Phosphorus–olefin chelation in coordinated atropisomeric chiral auxiliaries

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The atropisomeric chelating auxiliaries MeO-Biphep, Binap, MOP and selected monodentate phosphoramidite type ligands are all capable of using differing aromatic fragments as donors to stabilize coordinatively unsaturated 14- or 16-electron species. MeO-Biphep and Binap make use of a double bond immediately adjacent to one of the P-donors to turn these chelate ligands into six-electron donors. In addition to the P-atom, the MOP class uses the π-electrons of the naphthyl group, not attached to the phosphorus atom, to form a 4e chelate ligand. The MeO–MOP ligands often form weak σ-bonds, derived from the electrons in this naphthyl ring, rather than π-olefin complexes. Phosphoramidites, and some related ligands such as "simple-phos", use a pendant phenyl group to form an η^2-arene, P-chelate. The various bonding modes have been investigated *via* X-ray, NMR and DFT studies.

Introduction

The transition metal chemistry of complexed olefins continues to attract interest as these ligands represent substrates for a number of catalytic reactions. Although chelating diolefins,[1] or bidentate ligands containing N, P (or other) donors[2] together with an olefin, can afford relatively stable complexes,[3–8] see **1–6** in Scheme 1, the stability constants for monodentate olefins are not always very large.[2] Nevertheless, one finds a relatively rich literature for complexes of simple olefins containing the transition metals in Groups 8–10.[2] There are fewer examples of η^2-olefin complexes of benzene and arenes,[9–11] and the molecules in this latter group are often discussed in connection with C,H-activation chemistry. Occasionally one finds reference to η^1-olefin species,[12–15] see **7–10** in Scheme 2; however these are fairly rare.

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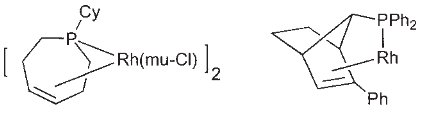
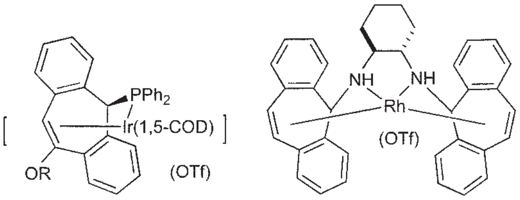
In connection with enantioselective catalysis, there is an increasing interest in the use of monodentate P-donor chiral auxiliaries.[16] The MOP class, **11**, prepared by Hayashi *et al.*,[17–20] has proven to be effective in enantioselective Heck and hydrosilylation chemistry (amongst others); however this group of ligands has been supplanted by the increasingly popular (and easier to synthesize) phosphoramidites, **12**.[21–24]



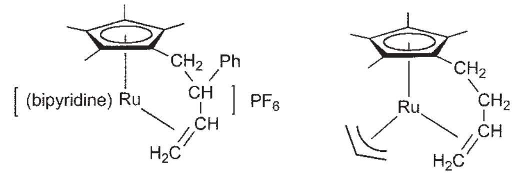
1[3]

2 The P,(olefin) chelate in $Rh_3(\mu\text{-}O)(\mu\text{-}OH)(chelate))_3]$[4]



3[5]

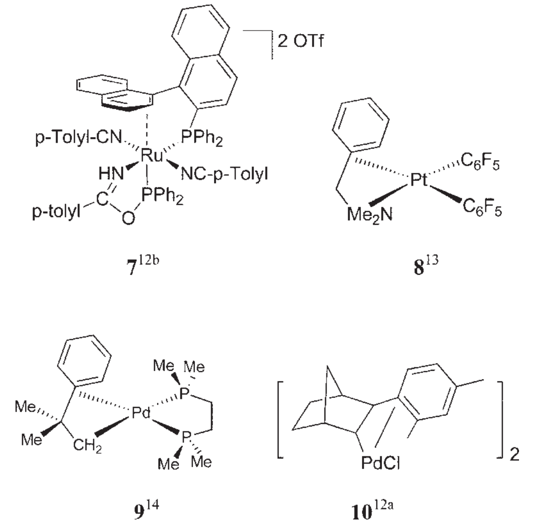
4[6]



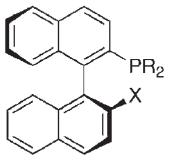
5[7]

6[8]

Scheme 1 Selected P or N ... *etc*., donor olefin chelate complexes from the recent literature.



Scheme 2 Selected complexes showing η^1-olefin bonding.



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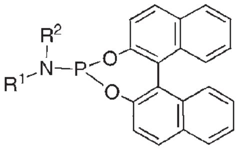

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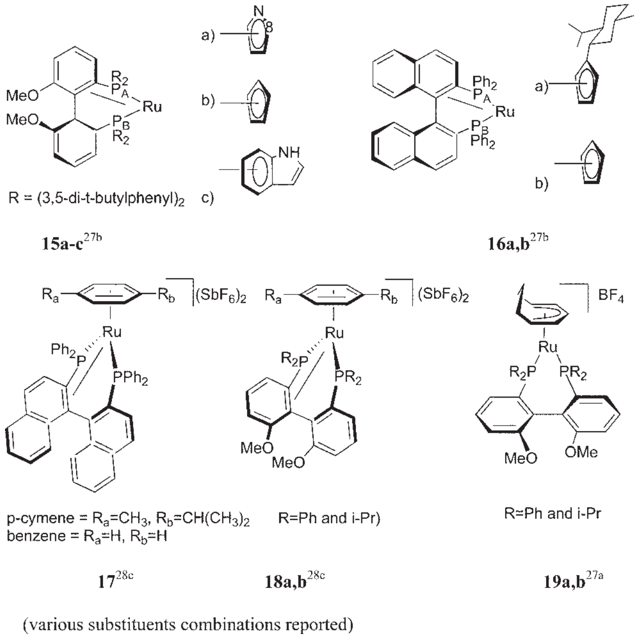
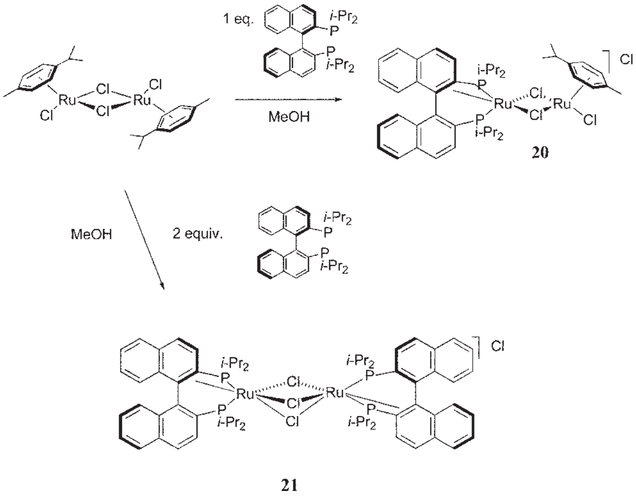
MeO-Biphep, Binap and related chemistry

