η^1 to η^6 Ru−Arene π Complexation: New Bonding Modes and P−C Bond Cleavage Chemistry

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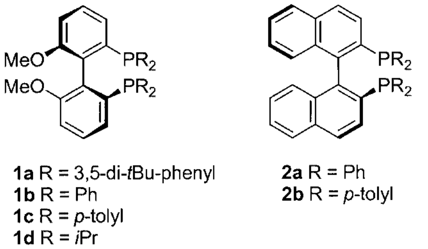
Keywords: P−C bond cleavage / π complexes / Unusual bonding / Stereospecific migration

Binap and MeOBiphep biarylbis(phosphane) complexes of Ru^{II} are shown to undergo a series of stereospecific P–C bond cleavage reactions. The products are novel cationic chiral arenebis(phosphane) compounds which contain stereogenic Ru centers. Upon further solvolysis in alcohols, additional P–C cleavage reactions lead to stereogenic P atoms. Several novel olefin π-bonding modes are recognised, including one in which only a single arene carbon atom i.e. an η^1 π-bond, weakly coordinates to Ru^{II}.

1. Introduction

There is an increasing interest in the area of enantioselective homogeneous catalysis[1] involving relatively small quantities of chiral catalytic materials that can produce substantial amounts of an enantiopure product. Although there are numerous examples of successful chiral nitrogen chelates,[2,3] as well as mixed P,N-ligands,[4] many auxiliaries are still based on chelating tertiary phosphanes.



1a R = 3,5-di-*t*Bu-phenyl
1b R = Ph
1c R = *p*-tolyl
1d R = *i*Pr

2a R = Ph
2b R = *p*-tolyl

The atropisomeric phosphanes MeO−Biphep **1**[5] and Binap **2**[6] are known to be excellent auxiliaries. These function exceptionally well in Ru-based homogeneous hydrogenation,[7,8] but can also be used in allylic alkylation,[9] and Heck reactions using palladium.[10] The syntheses of **1** and **2** are sufficiently flexible such that various R groups can be introduced and the backbone modified.[5,11] The catalyst precursor most often used in hydrogenation is the octahedral complex $Ru(OAc)_2$(**1**), $Ru(OAc)_2$(**2**), or a related trifluoroacetate complex.

Despite the widespread use of these biaryl ligands, not a great deal is known with respect to their fundamental organometallic chemistry. Several hydride compounds have been prepared,[12] e.g. $[RuH(i\text{PrOH})_2(\mathbf{1a})]BF_4$ (**3**),[13] however, olefin and alkyl compounds seem to have been neglected. Given the utility of **1** and **2**, it seems reasonable to ask how these might modify classical coordination behaviour. Moreover, if catalysts based on these ligands behave poorly or "die" in the course of the reaction, then perhaps knowledge of the possible decomposition pathways is important.

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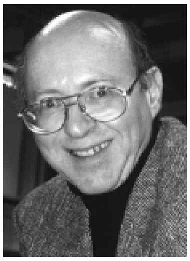

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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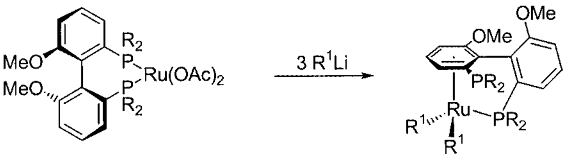
As an example, reaction of [Ru(OAc)$_2$(**1a**)] with 3 equiv. of methyllithium or trimethylsilylmethyllithium affords the dialkyl complexes [RuR$_2$(**1a**)] (**4a** or **4b**) in good yields [see Equation (1)].[14]



(1)

R = 3,5-di-*t*Bu-phenyl

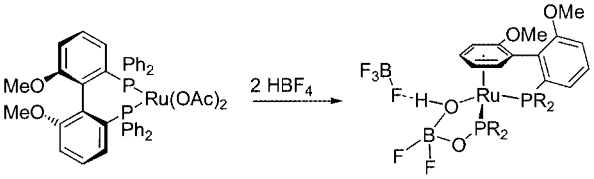
4a R^1 = Me
4b R^1 = CH$_2$SiMe$_3$

The molecule achieves this coordinatively saturated electronic structure by dissociating one tertiary phosphane donor, thereby making room (electronically) for an η^6-arene. This reduction from a bidentate to a monodentate ligand is hardly a common occurrence; however, we believe that this propensity for the Ru atom to complex one face of the biaryl ligand is related to the observation of facile P−C bond breaking. In this Microreview, we will focus on acid- and solvent-induced P−C bond cleavage in complexes containing the bidentate phosphane ligands **1** and **2**, and the array of arene−ruthenium bonding modes that are associated with these reactions.

2. P−C Bond Cleavage

2.1 Acid-Induced Cleavage

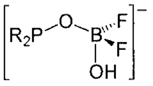
As the starting compound in hydrogenation chemistry is often protonated to open one or more coordination positions, we begin with a discussion of the chemistry of Ru(OAc)$_2$(**1** or **2**) on addition of a strong acid. Reaction of Ru(OAc)$_2$(**1**) with 2 equiv. of HBF$_4$ in dichloromethane afforded product **5**, in which a P−C bond is cleaved [see Equation (2)].[15]



(2)

5a R = 3,5-di-*t*Bu-phenyl
5b R = Ph
5c R = *p*-tolyl

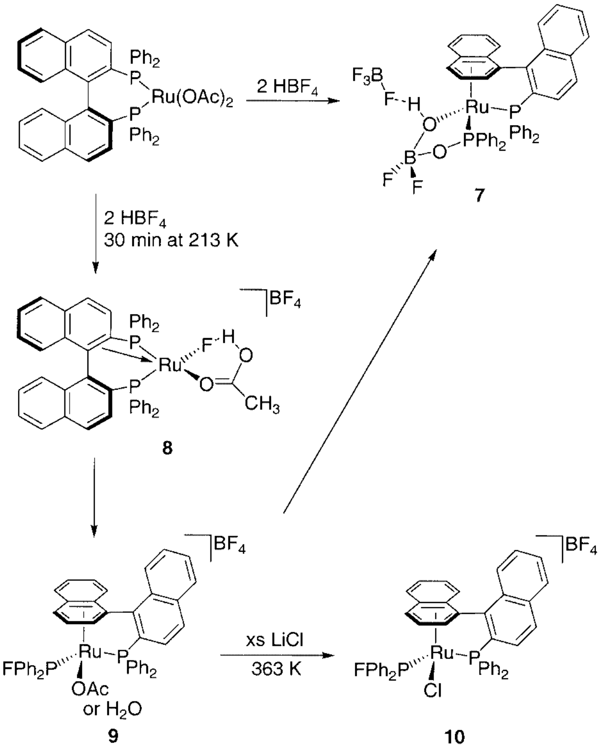
Complex **5** contains new P−O and B−O bonds, in addition to an unsymmetrical η^6 Ru−arene interaction, which arises from the complexation of the biaryl ring which loses the P-donor. The bis(phosphane) bidentate ligand has been cleaved affording two different chelating ligands.



