon atoms and their substituents, C(1)C(1′)C(2)C(2′) and C(3)C(3′)C(4)C(4′).

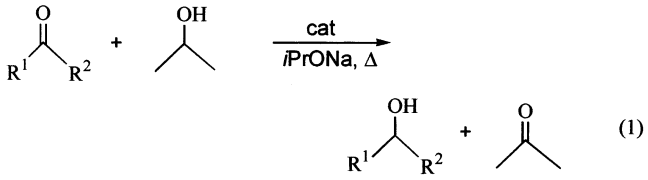
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 4 and 5b

compound **4**		compound **5b**	
Ru(1)−P(1)	2.280(2)	Ru(1)−P(1)	2.2764(14)
Ru(1)−P(2)	2.287(2)	Ru(1)−P(6)	2.2777(14)
Ru(1)−Cl(1)	2.421(2)	Ru(1)−Cl(1)	2.4321(15)
Ru(1)−Cl(2)	2.415(2)	Ru(1)−N(7)	2.174(4)
Ru(1)−N(1)	2.167(6)	Ru(1)−N(10)	2.202(4)
Ru(1)−N(2)	2.168(6)	Ru(1)−C(2)	2.188(4)
C(1)−C(2)	1.327(10)	Ru(1)−C(3)	2.247(4)
C(2)−C(3)	1.491(10)	C(2)−C(3)	1.431(7)
C(3)−C(4)	1.322(9)	C(3)−C(4)	1.505(6)
		C(4)−C(5)	1.340(6)
P(1)−Ru(1)−P(2)	91.79(7)	P(1)−Ru(1)−P(6)	93.54(6)
P(1)−Ru(1)−N(2)	173.18(19)	P(1)−Ru(1)−N(7)	163.02(10)
P(2)−Ru(1)−N(1)	173.25 (16)	P(1)−Ru(1)−N(10)	96.72(12)
N(1)−Ru(1)−N(2)	78.8(2)	P(6)−Ru(1)−N(10)	168.00(10)
P(1)−Ru(1)−N(1)	94.96(16)	P(6)−Ru(1)−N(7)	93.16(11)
P(2)−Ru(1)−N(2)	94.40(18)	Cl(1)−Ru(1)−C(3)	165.02(12)
Cl(1)−Ru(1)−Cl(2)	164.55(7)	Cl(1)−Ru(1)−C(2)	155.12(13)
Cl(1)−Ru(1)−N(1)	82.90(16)	Cl(1)−Ru(1)−P(1)	112.39(4)
Cl(1)−Ru(1)−N(2)	84.83(17)	Cl(1)−Ru(1)−P(6)	87.97(5)
Cl(1)−Ru(1)−P(1)	97.43(7)	Cl(1)−Ru(1)−N(7)	83.43(11)
Cl(1)−Ru(1)−P(2)	96.35(7)	Cl(1)−Ru(1)−N(10)	82.40(10)
Cl(2)−Ru(1)−N(1)	82.81(16)	P(6)−Ru(1)−C(3)	77.92(11)
Cl(2)−Ru(1)−N(2)	86.70(17)	P(6)−Ru(1)−C(2)	105.25(12)
Cl(2)−Ru(1)−P(1)	89.60(7)	P(1)−Ru(1)−C(3)	73.64(11)
Cl(2)−Ru(1)−P(2)	97.16(7)	P(1)−Ru(1)−C(2)	47.05(11)
Ru(1)−P(1)−C(1)	112.3(2)	Ru(1)−P(1)−C(2)	63.87(14)
P(1)−C(1)−C(2)	117.9(6)	Ru(1)−P(6)−C(5)	108.28(15)
C(1)−C(2)−C(3)	125.8(6)	P(1)−C(2)−C(3)	114.5(3)
C(2)−C(3)−C(4)	126.6(6)	C(2)−C(3)−C(4)	122.3(4)
C(3)−C(4)−P(2)	120.3(6)	C(2)−C(3)−Ru(1)	69.0(2)
C(4)−P(2)−Ru(1)	114.4(2)	C(3)−C(2)−Ru(1)	73.4(2)
		C(4)−C(3)−Ru(1)	117.3(3)

The bonding in the four-carbon tether is highly localized with the C(1)−C(2) and C(3)−C(4) bond lengths of 1.327(10) and 1.322(9) Å, respectively, close to that expected for a C(sp^2)−C(sp^2) double bond, and the C(2)−C(3) bond length of 1.491(10) Å, typical of a single bond between sp^2-hybridized carbon atoms.