Given the electron rich proximate arene backbones and P- and N-phenyl substituents in the ligands **11** and **12**, one may ask whether complexes formed from these phosphorus donors necessarily contain only monodentate ligands. One could readily imagine that the structures derived from these ligands might be somewhat more complicated due to some form of π–arene interaction. This idea derived from studies on ruthenium complexes involving the now well-known ligands MeO-Biphep,[25] **13** and Binap,[26] **14** ligands.

Ru(II) complexes containing these atropisomeric species are now recognized[27–29] to be capable of coordinating a seemingly remote double bond thereby turning these ligands into six (rather



Scheme 3 Ru-complexes with MeO-Biphep and Binap as 6e donors. These complexes contain various 6e donors to the Ru(II), *e.g.*, Cp-types, as in **15a,b** and **16**, or arenes, as in **15c**, **17** and **18** or a pentadienyl ligand, such an in **19**.



Scheme 4 Synthesis of the μ_2-dichloro-salt, **20**, and μ_3-trichloro-salt, $\mathbf{21}^{29c}$ with alkyl Binap ligands as 6e donors.

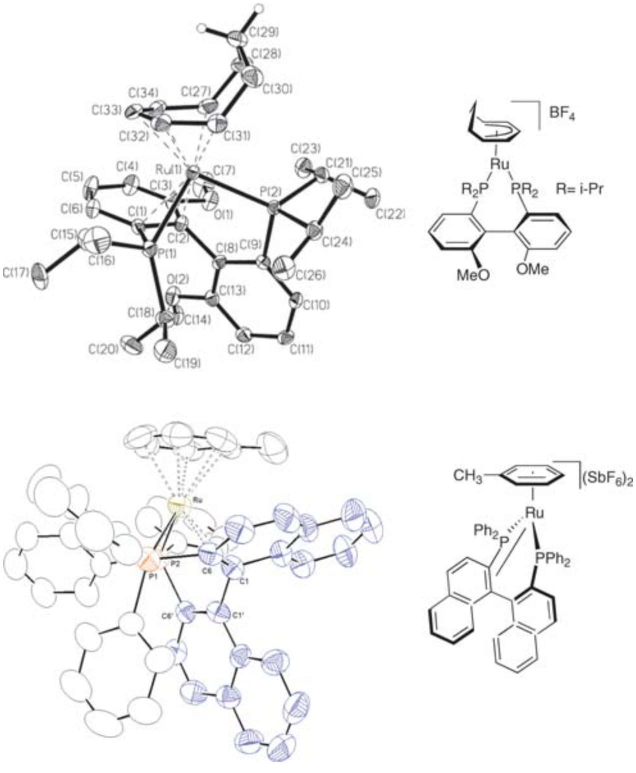
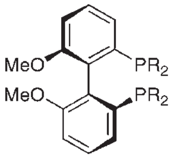


Fig. 1 Ru(η^5-pentadienyl $C_8H_{11}^-$ ligand))(MeO-Biphep) monocation, **19b** (top) and Ru(η^6-toluene)(Binap) dication (bottom) both showing the C1–C2 complexed double bond (in the solid-state structure, the two complexed carbons are labeled as C1 and C6).

than four) electron donors and a collection of literature examples is provided in Scheme 3, with complexes **15–19** and Scheme 4, with **20** and **21**.



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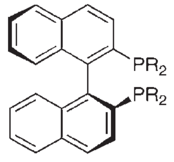

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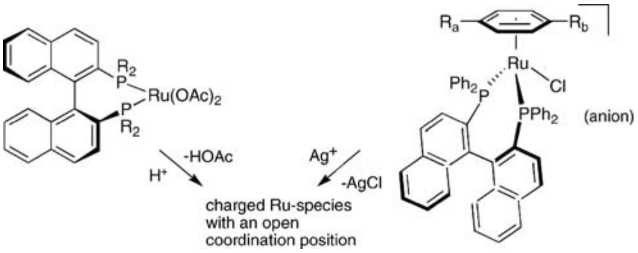
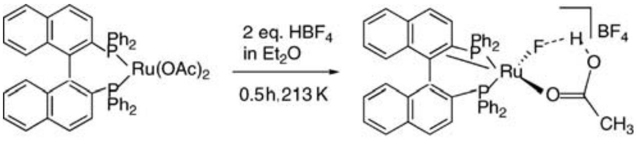
The occasional presence of *meta* di-*tert*-butylphenyl groups, in the schemes, is related to the ability of ligands containing these remote substituents to improve the enantioselectivity of selected catalytic reactions,[30] but is not important for the bonding. These phosphino-olefin complexes are usually prepared by opening a coordination position *via* either protonation of, *e.g.*, an acetate donor or extraction of a chloride ligand with Ag^+ in a suitable non-coordinating solvent, see eqn (1). Many of these ruthenium species are isolable and can be characterized in the solid-state *via* X-ray diffraction methods,[27–29] see Fig. 1.