6

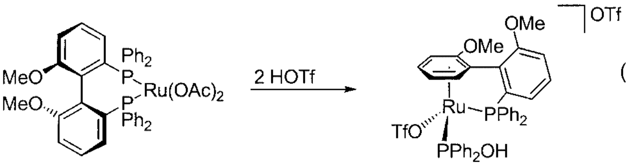
Formally, **5** contains the new phosphinite anion **6**, which arises by a hydrolysis reaction. The second BF$_4^-$ ion is held close by through a hydrogen bond. The major features of the structure of **5** were determined by one- and two-dimensional multinuclear NMR spectroscopy and X-ray crystallography.[15]

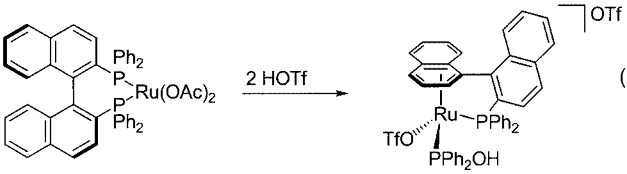
A more detailed NMR spectroscopic study of this protonation was carried out for the Binap analogue **7**, and these results are summarised in Scheme 1.[16] These reactions can be shown to involve an initial 6e$^-$ donor Ru−F complex **8** (and BF$_3$·Et$_2$O), followed by P−C bond splitting, yielding the monofluoro(phosphane) intermediate, whose structure is assigned as **9**. The ^{31}P and ^{19}F NMR spectra of the PR$_2$F ligand in **9** clearly show the expected $>$ 900 Hz one-bond $^1J_{P,F}$ values, as well as a very high-frequency ^{31}P chemical shift due to the strongly electronegative fluorine atom. Reaction of **9** with Cl$^-$ afforded the single diastereomeric chloro complex **10**. Obviously, this reaction produces Ru complexes that are sufficiently reactive to extract a fluoride from the BF$_4^-$ anion. Apart from their surprising structure, these compounds are noteworthy in that they demonstrate an undesirable side reaction, the potential loss of axial chirality.



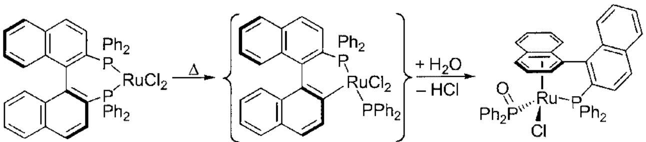
Scheme 1

The syntheses of the arene complexes **5** and **7** were complicated due to the slow, but concurrent BF$_4^-$ anion hydrolysis. To avoid this complication, [Ru(OAc)$_2$(**1** or **2**)], was allowed to react with slightly more than 2 equiv. of wet CF$_3$SO$_3$H in 1,2-dichloroethane at 363 K [see Equations (3) and (4)].[16] These reaction conditions gave the MeO−Biphep product **11** and the Binap analogue **12** in less then 2 h and in good yields. Formally, the H$^+$ cation protonates the acetate anion and the water molecule adds across the P–C bond. Interestingly, we observed only one of the two possible diastereomers (the metal atom is a stereogenic centre), thus this reaction is stereospecific. The ligand $P(OH)Ph_2$ is not very common, but there are a number of such (and related) complexes reported in the literature.[17,18]

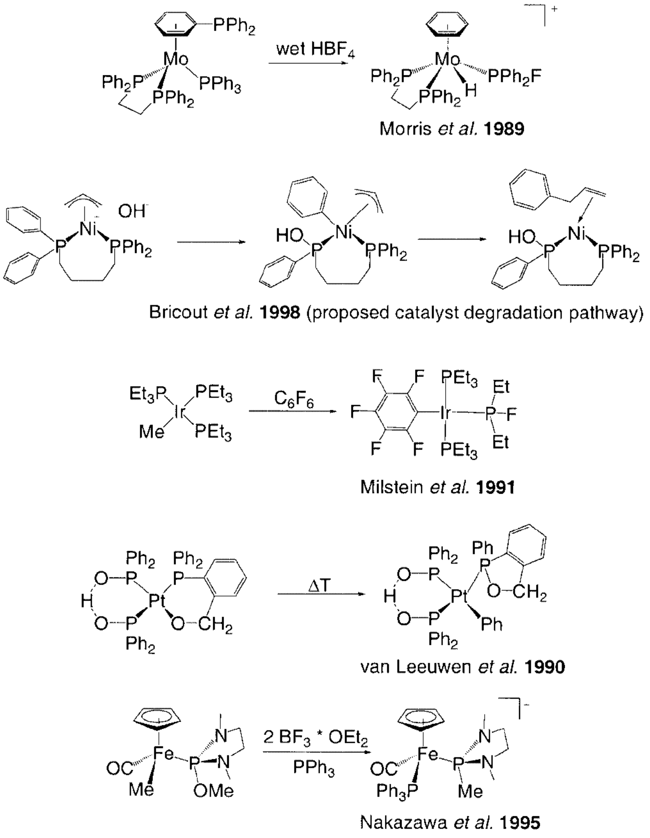

11 (3)


12 (4)

Apart from oxidative addition reactions,[19,20] there are not many examples of related P–C bond cleavage reactions in the literature and we show a selection of these in Scheme 2.[21–25] The first four examples involve the splitting of a P–C bond and the creation of a new P–X bond (X = electronegative group), whereas in the last reaction, a new P–C bond is formed at the expense of a P–O bond. Moreover, there are only a few examples of tethered phosphane–arene complexes,[26,27] e.g. **13** [see Equation (5)].[26a] Of course, lower valent Ru^0 clusters are also capable of cleaving P–C bonds.[28]


13 (5)

The structures of the new arene–phosphane compounds **11** and **12** were determined by X-ray diffraction and a view of the cation of **11** is shown in Figure 1. The six Ru–C(arene) bond lengths in both **11** and **12** are very different and seem to exist in three groups of two. Two bond lengths are relatively short [Ru–C1 and Ru–C6 (ca. 2.13–2.16 Å)] (but are fairly average),[29–33] two are slightly long [Ru–C4 and Ru–C5 (ca. 2.29–2.32 Å)], and two are quite long [Ru–C2 and Ru–C3 (ca. 2.35–2.48 Å)]. Inspection of the literature involving X-ray studies of arene complexes of Ru^{II} suggests that the usual Ru–C distances in a variety of substituted and simple Ru–arene complexes should be in the range 2.15–2.28 Å, with an average of ca. 2.23 Å. Specifically, the observed values of 2.480(5) and 2.477(5) Å for C2 and C3, respectively, in **11** suggest a weak interaction. The lengths of these bonds might be related to steric effects, since they involve the two sterically hindered fully substituted arene carbon atoms. We shall return to this theme in the discussion on possible flexible arene bonding in the next chapter.