Although we have been unable to grow crystals of **5a** suitable for X-ray analysis, crystals of **5b**, the perchlorate salt of **5a**, have been obtained from a concentrated methanol solution at room temperature. The molecular structure shown in Figure 5 clearly reveals **5b** to be monomeric and based on a severely distorted octahedral geometry with the η^4-six-electron diphosphine occupying a facial coordination environment, bonded through both phosphorus atoms and one of the double bonds of the butadiene backbone. The remainder of the coordination sphere consists of a bidentate 1,2-ethylenediamine and a chloride ligand, which occupies the site trans to the double bond. The C(2)−C(3) bond length of 1.431(7) Å shows the expected elongation upon η^2-coordination and is similar to those in **2a** and significantly longer than that of 1.340(6) Å for the uncoordinated double bond C(4)−C(5). The Ru−P bond lengths of 2.2764(14) and 2.2777(14) Å for Ru(1)−P(1) and Ru(1)−P(6), respectively, are longer than those in [Ru(H)(η^1-BH_4)-{(*R*)-BINAP}{(*R*,*R*)-dpen}][30] and [Ru(H)Cl{(*R*)-BINAP}-(dpen)][31] but are within the range reported for the ruthenium diphosphine−diamine complex [$Ru(H)_2$-{(*R*)-BINAP}(tmen)].[32] Coordination of C(1)−C(2) at the site trans to chloride results in a marked distortion of the P(1)−P(6)−N(7)−N(10) atoms from an ideal square planar geometry, as indicated by the dihedral angle of 18.3° between the planes containing P(1)−Ru(1)−P(6) and N(7)−Ru(1)−N(10), which is much larger than the corresponding distortion of 3.0° in **4**. Coordination of C(2)−C(3) also has a dramatic influence on the spatial arrangement of the P-phenyl rings such that both attached to P(1) adopt pseudoequatorial positions, while those attached to P(6) occupy pseudoequatorial and pseudoaxial sites. In comparison, the 1,2,3,4-Me_4-NUPHOS in **4** forms a seven-membered chelate ring with a distorted skew-boat conformation and an alternating edge−face arrangement of the four phenyl rings.

Catalytic Studies: Ruthenium-Based Transfer Hydrogenation of Ketones. Several features of the ruthenium-based coordination chemistry of 1,2,3,4-Me_4-NUPHOS have prompted us to investigate the performance of this diphosphine in the transfer hydrogenation of ketones (eq 1), in particular (i) possible stabilization



(1)

of a reactive 16-electron intermediate via coordination of the 1,2,3,4-Me_4-NUPHOS in a η^4-six-electron manner, (ii) the presence of N-H groups and phosphorus donors, a combination commonly used in ruthenium-catalyzed transfer hydrogenations,[33] and (iii) the similarity between 1,2,3,4-Me_4-NUPHOS coordinated in a facial manner as a six-electron donor and an η^6-arene, particularly since ruthenium(II) arene complexes in combination with amino alcohols form highly efficient catalysts for transfer hydrogenation.[34] Preliminary results for the reduction of a range of ketones using complexes **2a**, **2b**, **4**, and **5a** are summarized in Table 3. In a typical experiment, a propan-2-ol solution of the ruthenium complex and substrate was heated for 10 min, activated by addition of base (20 equiv), and the progress of the reaction monitored by GC. The volume of each reaction mixture was adjusted such that all catalytic runs were initiated with a substrate concentration of 0.1 M. For each substrate, comparative catalytic runs were performed using [$RuCl_2(PPh_3)_3$][35] as a standard in order to relate the results of our studies to those reported in the literature. For all substrates

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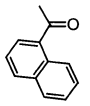
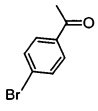
Table 3. Transfer Hydrogenation of Ketones Catalyzed by the Ru(II) Complexes 2a, 2b, 4, and 5a[a]

Substrate	Catalyst	Entry	Catalyst (mol%)	Time (min)	TOF[b]
	**2a**	1	0.0625	5	37600
	2b	2	0.0625	5	34600
	4	3	0.0625	5	2500
	5a	4	0.0625	5	3700
	$RuCl_2(PPh_3)_3$	5	0.0625	5	4500
	2a	6	0.125	10	2060
	**2b**	7	0.125	15	1860
	4	8	0.125	30	380
	5a	9	0.125	30	400
	$RuCl_2(PPh_3)_3$	10	0.125	30	290
	2a	11	0.125	15	1380
	**2b**	12	0.125	15	1220
	4	13	0.125	30	460
	5	14	0.125	30	380
	$RuCl_2(PPh_3)_3$	15	0.125	30	300
	2a	16	0.125	30	430
	**2b**	17	0.125	30	580
	4	18	0.5	30	70
	5a	19	0.5	30	100
	$RuCl_2(PPh_3)_3$	20	0.125	10	1200
	2a	21	0.125	30	1152
	**2b**	22	0.125	30	1050
	4	23	0.5	60	110
	5a	24	0.5	60	140
	$RuCl_2(PPh_3)_3$	25	0.5	60	80