(1)

It is not unusual for one (or both) of the Ru–C(olefin) bond lengths to be quite long. In the pentadienyl complex[27a] (top left in Fig. 1), the Ru–C(1), separation adjacent to the P-atom, is *ca.* 2.30 Å and the Ru–C(2) bond length *ca.* 2.37 Å. The X-ray studies show that the biaryl moiety distorts considerably[27,28] in order to open the π-face of the complexing arene towards the ruthenium atom. Not all of these complexes are very stable in solution. For example, the fluoride-complex[28b] shown in eqn (2) is not stable at ambient temperature; nevertheless, it can be readily characterized *via* low-temperature NMR studies.



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(2)

Typically, the ^{31}P NMR signal involved in the strained four-membered ring appears at unusually low frequency in the region of the uncoordinated phosphine.[27–29] For **22**, the ^{31}P chemical shift for the P-atom in the small ring, δ 6.3 is considerably different than that, δ 80.6, for the P-atom *pseudo trans* to fluorine,[28b] The ^{13}C resonances for the two coordinated olefin carbons are found, as expected, at relatively low frequency, often between 60 ppm and 100 ppm. The

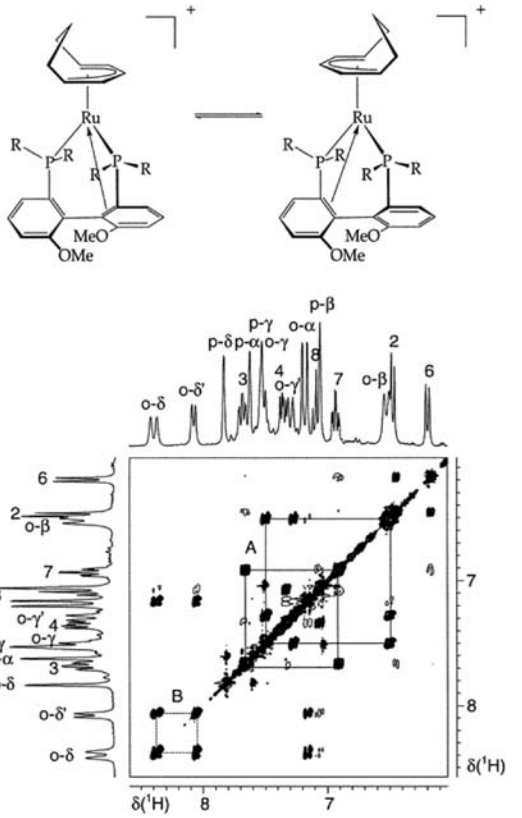
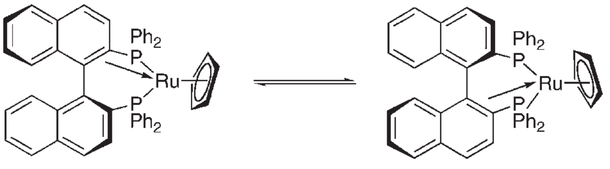


Fig. 2 2-D exchange spectrum showing the exchange between the two non-equivalent halves of the MeO-Biphep ligand.[27a] The protons H2, H3 and H4 represent the three biaryl protons of one of the two biaryl rings, and H7, H8 and H9 the three protons from the second biaryl ring. One finds that H2 is exchanging with H6 (upper right hand corner), H3 with H7 and H4 with H8 (both in the centre of the spectrum). The remaining exchange peaks arise from the aryl-groups of the P-atoms. A similar exchange spectrum is given in ref. 27c for the $Ru(Cp)(Binap)^+$ cation shown in eqn (3).

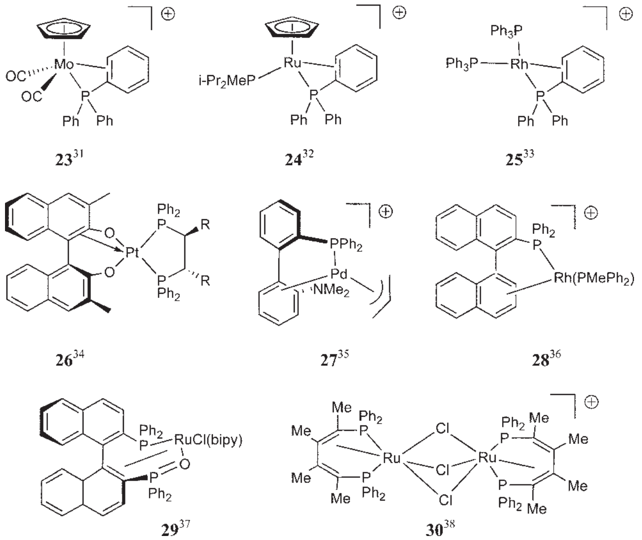
schemes show that this type of η^2-olefin bonding occurs in the presence of Cp-type ligands, η^6-arenes or bridging halogens, amongst others. Moreover, both aryl and alkyl P-substituents are compatible with this olefin-bonding.

As this η^2-olefin interaction is fairly weak, in solution one finds an equilibrium[27] in which the double bond of one of the biaryl-groups is replaced by the analogous olefin of the second biaryl fragment (see eqn (3)[27c] and Fig. 2). Eqns (1)–(3) have presented the Binap chemistry; however, as indicated in Schemes 3 and 4, the analogous complexes with MeO-Biphep are readily prepared.