Morris *et al.* **1989**

Bricout *et al.* **1998** (proposed catalyst degradation pathway)

Milstein *et al.* **1991**

van Leeuwen *et al.* **1990**

Nakazawa *et al.* **1995**

Scheme 2

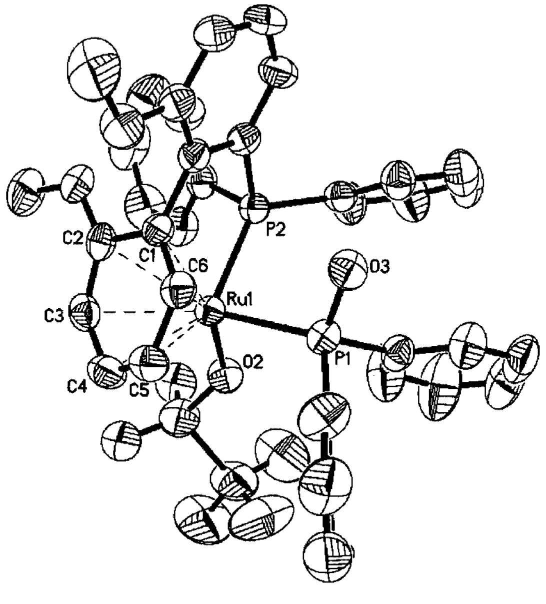


Figure 1. View of the cation of **11**

Although we reasoned that the presence of water was due to the wet triflic acid, there was another possible source. To test whether the acetate was a source of water, $Ru(OAc^{*})_2$(Binap) was synthesised containing > 98% ^{13}C-1 acetate (enriched at the carbonyl group).[34] The reaction of this complex with ca. 2.2 equiv. of high-purity (> 99%) triflic acid at 80 °C for 30 min in 1,2-dichloroethane was monitored by ^{13}C NMR spectroscopy (see Figure 2). The spectrum shows a coordinated acetate (δ ≈ 188 ppm), as well as acetic acid (δ ≈ 176 ppm) and acetic anhydride (δ ≈ 167 ppm). Clearly, the presence of acetic anhydride implies that water is produced.

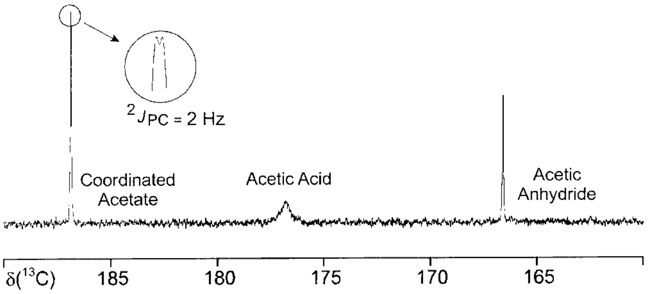
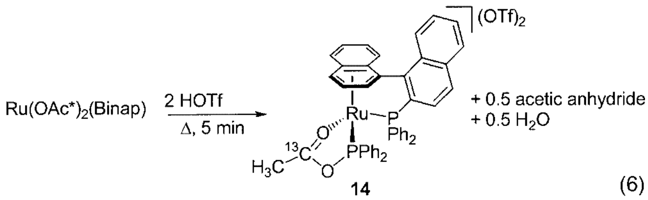


Figure 2. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction solution after 30 min at 80 °C, with peaks for complexed acetate, acetic acid and acetic anhydride; the expanded section shows the P−C coupling, ^{2}J = 2.0 Hz (75 MHz, 1,2-dichloroethane with D_2O capillary as internal lock)

Warming of a fresh sample of the enriched starting material to 80 °C for 5 min afforded a small amount (< 10%) of product **12**, a parallel amount of acetic anhydride (and thus water), in addition to a large quantity of a new compound, **14** [see Equation (6)].

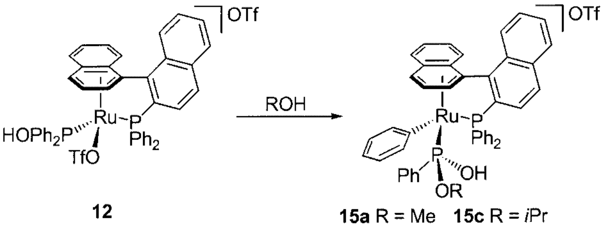


14 (6)

The ratio of **14** to **12** approaches unity after roughly 1 h. In the ^{31}P NMR spectrum of the new species, an AX ^{31}P spin system is seen, with one of the signals found at relatively high frequency (δ = 185.8 ppm). This new complex contains one acetate ligand as shown by ^{1}H and ^{13}C NMR spectroscopy. Interestingly, this intermediate species reacts quickly with water to form **12**. Indeed, workup of the NMR reaction solution, by simply pouring it into ether is sufficient to convert it immediately into **12**. The evidence for structure **14** is based on detailed NMR spectroscopic data.

2.2 Solvent-Induced Cleavage

We considered that the triflate compounds **11** and **12** might undergo solvolysis affording useful Lewis acids, so we treated these compounds with methanol. To our surprise we obtained good yields of the MeO−Biphep phenyl complex and its Binap analogue **15a**[35] [see Equation (7)].



12

15a R = Me **15c** R = *i*Pr
15b R = Et **15d** R = C_2H_4OH

(7)

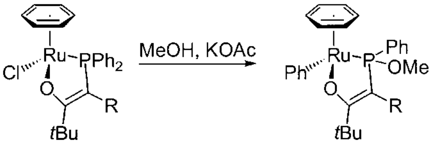
Additional compounds, **15b** and **15c**, have been prepared using EtOH and *i*PrOH, respectively. The new phenyl complexes are unique in that

a) they are produced in *only one diastereomeric form*, i.e. phenyl migration and P−O bond formation are specific,

b) they contain *three different forms of stereogenicity*: atropisomerism, from the biaryl moiety, a chiral transition metal atom and the newly formed stereogenic P atom, and

c) these are the first reported transition metal complexes of the ligands P(OH)(OR)Ph.

This kind of solvolysis and subsequent migration of a phenyl group from the phosphane group to the metal atom has been observed previously, see Equation (8).[36]



(8)

The solid-state structure of the *i*PrOH analogue **15c** was determined by X-ray diffraction methods and a view of the cation is shown in Figure 3. The immediate coordination sphere consists of the two phosphorus atoms, the π-arene and the η^{1}-phenyl ligand. While four of the Ru−C(arene) distances are fairly average and fall in the range

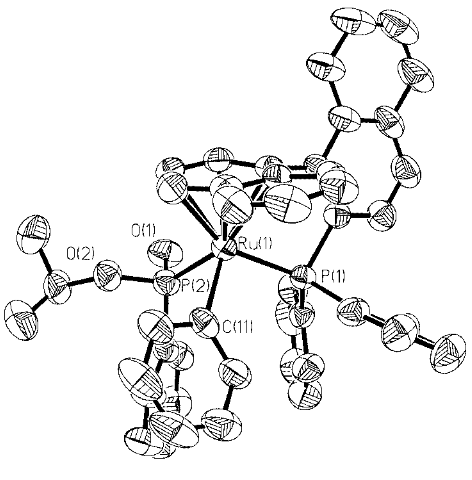
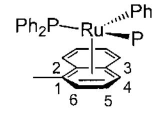


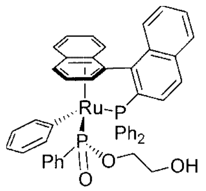
Figure 3. View of the cation of **15c**

2.217(7)−2.272(8) Å, again, the remaining two distances, involving the bridgehead carbon atoms C(2) and C(3), are quite long and suggest that little or no bonding to the metal atom occurs.