[a] Reaction was carried out in refluxing propan-2-ol using a solution 0.1 M in substrate and 20 equiv of *i*PrONa as base. [b] Initial TOF, determined by GC analysis of the reaction mixture after diluting with propan-2-ol and filtering through silica, based on formation of product. Average activity over three runs, reproducibility ±5%.

tested, catalysts formed from precursors **2a** and **2b** outperform those based on monomers **4** and **5a**, even assuming that each dimer generates 2 equiv of active catalyst. Catalyst mixtures based on **2a** and **2b** show good conversion rates for the transfer hydrogenation of cyclohexanone, acetophenone, 4-methylacetophenone, and 4-bromoacetophenone, with initial TOF up to an order of magnitude higher than that obtained with $[RuCl_2(PPh_3)_3]$. On the basis of initial TOF, acetonaphthone proved to be a particularly challenging substrate for this new series of catalysts (entries 16−19) and was most efficiently hydrogenated with $[RuCl_2(PPh_3)_3]$. This reversal in activity is somewhat surprising given that, for all other substrates studied, catalysts based on NUPHOS are consistently more active than that formed from $[RuCl_2(PPh_3)_3]$. Comparison of the initial TOF obtained using precursors **2a** and **2b** reveals that catalyst performance does not depend significantly on the nature of the counterion. Varying the catalyst-to-base ratio was found to have a dramatic effect on activity. In the absence of base, no reaction was observed and conversion rates increased with increasing catalyst/base ratio to give an optimum activity with 20 equiv per ruthenium (Table 4).

Under the conditions of base-accelerated transfer hydrogenation with catalysts generated from **2a** and **2b**, reduction most likely occurs via a dihydride mechanism.[36] In the absence of stabilization by solvent the active catalyst [RuH$_2$(1,2,3,4-Me$_4$-NUPHOS)] could be either 16- or 14-electron, depending on whether the phosphine coordinates as a six- or four-electron donor, respectively (Chart 4). An NMR study of the reaction between **2b** and *i*PrONa in propan-2-ol at reflux revealed that under these conditions a ruthenium hydrido species is formed, as evidenced by the presence of a broad high-field signal in the ^{1}H NMR spectrum, and that the diphosphine probably coordinates as a four-electron donor based on the absence of any high-field ^{31}P signals associated with η^4 six-electron coordination. There are several recent reports of the use of ^{1}H NMR spectroscopy to identify hydride species after activation of the catalyst precursor under basic conditions which include formation of a mixture of $[RuH_2(PPh_3)_3]$ and $[RuH_2(H_2)(PPh_3)_3]$ from $[Ru(PPh_3)_3Cl_2]$[36a] and generation of the hydrido anion $[Ru(PCP)(PPh_3)(H)(i\text{PrO})]^-$ (PCP = $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$) after treatment of [Ru(PCP)(PPh$_3$)(OSO$_2$CF$_3$)] with *i*PrOH/KOH in the absence of ketone.[37] However, at this stage comments about the nature of the active species are speculative and we cannot eliminate the possibility that the catalyst could be a dimer such as $[Ru_2(H)_2(\mu\text{-Cl})_2(1,2,3,4\text{-Me}_4\text{-NUPHOS})_2]$ (Chart 4), acting either as a 16-electron monohydride or as a bimetallic dihydride.

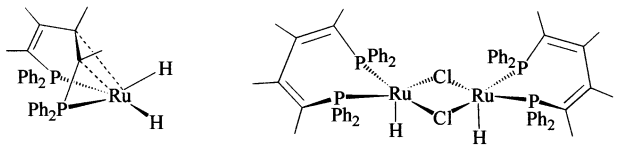
In the case of transfer hydrogenation with **4** and **5a**, we must consider an alternative mechanism since the N-H groups of 1,2-ethylenediamine are capable of stabilizing a six-membered transition state involving the Ru-H and the carbonyl group of the ketonic substrate. The accelerating effect of an N-H group on the rate of transfer hydrogenation was first noted for a ruthenium

Table 4. Influence of Base Concentration on Transfer Hydrogenation Activity of Acetophenone Catalyzed by the Ru(II) Complexes 2a and 4[a]

catalyst	catalyst (mol %)	*i*PrONa (equiv)	time (min)	TOF[b]
2a	0.125	0	10	20
2a	0.125	5	10	1300
2a	0.125	10	10	1390
2a	0.125	20	10	1920
2a	0.125	40	10	1820
4	0.125	0	30	0
4	0.125	5	30	140
4	0.125	10	30	260
4	0.125	20	30	380
4	0.125	40	30	360

[a] Reaction was carried out in refluxing propan-2-ol using a solution 0.1 M in substrate and equivalents of *i*PrONa as base. [b] Initial TOF (mol of product per mol catalyst per hour), determined by GC analysis of the reaction mixture after diluting with propan-2-ol and filtering through silica, based on formation of product.