(3)

Subsequently, a number of studies[31–38] have appeared reporting on complexes in which various remote olefin

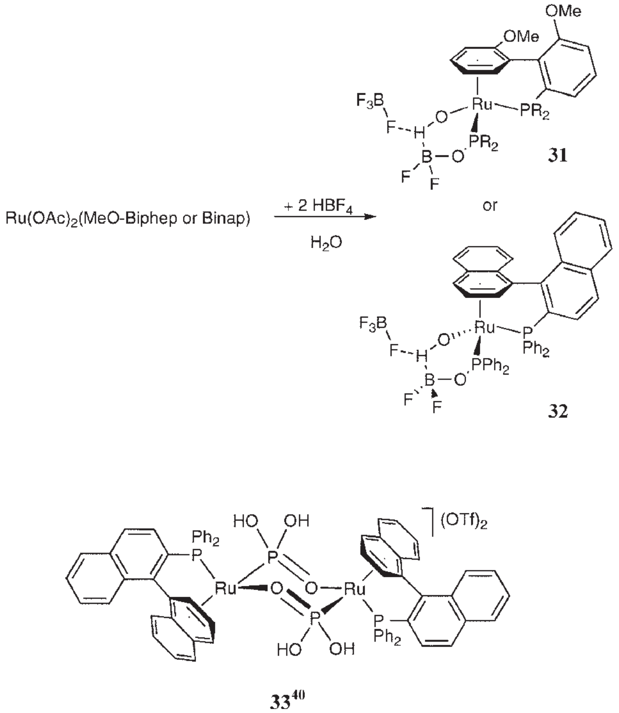


Scheme 5 Metal complexes, **23–30**, with remote olefin interactions.

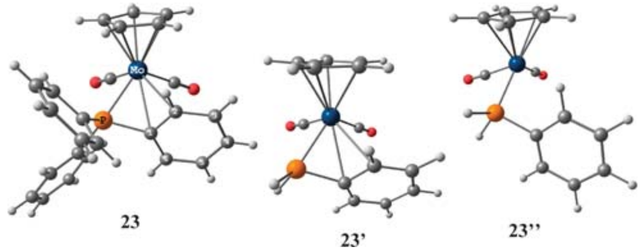
fragments have been shown to coordinate transition metals, see Scheme 5, for complexes **23–30**. These include several examples[31–33] in which the immediately adjacent double bond of a PPh_3 donor is involved. Indeed, one of the oldest examples of this kind concerns the $Rh(PPh_3)_3^+$ cation, **25**, characterized quite early by Hawthorne and co-workers,[33] which achieves a 16e count as a consequence of a coordinated phenyl C=C bond with Rh–C distances of 2.236 and 2.502 Å.

Occasionally, if the solvent contains some water, the open coordination position, when combined with the electrophilic nature of the Ru(II), can lead to rather exotic products which arise from P,C bond splitting reactions and subsequent anion hydrolysis[39*a*,*b*] (see eqn (4) and Fig. 3). Under the correct conditions, it is possible to cleave all three P–C(aryl) bonds and eventually isolate the dinuclear phosphorus acid complex **33**.[40] These and related salts derived from P–C-bond breaking reactions, have been isolated and characterized *via* multinuclear NMR and X-ray diffraction studies.[29*b*]

Given that the Binap-type is an extremely relevant chiral ligand in active catalytic systems, and that PPh_3 is a quite commonly used P-donor, Calhorda and co-workers[41] have carried out a series of DFT calculations on the cations $[CpRu(Binap)]^+$, **16b**,[42] and $[CpMo(CO)_2(PPh_3)]^+$, **23**.[31] The optimized geometries for $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]^+$ **23**, plus two models **23′** (with PH_2 instead of PPh_2) and **23″** (without the olefin interaction) are shown below.



(4)



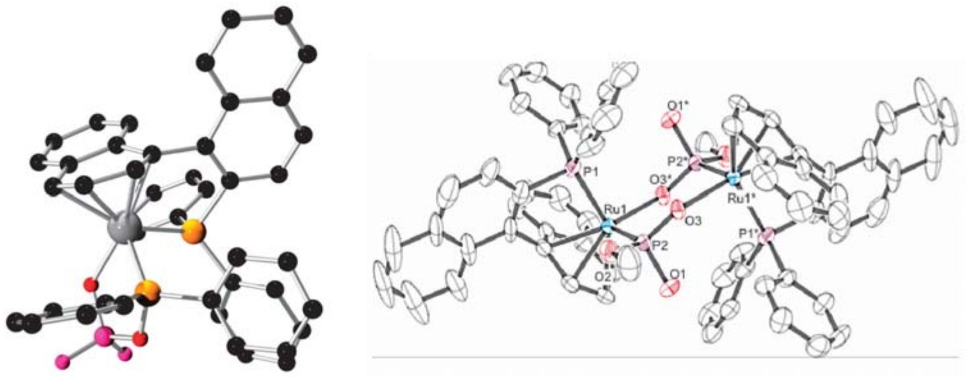
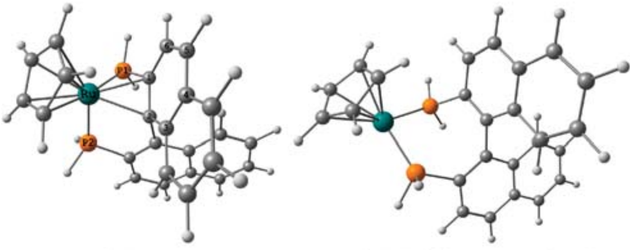


Fig. 3 The solid-state structures of the BF_4 hydrolysed Ru arene complex, **32** (left) showing the BO_2F_2 chelate ligand[39*a*,*b*] and the dinuclear Ru(arene) $P(=O)(OH)_2$ bridged species, **33**[40] (right).