Ru–C2 = 2.433(7) Å Ru–C3 = 2.419(8) Å

The Ru{P(OH)(OR)Ph} fragment is readily deprotonated and in some cases, e.g. the ethylene glycol derivative, **16**, rather than **15d**, was isolated.



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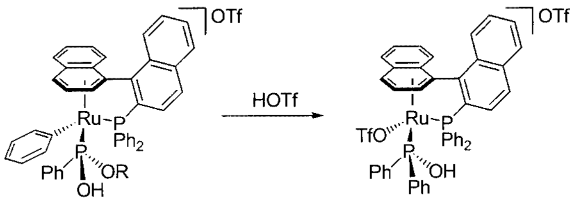
2.3 Stereochemistry and Protonation Studies

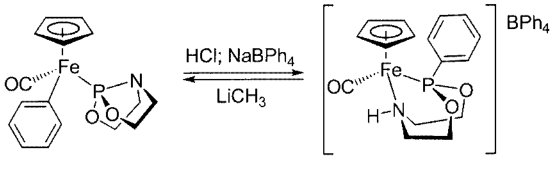
With a view to preparing chiral complexes with an open coordination site, two of the Ru−{P(OH)OR)Ph} compounds (**15a**: R = Me; **15c**: R = *i*Pr; both with racemic phosphane ligands), were allowed to react with excess triflic acid in dichloromethane.



15a R = Me
15c R = *i*Pr
12

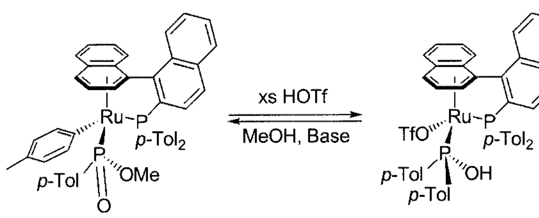
(9)

Instead of removing the Ru−phenyl ligand, the observed protonation product was either exclusively **12** (methoxy), or primarily **12** (isopropoxy).[37] For these acid reactions only a single diastereomer is observed, i.e. epimerisation at the Ru atom is not found. This type of migration reaction is known, but rare. A relevant example is shown in Equation (10).[38]



(10)

As an additional check on the stereospecificity of the transformation, we carried out several protonation reactions using the commercially available, optically pure (*S*)-(−)-*p*-tolyl−Binap **2b**. While only marginally different from **2a**, this ligand afforded yet another subset of complexes, **17**.



17 **18**

Addition of excess triflic acid to **17** immediately afforded only one diastereomeric form of **18**. Consequently, both the formation of the MeO analogue **15a** and the reformation of **12** proceeded stereospecifically. It was recognised that epimerisation at Ru can (but need not always) be facile.[39−41] Therefore, we repeated the protonation of **17** with excess triflic acid in dichloromethane at dry ice/acetone temperatures. After addition of HOTf to a precooled NMR probe at 220 K, we observed only a single product with a broad resonance at δ = 123.2 ppm and a sharp doublet at δ = 52.4 ppm. Slowly warming to 270 K using 10° increments, afforded a sharp peak in the ^{31}P NMR spectrum of the pure P(OH)(*p*-tolyl)$_2$ analogue of **12**. Since there is no evidence for a second diastereomer, we concluded that the reaction is very facile and, indeed, proceeds stereospecifically.

2.4 Kinetics of the Formation of 15a−c

The rates of reaction for **12** with ROH were not all identical. Consequently, these reactions were monitored by ^{31}P NMR spectroscopic methods. Reaction of **12** using either methanol or ethanol as the solvent proceeded essentially within mixing time to afford **15a** and **15b**, respectively. The difference in reaction rates as a function of the alcohol concentration becomes obvious when **12** is allowed to react using 4:1 alcohol/[D$_6$]benzene mixtures at 21 °C.

To reduce the reactivity of complex **12** with methanol and to obtain rate data at similar alcohol concentrations, 1:4 MeOH/[D$_6$]benzene mixtures were studied. The observed rate constant at 21 °C for the formation of **15a** is $k_{obs} = 6.4 \cdot 10^{-4}$ s^{-1}. For the reaction of **12** with ethanol under similar conditions, $k_{obs} = 5.6 \cdot 10^{-4}$ s^{-1}; therefore, for these somewhat more dilute alcohol solutions, the reactions with both MeOH and EtOH proceed at similar rates. In both cases, a new intermediate in the ^{31}P NMR spectrum is observed.[37] Due to its relatively slow rate, the reaction with 2-propanol was carried out at 27 °C, and not 21 °C. The major peaks observed are those of the starting material, together with a weak, unresolved resonance at $\delta \approx 94$ ppm. The product **15c** reacts slowly with traces of water to form a new species, which we believe to be a dinuclear complex. After 16 h, the two products are present in similar amounts. The observed reaction rate, $k_{obs} = 8.8 \cdot 10^{-5}$ s^{-1} (27 °C), was calculated using the disappearance of the substrate. Obviously, the reaction with 2-propanol can be considered to be one order of magnitude slower than with either methanol or ethanol.

We have recently managed to isolate two of the dinuclear species, **19** and **20**, and the crystallographic results for **19** are shown in Figure 4.[42]

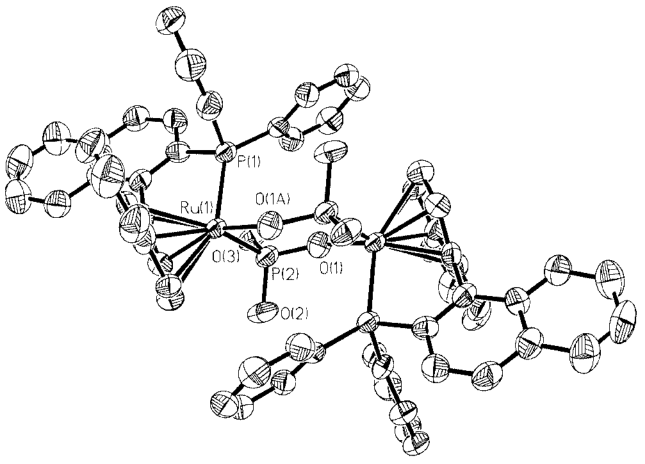
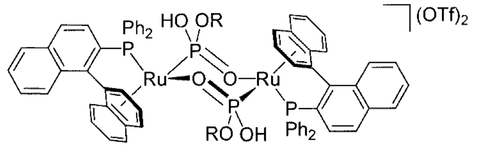