Chart 4



(36) (a) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun.* **1999**, 351. (b) Pàmies, O.; Bäckvall, J.-E. *Chem. Eur. J.* **2001**, *7*, 5052. (c) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533.

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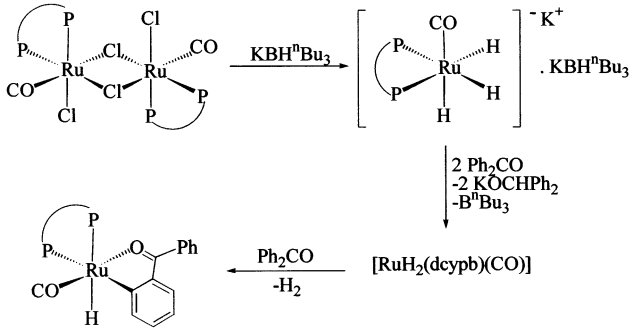
complex of the C_2-symmetric diphosphine−diamine *N,N*-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine, which showed a markedly higher activity than its imine counterpart.[38] Numerous additional reports have subsequently appeared that support the role of an N-H in delivering the hydrogen atom from a metal-hydride to the ketone.[39] For example, Morris and co-workers have provided convincing evidence that the *cis*-M−H- -H−N bifunctional moiety is a key feature of the highly active ruthenium-based hydrogenation catalyst [$RuH_2(PPh_3)_2$\{(*R,R*)-cyclohexyldiamine\}] and have suggested that the first step in the catalytic hydrogenation of ketones involves concerted transfer of the hydride to the carbonyl carbon and N-H proton to the oxygen.[39b] The low initial TOF obtained with catalyst precursors **4** and **5a** could be taken as evidence of a dihydride mechanism since hydrogenation involving concerted transfer of Ru-H and N-H would be expected to lead to much higher initial TOF. Indeed, the low initial TOF obtained with catalysts generated from **4** and **5a** compared with those generated from **2a** and **2b** suggests that coordinative unsaturation and substrate coordination are important features of the catalytic cycle. In the case of **4** and **5a** the active species [RuH_2(1,2,3,4-Me_4-NUPHOS)(en)] would be coordinatively saturated and reluctant to interact with substrate, which would account for the poor performance of these catalysts if the dihydride mechanism operates. In contrast, the higher activities obtained with catalysts generated from **2a** and **2b** are not surprising since the active dihydride would be coordinatively unsaturated. In this regard, there is an emerging body of evidence that suggests coordinative unsaturation can be more important than H-bonding in conferring hydrogenation activity. Gimeo has reported that the five-coordinate complexes [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH{=}NtBu)(PPh_3)$], [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH_2NHtBu)(PPh_3)$], and [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH_2NHtBu)$(DMSO)] are more active then the octahedral [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH{=}NtBu)(DMSO)_2$] and that the phosphino-imine complex [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH{=}NtBu)(PPh_3)$], devoid of an N-H functionality, has an activity similar to that of its corresponding phosphino-amine derivative [$RuCl_2(\kappa^2$-*P,N*-2-$Ph_2PC_6H_4CH_2NHtBu)(PPh_3)$].[40] However, it should be noted that this apparent absence of an N-H effect could be due to the bulky secondary amine, preventing formation of a hydrogen bond. Fogg and co-workers recently reported that *fac*-[RuH_3(CO)(dcypb)]K [dcypb = 1,4-bis(dicyclohexylphosphino)butane] effects reduction of benzophenone with an activity comparable to that of the Noyori system, which is based on a combination of a chelating diphosphine and 1,2-diamine.[20a] The high activity achieved with *fac*-[RuH_3(CO)(dcypb)]K provides further evidence that an N-H group is not a necessary requirement for achieving efficient ketone hydrogenation. The orthometalated [RuH\{*o*-C(O)(Ph)C_6H_4\}(dcypb)-(CO)] (Scheme 2) was identified as the catalyst resting state in the catalytic hydrogenation of benzophenone via *fac*-[RuH_3(CO)(dcypb)]K, and the most likely origin of the high activity was suggested to be the generation of a vacant coordination site by reversible insertion of ruthenium into the ortho C−H bond. Clearly, the higher activity achieved with catalysts generated from **2a** and **2b** compared with those formed from **4** and **5a** lends further support to the important role of coordinative unsaturation in determining activity, particularly if a pathway involving concerted transfer of N-H and Ru-H is not available. The marked dependence of activity on the concentration of base also strongly suggests that reduction occurs via a hydride mechanism rather than the concerted hydride proton transfer commonly associated with catalysts supported by ligands containing protic groups. Further studies are clearly required to distinguish between the two mechanisms possible for catalysts generated from **4** and **5a**.