An analysis of the resulting data reveals excellent agreement between the calculated metric parameters and the experimental structural results. The distances between the molybdenum centre and the two olefinic carbons, 2.566 and 2.647 Å in the X-ray structure, are reproduced in the optimized structure (2.594 and 2.647 Å). It is worth noting that, although these are relatively long Mo–C bonding distances, the ^{13}C data[31] clearly show complexation in solution. The substitution of two phenyl groups by two hydrogen atoms, **23′** leads to shortening of the Mo–P distance in comparison with **23**, while the Mo–C1 and Mo–C2 bond lengths slightly increase. The model **23″** a formally 16-electron species, is higher in energy by 13.4 kcal mol^{-1} than that for **23′**. The calculated Mo–C1 and Mo–C2 distances in **23″** are long, 3.333 and 3.526 Å, respectively) and, therefore, consistent with a "normal" phosphine bonding mode.



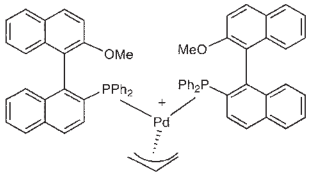
16b' **16b''** (olefin not complexed).

The optimized geometry for the Ru-model, **16b′** (indicated above, again, with PH_2 instead of PPh_2) agrees well with the experimental structure, despite the absence of the phenyl groups on phosphorus. The structures for **16b′** and **16b″** show that C1 and C2 are bound to Ru in **16b′**, but are not coordinated in **16b″**. The calculated Ru–C(olefin) distances, 2.311 and 2.383 Å, in **16b′** are in excellent agreement with those found in the experimental solid-state structure and are also very close to the Ru–C bond lengths in related complexes. For this cation, the energy of the model **16b″** is 21.4 kcal mol^{-1} higher than that of **16b′**. Using an energy decomposition analysis, the η^2–arene interaction was calculated as 8.58 and 13.74 kcal mol^{-1}, for Mo and Ru, species, respectively.[41]

All in all, this perhaps unexpected olefin bonding affords an increasing number of accessible and modestly stable complexes.

MOP chemistry

Given that the arene backbones of both MeO-Biphep and Binap can be involved in the bonding to ruthenium, it was interesting to prepare complexes of the presumed monodentate phosphine ligand, MOP, and look closer at their bonding modes. Since the MOP ligands have been used extensively with palladium, several Pd–allyl derivatives were prepared. Initial preparative experiments[43] afforded a mixture of **34**, **35** and **36**, all of which confirmed that Pd(II) was capable of coordinating two very bulky MOP ligands in *cis* positions. Complex **35** represents a relatively rare example of a chiral η^1-allyl Pd-complex (and **37** is yet another[44]). The ^{13}C NMR data for **36** suggested that this salt contained an η^2-olefin bond, in that the two naphthyl olefinic CH-carbons immediately adjacent to the C–O bond were found at δ 86.3 and 80.4.[43]



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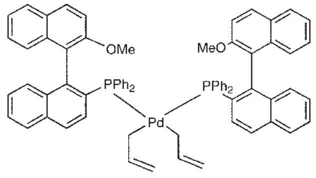

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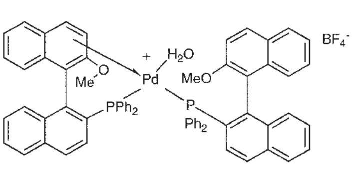

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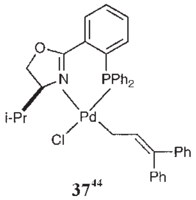
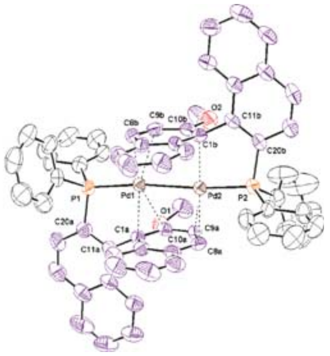
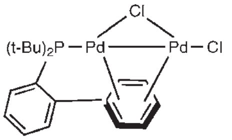


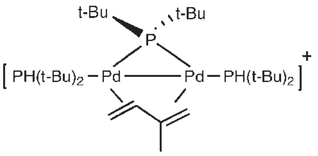
37[44]

Subsequently, a MeO–MOP Pd(I) dinuclear salt, **38**, was prepared.[45] The solid-state structure of this dication shows one ring of the MeO–MOP naphthyl acting as a bridging diene across the Pd–Pd bond, with each Pd atom involved in η^2-olefin interaction. Although this is a known coordination mode for Pd(I) dinuclear diene derivatives (see **39**[46] and **40**[47]), it provided a hint that the MOP class was capable of various coordination types and certainly more than just simple P-coordination.



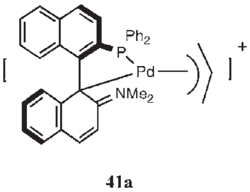


39[46]

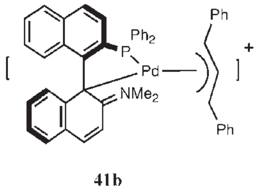


40[47]

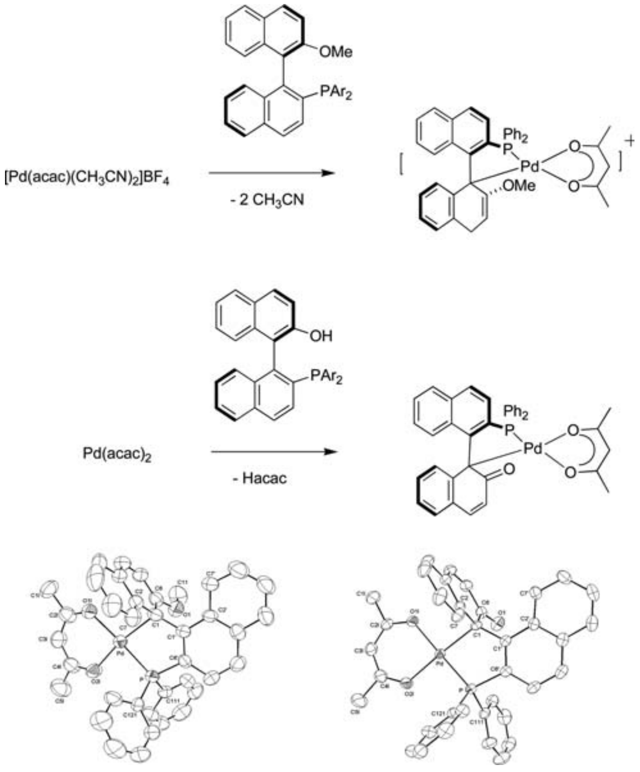
Interestingly, earlier studies using MAP (the dimethylamino-version of MOP) had suggested that an even more marked polarization was possible. The allyl salts **41a**[48] and **41b**[49] were shown to exist with Pd–C σ bonds.