Figure 4. View of the dication of **19**

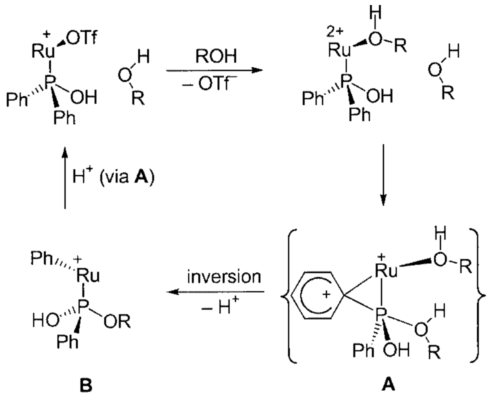


19 R = H
20 R = Me

The structures show that water from the alcohol competes favourably for the P atom, and indeed, one of these two species was prepared by a reaction involving *tert*-butyl alcohol, i.e. the *tert*-butyl alcohol reacts even more slowly than 2-propanol, relative to water.

The reaction of **12** with 2-propanol was also studied in the presence of an excess of sodium triflate. The starting material was consumed after 4 h, whereas in the same time, without added sodium triflate, ca 70% of substrate had reacted, i.e. addition of triflate increases the reaction rate. From a mechanistic point of view, if triflate dissociation was important, the rate should be slower. The kinetic data suggest that the reaction with 2-propanol, as well with methanol and ethanol, are first order with respect to complex **12**. A comparison of the values of k_{obs} obtained using different concentrations of ethanol supports a rate dependence on the concentration of the alcohol.

A possible reaction pathway, which rationalises the stereospecific transformation of complex **12** into the products is shown in Scheme 3 (only the reactive sites of these molecules are shown). Solvent substitution is followed by arene migration to afford a Ru−Ph complex. Protonation of the OR group in the Ru−Ph complex restores the $P(OH)Ph_2$ compound. Using the alcohol as the solvent favours the formation of the dicationic solvent complex (as might the presence of excess charged triflate). Presumably, these solvent complexes are the unknown compounds that appear in the ^{31}P NMR studies, when diluted with benzene. There is always solvent alcohol in close proximity, partially due to the hydrogen bonding to both the triflate anion and POH moieties (another possible source of an intermediate structure). In the transition state, the complexed solvent begins to dissociate. Simultaneously, the phenyl group bridges the Ru and P atoms and the proximate H-bonded solvent begins to form the new P−O bond through a pseudo-backside attack. Possibly, these steps occur sequentially, although the alcohol must be in the rate-determining step. This mechanism is reminiscent of the formation of a nonclassical arenium ion (a typical intermediate in 1,2 shifts of aryl rings), and would be consistent with the observed stereospecificity. Since the alcohol is involved in the transition state, it is reasonable that both its concentration and size affect the kinetics.



Scheme 3

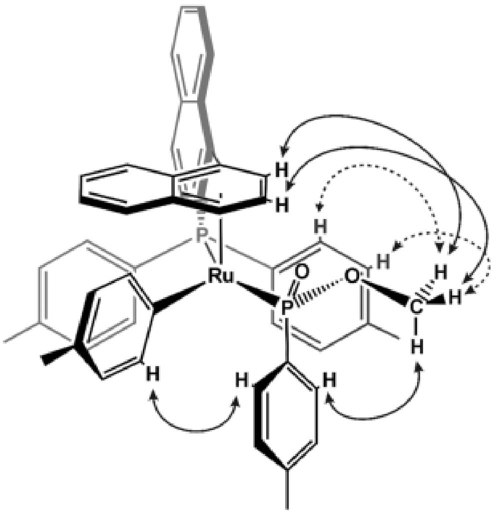
To support this mechanism we have determined the 3-D solution structure of {P(=O)(OMe)(*p*-tolyl)} complex **17** in dichloromethane, using NOE methods (see Scheme 4).[37,43,44] From these and additional NOE results, it can be seen that the Ru−aryl ring is positioned in an approximately antiperiplanar position relative to the methoxy group. This structural feature allows us to rationalise both the ease and specificity of the reactions indicated in Scheme 3. The positive charge which would develop from facile protonation of the P(OR) group by the strong acid, can be stabilised by the Ru−*p*-tolyl group, again in analogy with carbon cation chemistry (see structure **A**, Scheme 3). Complete transfer of the aryl group to the P atom is then accompanied by rapid triflate capture by the ruthenium cation affording the product, e.g. **15**. Since **A** and **B** are positively charged, in dichloromethane the triflate anion will be nearby. The excess triflic acid helps to facilitate rapid capture before epimerisation.

3. Flexible Arene Bonding

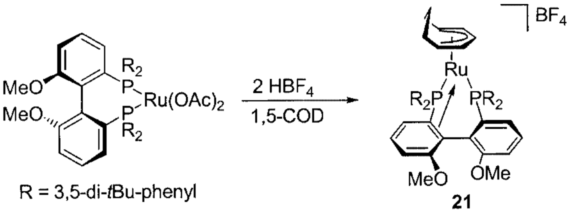
3.1. Olefin-Type Coordination

We noted above, without comment, that a proximate biaryl double bond can complex the Ru^{II} atom, e.g. the middle structure in Scheme 1. We believe this type of complexation to be surprisingly common.

In dichloromethane, $Ru(OAc)_2$(**1a**) reacts with 1,5-COD and HBF_4 to afford **21** in a good yield [see Equa-

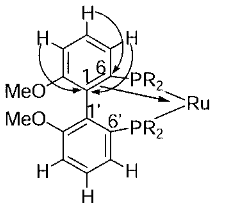


Scheme 4



(11)

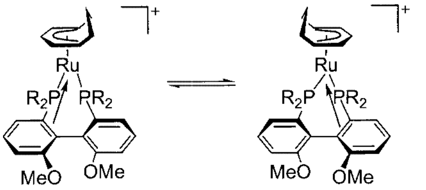
tion (11)].[45] The ^{31}P NMR spectrum shows a routine AX spin system; however, the chemical shifts at δ = 69.6 and −11.2 ppm (!) are unexpected, with the latter in a region often associated with uncoordinated phosphane. The nature of the organometallic ligand in **21** was not immediately obvious; however, a routine 2-D ^{13}C,^{1}H-correlation showed only three aliphatic CH$_2$-type signals, and five CH absorptions in the region δ = 57−114 ppm. These ^{13}C chemical shift data are strongly suggestive of the cyclooctapentadienylruthenium fragment, Ru(η^6-C_8H_{11}).[46] At this point, we noted two ^{13}C resonances of *nonprotonated* carbon atoms at δ = 74.5 ppm as a strong doublet, and at δ = 95.1 ppm as a very weak triplet. A long-range ^{13}C,^{1}H-correlation revealed connectivity between both of these nonprotonated carbon atoms and the proton *ortho* to the P atom, plus further $^3J(^{13}C,^{1}H)$ correlations, as indicated.