Scheme 2



Conclusion

These studies have demonstrated that 1,2,3,4-Me_4-NUPHOS can readily interconvert between coordination as a four-electron bidentate diphosphine and a six-electron donor via reversible coordination of one of the carbon−carbon double bonds of the four-carbon tether. Complexes **2a**, **2b**, **4**, and **5a** form catalysts that are active for the transfer hydrogenation of a range of ketones, and preliminary NMR studies suggest that a hydride mechanism operates. For all substrates tested, there is a significant differential between the performance of catalysts formed from the coordinatively unsaturated binuclear precursors **2a**,**b** and the 18-electron diphosphine−diamine complexes **4** and **5a**. As a result of these encouraging transfer hydrogenation studies, detailed synthetic and mechanistic investigations to establish the identity of the active catalyst and the mechanism of transfer hydrogenation, the use of amino-alcohols in combination with ruthenium(II) complexes of η^4-six-electron-1,2,3,4-Me_4-NUPHOS for asymmetric transfer hydrogenation, and the use of chiral diamines for asymmetric activation of ruthenium(II) complexes of 1,2,3,4-Me_4-NUPHOS toward enantioselective hydrogenation are currently underway.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in an inert atmosphere glovebox or using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from potassium/sodium alloy, tetrahydrofuran from potassium, dichloromethane from calcium hydride, and methanol from magnesium. Unless

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otherwise stated, commercially purchased materials were used without further purification. The ruthenium complexes [$RuCl_2$(nbd)(py)$_2$] and [$RuCl_2$(*rac*-BINAP)(py)$_2$] were prepared as previously described.[17] Deuteriochloroform was predried with calcium hydride and vacuum transferred and stored over 4 Å molecular sieves. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on JEOL LAMBDA 500 or Bruker AC 200, AMX 300, and DRX 500 machines. GC analyses were conducted on a Varian CP3800 connected to a Varian C8400 auto sampler with a CHIRASIL-DEX CB column.

Synthesis of [Ru$_2$Cl$_3$(1,2,3,4-Me$_4$-NUPHOS)$_2$]Cl (2a). A solution of [$RuCl_2$(nbd)(py)$_2$] (0.5 g, 1.18 mmol) in chloroform (10 mL) was treated with a chloroform solution (4−5 mL) of 1,2,3,4-Me$_4$-NUPHOS (0.564 g, 1.18 mmol) and stirred vigorously overnight, after which time the reaction mixture was filtered and the solvent removed to leave a deep orange solid residue. Crystallization by slow diffusion of *n*-hexane into a dichloromethane solution at room temperature gave **2a** as orange crystals in 78% yield (0.60 g). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): major isomer, 87.6 (d, $^2J_{PP}$ = 49.8 Hz, P_{A1}), 83.4 (d, $^2J_{PP}$ = 49.8 Hz, P_{A2}), 13.3 (d, $^2J_{PP}$ = 49.8 Hz, P_{X1}), 6.4 (d, $^2J_{PP}$ = 49.8 Hz, P_{X2}); minor isomer, 86.8 (d, $^2J_{PP}$ = 49.8 Hz, P_A), 10.5 (d, $^2J_{PP}$ = 49.8 Hz, P_X). ^{13}C{^{1}H} NMR (125.45 MHz, $CDCl_3$, δ): 159.3 (d, J_{PC} = 26.3 Hz, *C*Me), 158.7 (d, J_{PC} = 26.3 Hz, *C*Me), 157.7 (d, J_{PC} = 26.9 Hz, *C*Me), 136.3−122.6 (m, C_6H_5 + *C*Me), 89.6 (dd, J_{PC} = 7.0, 5.0 Hz, *C*Me), 88.6 (dd, J_{PC} = 7.0, 5.5 Hz, *C*Me), 87.0 (dd, J_{PC} = 7.0, 4.4 Hz, *C*Me), 52.3 (d, J_{PC} = 35.4 Hz, *C*Me), 51.4 (d, J_{PC} = 34.5 Hz, *C*Me), 51.3 (d, J_{PC} = 34.9 Hz, *C*Me), 23.7 (m, *C*H$_3$), 23.1 (d, J_{PC} = 7.8 Hz, *C*H$_3$), 20.6−20.0 (m, *C*H$_3$), 16.9 (d, J_{PC} = 6.0 Hz, *C*H$_3$), 16.6 (d, J_{PC} = 5.4 Hz, *C*H$_3$), 15.0 (d, J_{PC} = 5.4 Hz, *C*H$_3$), 13.5 (s, *C*H$_3$). ^{1}H NMR (500.1 MHz, $CDCl_3$, δ): 8.29−6.75 (m, 40H, C_6H_5), 2.0 (s, 3H, C*H*$_3$, major isomer), 1.98 (s, 3H, C*H*$_3$, major isomer), 1.95 (s, 3H, C*H*$_3$, major isomer), 1.93 (s, 6H, C*H*$_3$, minor isomer), 1.85 (d, J_{PH} = 8.8 Hz, 3H, C*H*$_3$ major isomer), 1.70 (s, 3H, C*H*$_3$, major isomer), 1.64 (d, J_{PH} = 8.4 Hz, 6H, C*H*$_3$, minor isomer), 1.30 (s, 6H, C*H*$_3$, minor isomer), 1.07 (d, J_{PH} = 8.8 Hz, 3H, C*H*$_3$, major isomer), 0.90 (d, J_{PH} = 9.6 Hz, 3H, C*H*$_3$, major isomer), 0.83 (d, J_{PH} = 9.6 Hz, 3H, C*H*$_3$, major isomer), 0.79 (s, J_{PH} = 9.6 Hz, 6H, C*H*$_3$, minor isomer). Anal. Calcd for $C_{64}H_{64}Cl_4P_4Ru_2$: C, 62.04; H, 5.21. Found: C, 62.41; H, 5.32.