41a

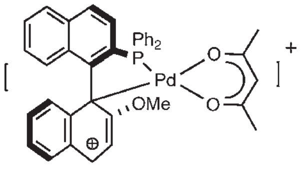


41b



Scheme 6 Synthesis of the MOP acac-complexes with Pd–C σ-bonds.

These results prompted us to prepare the model palladium acetyl acetonate complexes[50] shown in Scheme 6. In both the solid and solution states, the MeO–MOP and OH–MOP ligands afford P,C-chelate derivatives. The Pd–C bond length in **43**, derived from the OH–MOP complex, is much shorter than that stemming from MeO–MOP, **42**. Taken together with the ^{13}C NMR data, **43** is best described as containing an α,β-unsaturated ketone fragment. In **42** the positive charge is delocalized throughout the naphthyl moiety.



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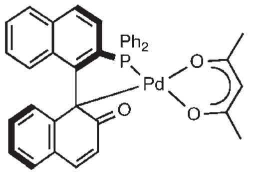

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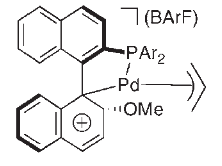
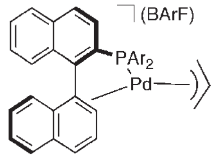


Ar= 3,5-Di-*t*-Bu-Phenyl

44

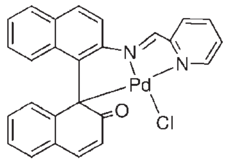


Ar= 3,5-Di-*t*-Bu-Phenyl

45

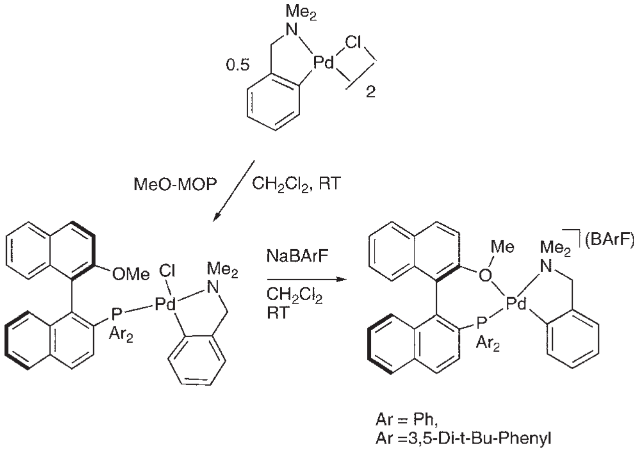
NMR studies on the related Pd-allyl complexes **44** and **45** suggested[51] that **45** is best described as an olefin complex. It would seem that, within the sub-group of MOP-allyl derivatives, the naphthyl backbone in these atropisomeric phosphines can be involved in both π- and σ-bonding to the Pd(II), depending on the MOP substituent. Similar conclusions have been reached for several Pt(η^3-allyl)(MOP) complexes.[51]

Although not directly related to the MOP chemistry, Xu *et al.*[52] have recently reported the neutral Pd complex **46** with its Pd–C σ bond and α,β-unsaturated ketone fragment.



46

The MOP complexes, **47**, containing an N,C-chelate ligand, were prepared *via* the usual bridge cleavage reactions, see eqn (5).[50] The decision to study a Pd-cyclometallated complex containing MOP was based on the fact that a number of catalytic processes involving palladium (*e.g.*, hydrosilylation or cross-coupling) contain a reactive species with a metal–carbon σ-bond.



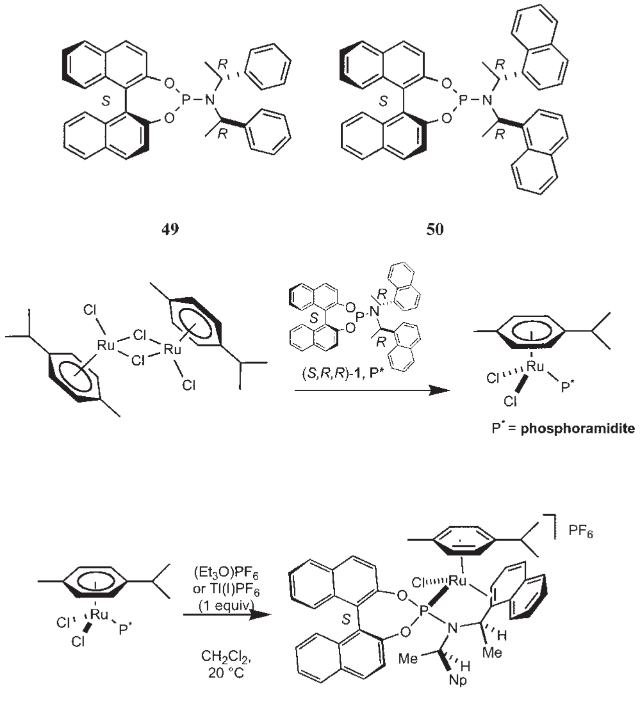
Ar = Ph,
Ar =3,5-Di-t-Bu-Phenyl

47 **48** (5)

Extraction of the chloride with Na(BArF), in dichloromethane solution, afforded the new, rather conventional derivatives, **48**, in which the methoxy-oxygen atoms (rather than some part of the MOP ligand backbone) are now complexed to the Pd(II).[50] Perhaps the strong *trans* influence of the σ-bound carbon donor (relative to the modest *trans* influence of an η^3-allyl) favors the ether-oxygen complexation. The geometry shown, which places the MeO- and Me$_2$N-groups close to one another, is supported by ^{1}H,^{1}H Overhauser experiments. In any case, the bonding modes for the MOP ligands need not always involve the neighboring π-system.