δ C(1) = 95.1 ppm δ C(6) = 74.5 ppm

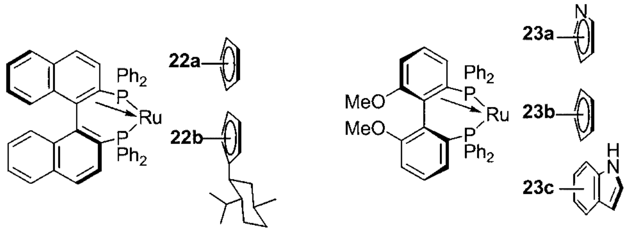
The ^{13}C signals for the noncomplexed analogous carbon atoms (C1′: δ = 139.7 ppm; C6′: δ = 135.4 ppm) are at a higher frequency. Given these assignments we conclude that the C1−C6 biaryl double bond is coordinated to the metal atom, thereby affording an 18e$^-$ coordinatively saturated complex, and thus making the ligand **1a** a six-electron donor to the metal atom. The low-frequency ^{31}P signal at δ = −11.2 ppm is associated with the unexpected coordination mode.

The ^{1}H phase-sensitive NOESY spectrum[44,45] for **21** at ambient temperature reveals a slow exchange process in which the two halves of the MeO−Biphep ligand are exchanged. Since the product has exactly the same structure, one observes only one set of resonances. Presumably, the biaryl double bond dissociates, thus making room for its counterpart in the second biaryl ring [see Equation (12)].

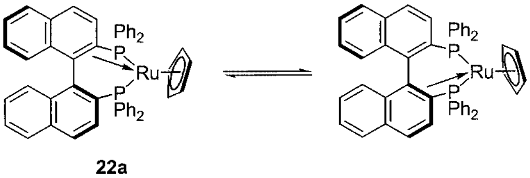


(12)

This new type of pseudo-allylic olefin bonding is unusual; however, White and co-workers reported[47] the solid-state structure for [Ru(Cp)(Binap)]CF$_3$SO$_3$, in which they found the same type of six-electron donation from the Binap ligand. They also noted widely dispersed ^{31}P chemical shifts at δ = 74.0 and 14.1 ppm. They were kind enough to provide us with samples of two Cp complexes, **22a** and **22b**, for NMR spectroscopic studies (see Scheme 5). These show both the typical ^{13}C shifts and exchange dynamics [see Equation (13)].[48]



Scheme 5



(13)

Subsequently, we prepared the complexes **23a**−**c**, and the solid-state structures of **23b** and **23c** are shown in Figure 5 and Figure 6, respectively. All of these compounds contain the complexed proximate double bond.

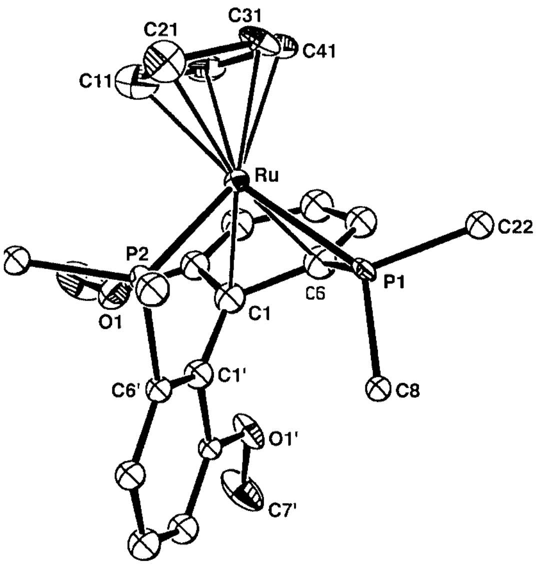


Figure 5. View of a part of the cation **23b**

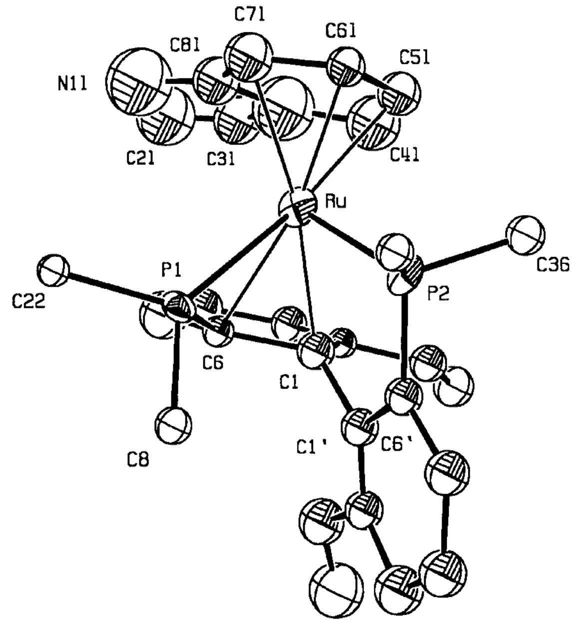
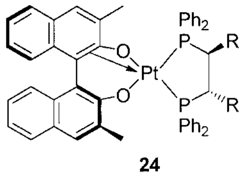


Figure 6. View of part of the cation **23c**

In recent literature reports, we found two related cases of this type of bonding: The Pt complex **24**[49] is clearly related, whereas the Mo complex **25**[50] might be of a more general nature due to the ubiquitous triphenylphosphane.



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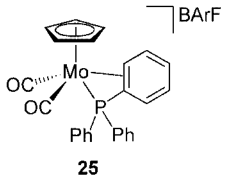
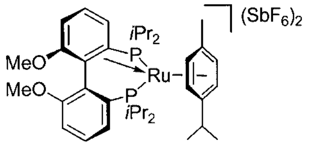