Synthesis of [Ru$_2$Cl$_3$(1,2,3,4-Me$_4$-NUPHOS)$_2$][SbF$_6$] (2b). A chloroform solution of [Ru_2Cl_3(1,2,3,4-Me$_4$-NUPHOS)$_2$]Cl (0.40 g, 0.306 mmol) was stirred overnight with a slight excess of $NaSbF_6$ (0.129 g, 0.5 mmol). The reaction mixture was filtered, the solvent removed, and the residue crystallized by slow diffusion of methanol into a dichloromethane solution at room temperature, to give X-ray quality crystals of **2b** in 66% yield (0.302 g). Anal. Calcd for $C_{64}H_{64}Cl_3F_6P_4Ru_2Sb$: C, 51.20; H, 4.30. Found: C, 51.53; H, 4.45.

Synthesis of [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(py)$_2$] (3). A tetrahydrofuran solution of [$RuCl_2$(nbd)(py)$_2$] (0.50 g, 1.18 mmol) and 1,2,3,4-Me$_4$-NUPHOS (0.564 g, 1.18 mmol) was stirred overnight, after which time the reaction mixture was filtered and the solvent removed to leave a solid yellow residue. The product could be isolated by extraction of this residue into toluene and precipitation by addition of diethyl ether to give **3** as a spectroscopically pure fine yellow powder. However, compound **3** was typically generated in THF and reacted with 1,2-ethylenediamine without further purification. ^{31}P{^{1}H} NMR (121.4 MHz, THF, δ): 48.05 (s, PPh_2). ^{1}H NMR (500.13 MHz, C_6D_6, δ): 9.0−6.1 (m, 30H, C_6H_5, C_5H_5N), 2.17 (t, J = 4.5 Hz, 6H, C*H*$_3$), 0.64 (br s, 3H 6H, C*H*$_3$).

Thermolysis of [RuCl$_2$(*rac*-BINAP)(py)$_2$]. In a typical experiment a sample of [$RuCl_2$(*rac*-BINAP)(py)$_2$] (0.055 g, 0.057 mmol) was dissolved in deuteriochloroform (ca. 0.5 mL) and transferred via cannula to an NMR tube. A capillary containing PPh_3 (0.020 g, 0.076 mmol) in chloroform was used as an internal standard. A time zero spectrum was recorded, the sample heated at 60 °C, and the progress of the thermolysis monitored by ^{31}P NMR spectroscopy.