Phosphoramidite chemistry

As the MeO-Biphep, Binap and MOP ligands all are capable of using the neighboring biaryl fragments to coordinate, it seemed logical to ask whether the now fashionable phosphoramidites might also follow suit. Mezzetti and co-workers[53,54] have begun a systematic study of this chemistry and Scheme 7



49

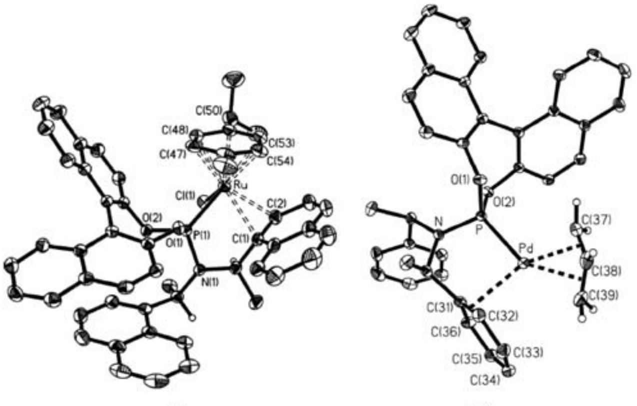
50

51

Scheme 7 Synthesis of the ruthenium phosphoramidite complexes.

shows the route to **51**, one of two recently reported cationic Ru(II) complexes using ligands **49** and **50**.

Once again an η^2-olefin complex, Ru(*p*-cymene)(**50**)$^+$, **51**, is produced; however, for this cation, the coordinated double bond stems not from the biaryl moiety but rather from one of the two pendant N-naphthyl substituents. The solid-state structure for **51** (see Fig. 4), reveals Ru–C(olefin) distances of 2.379(2) Å and 2.386(2) Å. These are fairly long separations, but consistent with values found in the X-ray structures for the η^2-olefin complexes mentioned above. The ^{13}C signals for the two coordinated olefinic carbons in **51** appear at 100.9 ppm and 96.8 ppm, for the *ipso* and CH-resonances, respectively. These resonances appear at higher frequency than those for the Ru–MeO-Biphep and Binap species discussed above; nevertheless, these NMR data are consistent with weak olefin complexation.

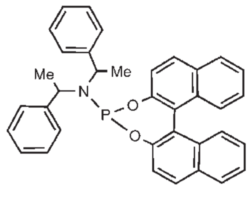


51 **54**

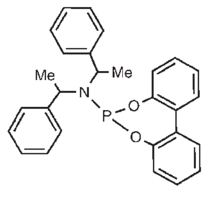
Fig. 4 The solid-state structures for the Ru(*p*-cymene) phosphoramidite cation, **51** (left) and the Pd(allyl) phosphoramidite cation, **54** (right).

In addition to the X-ray structure for **51**, the rhodium and palladium cationic complexes [Rh(NBD)(1,2-η-Ph-1-κP)]$^+$, (**52**), [Rh(1,5-COD)(1,2-η-Ph-1-κP)]$^+$, (**53**), and [Pd(η^3-C_3H_5l)(1,2-η-Ph-1-κP)]$^+$ (**54**) were prepared[55] and Fig. 4 shows a view of the Pd-cation from **54**. The two Rh–C(olefin) bond lengths in **52**, Rh–C(1) = 2.320(4) Å and Rh–C(2) = 2.305(3) Å, are much shorter, than the observed separations in the Pd-cation, **54**, Pd–C(31) = 2.513(2) Å and Pd–C(32) = 2.413(2) Å. A 1,2-η^2-arene interaction for a rhodium complex is not unprecedented, and as indicated in Scheme 5, the formally three-coordinate [Rh(PPh$_3$)$_3$]$^+$ **25**, is stabilized by 1,2-η^2-Ph-coordination arising from of one PPh$_3$ phenyl ring.[33] The ^{13}C coordination chemical shifts for the two olefinic carbons in these rhodium and palladium complexes can be comparable to those found in the ruthenium cation, **51**; however, due to solution dynamics these can also be somewhat smaller.

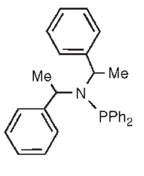
In order to study these dynamics, the ligands **49**, **55** and **56** were used to prepare a series of Pd and Pt allyl complexes,[56] *e.g.*, **57**.



49 (from Scheme 7)



55



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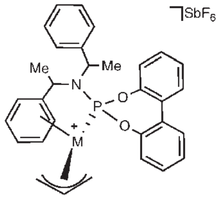


57, M = Pd, Pt

The Pd salts are all dynamic on the NMR time scale and Fig. 5 shows a shows a set of variable-temperature ^{1}H measurements for **57**, M = Pd. These NMR spectra reveal that the allyl protons are relatively sharp, but the α-phenethyl side-chain signals are very broad at ambient temperature. Therefore, the possible η^3 to η^1 allyl-isomerization is fairly slow and not responsible for the observed broad lines. The α-phenethyl side-chain methine CH-signals, do become relatively sharp at *ca.* 233 K and are found at δ 4.3 and 4.9. However, as suggested by the line shapes, the phenyl protons "H2, H6" are still exchanging even at 213 K (see the shapes of the signals between 6.0 ppm and 6.5 ppm). Most likely, the metal can slide across the π-donor and/or the olefin can dissociate and rotate around the C1–C(Me)N bond (see eqn (6)).