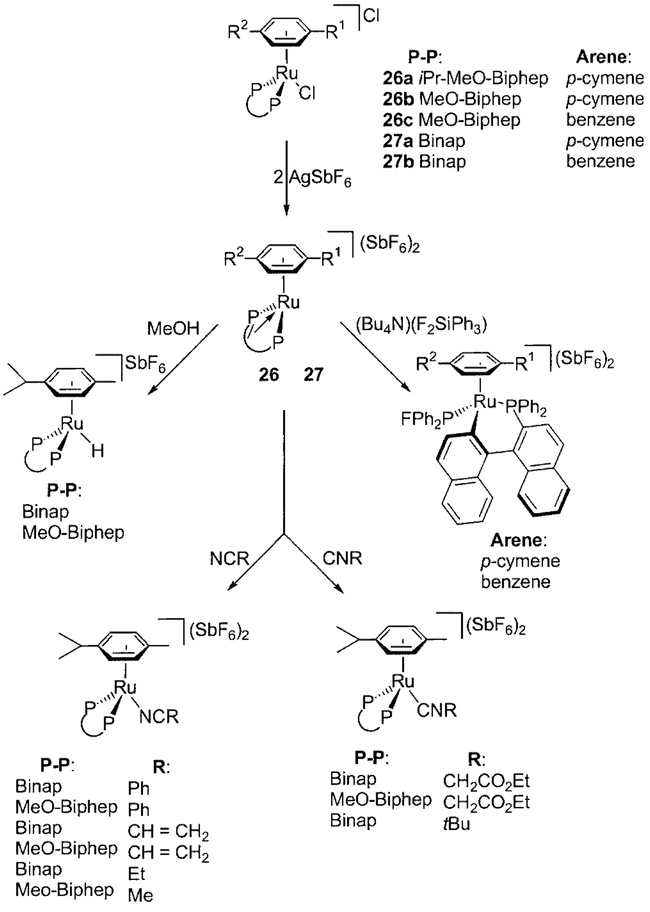
25

Once it is known that **21−23** are stable, then it is a relatively simple task to extend the known range of complexes showing this type of bonding by extracting chloride from [RuCl{bis(phosphane)}(arene)]Cl to afford the cymene complex **26a**.[51]



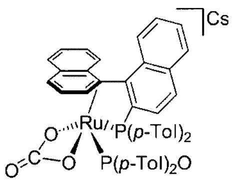
26a

Compound **26a** and related species are shown in Scheme 6, along with several other derivatives, and selected NMR spectroscopic data are given in Table 1.[51]



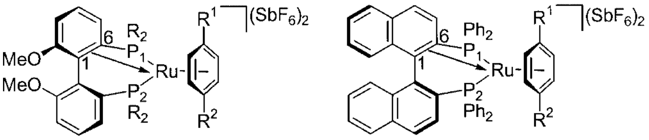
Scheme 6

Reaction of **12** with Cs_2CO_3 gave compound **28,** which also shows an η^2-olefin interaction, albeit of a different nature. Interestingly, the two carbon atoms complexed are those which can coordinate before P−C cleavage.



28

Table 1. Selected NMR chemical shifts for the carbon and phosphorus donors in Ru−arene complexes **26** and **27**



26a R = *i*Pr; *p*-cymene
26b R = Ph; *p*-cymene
26c R = Ph; benzene

27a *p*-cymene
27b benzene

	C1	C6	P1	P2
26a	102.5	79.1	27.3	82.6
26b	93.0	80.1	7.7	67.1
26c	90.9	86.0	15.4	64.7
27a	98.0	67.5	3.3	68.7
27b	101.7	73.0	19.0	64.0

A section of the ^{13}C long-range correlation for **28** is given in Figure 7 and reveals two "typical" chemical shifts for C1 and C6, the carbon atoms coordinated to the ruthenium atom. The four remaining ring carbon atoms show normal NMR characteristics.

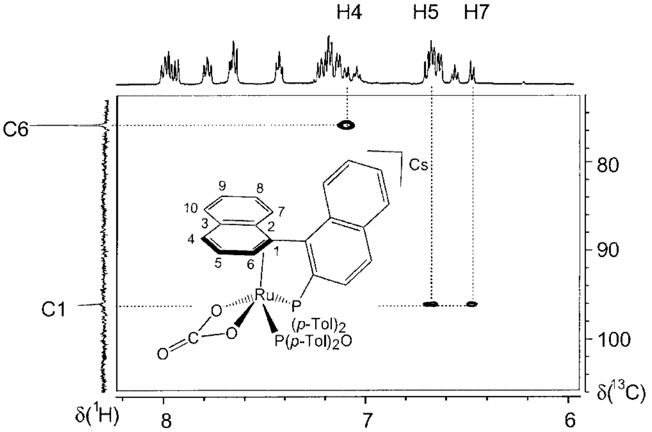
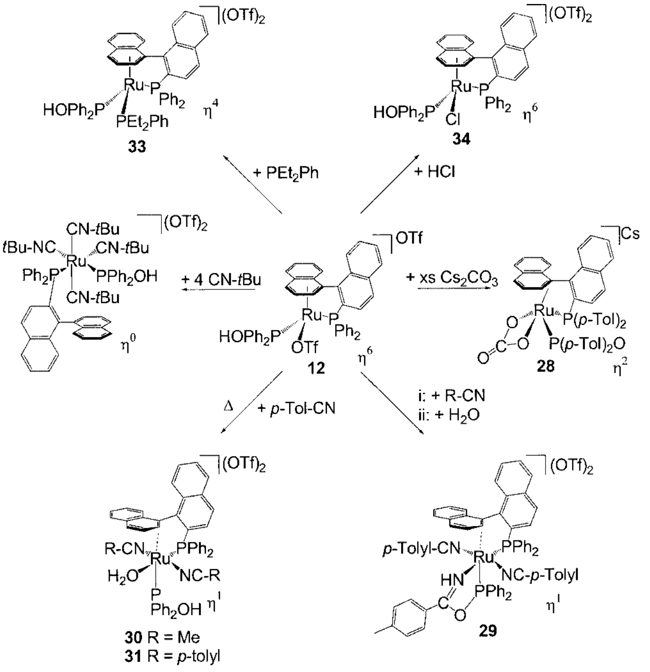


Figure 7. C,H long-range correlation for **28** showing the cross peaks for the two coordinated carbon atoms C6 and C1 stemming from the interaction of the *meta*-protons H4 and H5, and H7, respectively

3.2. Coordination from a Single Arene Carbon Atom

A number of derivatives of the $[Ru-P(OH)Ph_2]$ complexes **11** and **12**, containing nitrile, isocyanide and phosphane donors have been prepared (see Scheme 7).[52] In these compounds the arene has either been partially or fully displaced. On the surface, all of the apparent five-coordinate nitrile complexes appear to have structures in which the η^6-arene bonding has been completely displaced. However, these nitrile complexes contain an interesting and unexpected feature as shown by their ^{13}C NMR spectroscopic data. Just *one* of the (previously η^6-arene) biaryl carbon atoms (C6) remains situated in a pseudo-sixth coordination position, and its ^{13}C resonance is shifted to δ = 105−112 ppm from that of a "normal" arene hydrocarbon, which we estimate to be at $\delta \approx$ 127−130 ppm.[53] This difference in carbon chemical shift is much too large to arise from local anisotropic effects. The signals of the adjacent carbon atoms C1 and C5 are found at $\delta \approx$ 130−140 ppm, i.e. in rather typical positions, so that an η^2 description is not suitable for these molecules. The protons on C6 in these nitrile compounds (δ = 7.69−8.27 ppm) are also of a routine nature.



Scheme 7

Specifically, complex **29**, which arises from attack of the P−OH on a complexed nitrile ligand, shows this type of novel η^1 bonding.