Synthesis of [RuCl$_2$(1,2,3,4-Me$_4$-NUPHOS)(en)] (4). A tetrahydrofuran solution of [$RuCl_2$(1,2,3,4-Me$_4$-NUPHOS)(py)$_2$] (0.35 g, 0.432 mmol) and 1,2-ethylenediamine (0.033 mL, 0.5 mmol) was stirred at room temperature under an inert atmosphere for 7−8 h, after which time the solvent was removed to leave an orange-yellow residue, which was purified by crystallization from a concentrated toluene solution at room temperature to give **4** in 71% yield (0.22 g). ^{31}P{^{1}H} NMR (121.4 MHz, THF, δ): 49.7 (s, PPh_2). ^{1}H NMR (500.13 MHz, C_6D_6, δ): 8.8 (br, 4H, C_6H_5), 8.5−6.9 (m, 16H, C_6H_5), 2.8 (br, 2H, N*H*$_2$), 2.0 (m, 6H, C*H*$_3$), 1.98 (br, 6H, C*H*$_2$ + N*H*$_2$), 0.75 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (125.45 MHz, C_6D_6, δ): 159.0 (s, *C*Me), 144−123 (m, C_6H_5 + *C*Me), 43.0 (s, N*C*H$_2$), 20.1 (t, J_{PC} = 3.4 Hz, *C*H$_3$), 18.7 (t, J_{PC} = 3.1 Hz, *C*H$_3$). Anal. Calcd for $C_{34}H_{40}Cl_2N_2P_2Ru$: C, 57.47; H, 5.67; N, 3.94. Found: C, 57.67; H, 5.78; N, 4.02.

Synthesis of [RuCl(1,2,3,4-Me$_4$-NUPHOS)(en)]Cl (5a). Compound **4** (0.330 g, 0.463 mmol) was dissolved in ca. 20 mL of chloroform and stirred under an inert atmosphere overnight. The solvent was removed and the product purified by slow diffusion of a hexane into a chloroform solution at room temperature to give **5a** as a yellow powder in 92% yield (0.462 g). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 79.9 (d, J_{PP} = 50.2 Hz), 5.1 (d, J_{PP} = 50.2 Hz). ^{1}H NMR (500.13 MHz, $CDCl_3$, δ): 7.97 (dd, J = 8,9, 7.4 Hz, 2H, C_6H_5), 7.90 (dd, J = 12.1, 7.0 Hz, 2H, C_6H_5), 7.90−7.38 (m, 10H, C_6H_5), 7.23 (dd, J = 11.3, 7.5 Hz, 2H, C_6H_5), 7.16 (t, J = 7.3 Hz, 2H, C_6H_5), 6.99 (dt, J = 7.6, 2.2 Hz, 2H, C_6H_5), 3.68 (br m, 1H, N*H*), 2.98 (br m, 1H, N*H*), 2.87 (br m, 1H, N*H*), 2.48 (br m, 2H, N*H* + C*H*$_2$), 2.39 (br m, 1H, C*H*$_2$), 2.32 (br m, 1H, C*H*$_2$), 2.06 (s, 3H, C*H*$_3$), 1.64 (br m, 1H, C*H*$_2$), 1.78 (s, 3H, C*H*$_3$), 1.75 (d, J_{PH} = 7.8 Hz, 3H, C*H*$_3$), 0.97 (d, J_{PH} = 9.3 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (125.45 MHz, $CDCl_3$, δ): 159.7 (dd, J_{PC} = 29.4, 5.1 Hz, *C*Me), 138−125 (m, C_6H_5 + *C*Me), 87.1 (d, J_{PC} = 7.9, 4.0 Hz, *C*Me), 51.5 (d, J_{PC} = 31.9 Hz, *C*Me), 44.9 (s, N*C*H$_2$), 42.5 (s, N*C*H$_2$), 23.0 (d, J_{PC} = 7.5 Hz, C*Me*), 21.7 (d, J_{PC} = 18.7, C*Me*), 15.0 (d, J_{PC} = 4.9 Hz, C*Me*), 14.3 (d, J_{PC} = 2.8 Hz, C*Me*). Anal. Calcd for $C_{34}H_{40}Cl_2N_2P_2Ru$: C, 57.57; H, 5.67; N, 3.94. Found: C, 57.49; H, 5.71; N, 4.07.

Synthesis of [RuCl(1,2,3,4-Me$_4$-NUPHOS)(en)][ClO$_4$] (5b). A chloroform solution of **5a** (0.25 g, 0.35 mmol) as stirred overnight with a slight excess of $NaClO_4$ (0.06 g, 0.5 mmol). The reaction mixture was filtered, the solvent removed, and the residue crystallized from a concentrated methanol solution at room temperature to give **5b** in 66% yield (0.180 g). X-ray quality crystals of **5b** were grown by slow diffusion of methanol into a chloroform solution at room temperature. Anal. Calcd for $C_{34}H_{40}Cl_2N_2O_4P_2Ru$: C, 52.72; H, 5.20. Found: C, 52.87; H, 5.45.