One could consider the observed bonding as arising from a "remote agostic", i.e. weak, interaction of the metal atom with the biaryl C−H bond.[54,55] However, we do not believe this to be correct based on the normal observed values of $^1J_{C,H}$ (from the C,H correlations) and the H6 chemical shifts, both of which seem rather unaffected by the bonding. The most reasonable explanation involves a weak η^1-π bonding mode from a single CH biaryl arene carbon atom to the ruthenium atom. A strong interaction might induce larger coordination chemical shifts and shorter bond lengths.

Crystals of the two aquo(nitrile) complexes **30** and **31** were grown and their solid-state structures determined by X-ray diffraction. Figure 8 and Figure 9 show views of the cations and, although there is strong disorder in these crystals (the *R* values are not excellent), the coordination sphere around the ruthenium centre is clear.[52] Atom C(6) occupies the sixth position in both structures and P(2), possessing the P(OH) group, is in a pseudo-*trans* position to this arene carbon atom. The Ru−C(6) distances of 2.62 and 2.63 Å, for complexes **30** and **31**, respectively, are clearly too long for a routine σ-bond, but approach the upper end of what is known[56] for weak Ru−olefin interactions. The distances from the ruthenium atom to C(5) are both rather long for a bonding interaction, ca 3.3 Å, which is consistent with the ^{13}C NMR results. Placing the H atom at a ca. 1 Å distance from C(6) affords Ru···H distances in the region of 2.69−2.70 Å, i.e. there is no reason to invoke a C−H agostic interaction.

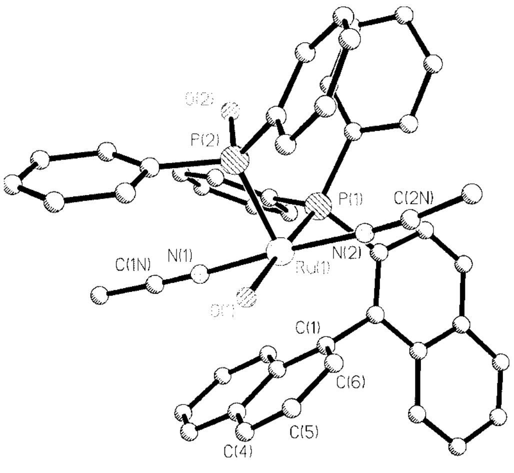


Figure 8. View of the cation **30**; note the position of C(6), occupying the 6th coordination site

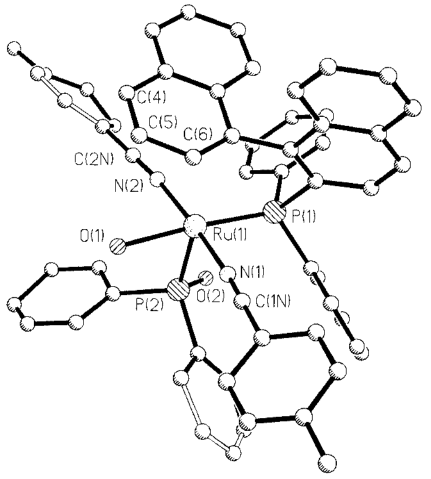
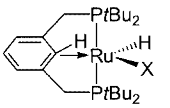


Figure 9. View of the cation **31**; note the position of C(6), occupying the 6th coordination site

We are not aware of many examples of η^1 Ru−CH bonds; however, Gusev et al.[57] have recently assigned the Ru−CH interaction in **32** as a strong agostic interaction based on the short M−C distance, ca. 2.1 Å.



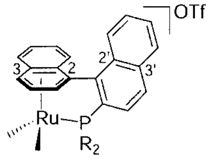
32

Indeed the reported *high frequency* carbon chemical shift of this Ru−CH carbon atom (δ ≈ 152 ppm) is consistent with a strong M−C σ-bond character.[58] This interaction is obviously different from those found in our Ru compounds.

3.3. η^4 or η^6 Bonding?

The PEt$_2$Ph complex **33** in the upper half of Scheme 7 is assigned to an η^4 diolefin structure. Although only slightly different from **12**, based on X-ray and NMR spectroscopic data, there are clearly two complexed double bonds and one remote, perhaps weak, interaction.

The question of η^6 vs. η^4 arene bonding in **12** and its derivatives is one that is discussed using ^{13}C NMR data. Despite the observed Ru−C distances (ca 2.4 Å or more), we believe that the bonding is best described as strongly asymmetric η^6. The ^{13}C chemical shifts for the two carbon atoms in question, C-2 and C-3, are shown together with three model compounds **28**, **33** and **34** (see Scheme 7).



	C-2	C-3	C-2'	C-3'
28	136.6	133.7	133.8	134.8
33	116.4	116.2	131.5	134.9
34	111.6	114.0	131.8	135.1

Assuming that a "normal" ^{13}C position (pure η^4 arene bonding) would be at δ ≈ 130 ppm, then both C-2 and C-3 experience some effect of the proximate Ru atom. Consequently, it is somewhat superficial to draw the line between the η^6 and η^4 description; however, as expected, the presence of stronger donating groups (e.g. phosphane vs. chloride), leads to a weaker arene−Ru interaction and thus to a shift towards higher frequency for the signals of C-2 and C-3.

4. Comments

The biaryl chelating phosphanes **1** and **2** do not display "routine" coordination/organometallic chemistry. In general, for Ru complexes of **1** and **2**, the nature of the other ligands bound to the ruthenium atom determines whether these bis(phosphanes) function as 4e$^-$ or 6e$^-$ donors. There is a definite propensity for this metal to "reach" for the electrons of the biaryl π-system (as in **21**−**27**) as soon as the electron count for ruthenium is only 16e$^-$. In order to achieve this, the biaryl is severely twisted.[43,46] Once the Ru atom has complexed the double bond next to the P atom, it is reluctant to release it, and all of the X-ray data show that the Ru−C1 and Ru−C6 distances are the shortest. When the P−C bond has been broken, and a new π-ligand formed, the nature of the different donor ligands (phosphanes, nitriles, carbonate etc.) determines whether the ring of the biaryl ligand slips from a weak six- to a normal four-, and then down to a two-atom donor. Rather than completely forsake this nearby π-system, these complexes can adopt the novel η^1-π bonding mode, as in **29−31**; the weakest interaction with the π-system manageable. This interest in holding the π-cloud may well be responsible for the observed ease of P−C bond breaking in bidentate biarylphosphane compounds. In any case, the chemistry of **1** and **2** affords a variety of novel, new chiral phosphane complexes of Ru^{II} in which arene complexation plays a major role.

The undesirable second and third P−C bond breaking reactions, i.e. the formation of **19** and **20**, prohibits a controlled synthesis of $16e^-$ intermediates. Nevertheless, both **19** and **20** are unique and offer opportunities for studying interactions of these with additional harder metal centres, e.g. the preparation of phosphorus-containing chiral complexes of metals in higher oxidation states.

Acknowledgments

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