General Procedure for Transfer Hydrogenation Reactions. A Schlenk flask was charged with the catalyst precursor (0.0025 mmol), 19.5 mL of *i*PrOH, substrate (2 mmol), and *n*-decane internal standard (2 mmol). The solution was heated at 82 °C for 10 min, and then 0.5 mL (0.05 mmol) of a solution of *i*PrONa in *i*PrOH (0.1 M) was added. The volume of *i*PrOH was adjusted so that all catalytic reactions were conducted with an initial substrate concentration of 0.1 M. The addition of *i*PrONa was taken as the starting time for the reaction. The extent of conversion was determined by gas chromatography. GC conditions: initial temperature 100 °C for 5 min, final temperature 200 °C, ramp rate 8 °C/min, injection temperature 200 °C, detector temperature 300 °C, carrier gas He at 25 mL/min, column Varian WCOT fused silica, 25 m × 0.32 mm i.d., coating CP CHIRASIL-DEX CB.

Crystal Structure Determinations of 2b, 4, and 5b. Data were collected on a Bruker-AXS SMART diffractometer using SAINT-NT[41a] software with graphite monochromated Mo Kα radiation and are tabulated in Table 5. The structures were solved using direct methods and refined with SHELXTL version 5,[41b] and all non-hydrogen atoms (unless disordered) were refined with anisotropic thermal parameters. Close

Table 5. Summary of Crystal Data and Structure Determination for Compounds 2b, 4, and 5b

	2b	4	5b
formula	$C_{75}H_{73}Cl_8F_6OP_4Ru_2Sb$	$C_{34}H_{40}Cl_2N_2P_2Ru$	$C_{35}H_{44}Cl_2N_2O_5P_2Ru$
M_r	1745.63	710.59	806.63
cryst color	orange	yellow	yellow
cryst size, mm	0.34 × 0.26 × 0.12	0.58 × 0.33 × 0.30	0.40 × 0.35 × 0.32
temperature, K	298	298	153
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	12.921(9)	10.241(2)	11.545(6)
b, Å	17.770(15)	12.076(3)	15.876(9)
c, Å	32.10(2)	14.071(4)	19.742(11)
α, deg		71.79(3)	
β, deg	92.41(2)	88.47(4)	101.758(11)
γ, deg		81.04(2)	
V, Å^3	7364(10)	1632.3(7)	3543(3)
Z	4	2	4
D_{calc}, g cm^{-3}	1.575	1.446	1.512
$F(000)$	3500	732	1664
μ(Mo Kα), mm^{-1}	1.202	0.768	0.710
θ_{max}, deg	23.31	28.63	28.46
no. of reflns measd	44 728	4730	19 044
no. of unique reflns	10 598	4711	7445
R_{int} (on F^2)	0.2598	0.0324	0.1777
no. of params	674	373	427
$R^a[F^2 > 2\sigma(F^2)]$	0.1058	0.0452	0.0543
$R_w{}^b$(all data)	0.3229	0.1433	0.1587
GOF^c (S)	1.102	0.958	1.107
max., min. diff map, e Å^{-3}	1.32, −1.604	0.624, −0.479	1.186, −1.334

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [c] GOF $= [\sum w(F_o^2 - F_c^2)^2/(\text{no. unique reflns} - \text{no. of params})]^{1/2}$.

inspection of the atomic displacement parameters for the three crystal structures revealed that they all had some disorder associated with either the ligands or the anions. In **2b** four of the phenyl rings and two of the CH_2Cl_2 solvent molecules were disordered and have been modeled as having two major positions in a 50:50 ratio. The remaining CH_2Cl_2 solvent molecule is not disordered but has an occupancy factor of 50%. The 1,2-ethylenediamine ligand in **4** is disordered over two positions with occupancy factors of 50%, and the perchlorate ions in **5b** are also disordered and have been modeled as having two positions with occupancy factors of 50%. Hydrogen atom positions were added at idealized positions with a riding model and fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for methyl)). The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

(41) (a) *SAINT-NT*, program for data collection and data reduction; Bruker-AXS: Madison, WI, 1998. (b) Sheldrick, G. M. *SHELXTL* Version 5.0, A System for Structure Solution and Refinement; Bruker-AXS: Madison, WI, 1998.

Acknowledgment. We gratefully acknowledge the Queen's University of Belfast and the McClay Trust for funding and Johnson Matthey for loans of palladium salts.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, and anisotropic thermal parameters for compounds **2b**, **4**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available from the authors upon request.

OM020861B