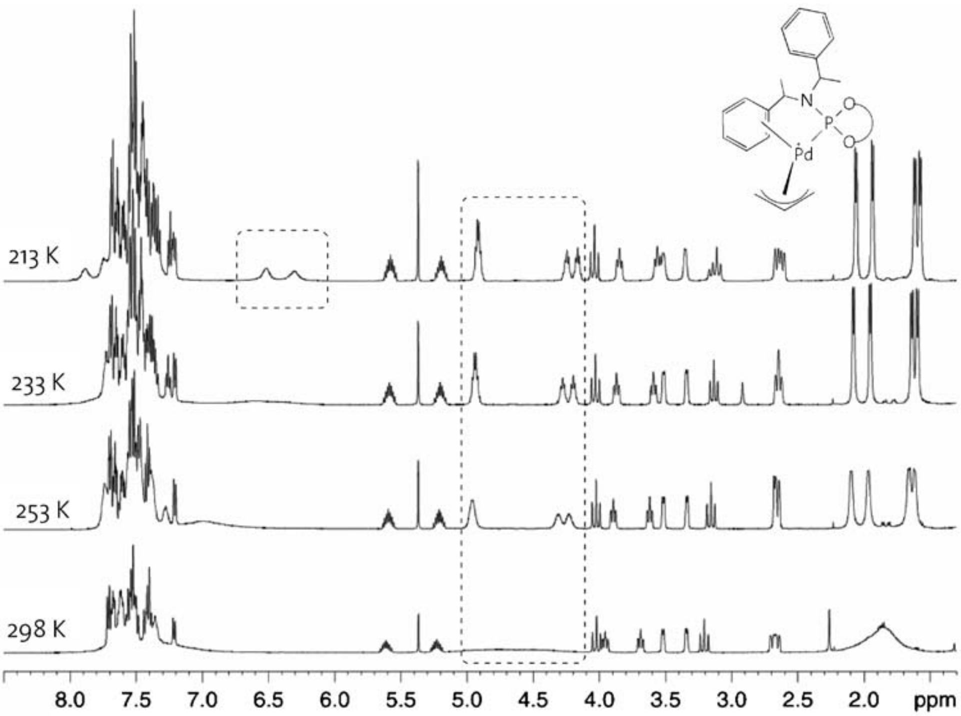
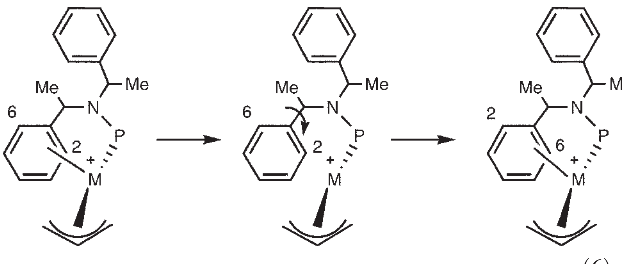


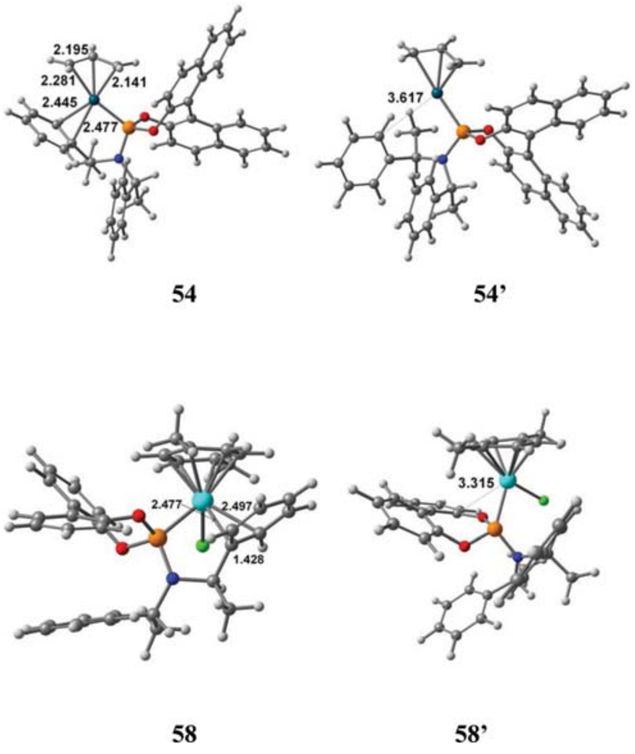
Fig. 5 A set of variable-temperature ^{1}H NMR spectra for the Pd-complex **57**, M = Pd. Note that the side-chain CH and CH_3 signals are very broad at ambient temperature, but that the allyl resonances, *e.g.*, the two central allyl protons between δ 5.0 and 5.7, are relatively sharp. There is still exchange at 213 K (see eqn (6)).



(6)

This results in some averaging of the ^{13}C chemical shifts over both C2 and C6, thus decreasing the magnitude of the observed coordination chemical shift for C2, the carbon in the complexed double bond. Unfortunately, lowering the temperature further does not sharpen the lines due to the onset of restricted rotation around various N–C(aryl) or P–C(aryl) bonds, with the result that all of the lines broaden significantly. This problem is not so severe for several platinum analogs whose dynamics are somewhat slower.[56] It is worth noting that these Pd(allyl) η^2-olefin complexes are not limited to naphthyl-based phosphoramidites but that complexes containing either **55** or (bis α-phenethyl)aminodiphenylphosphine ("simple phos"), **56**, prepared and used by Alexakis *et al.*,[57] also reveal this type of bonding.

Since the source of the observed preference for N-aryl η^2-olefin bonding in **51** and **57** was not obvious, DFT calculations[56] were performed for the Pd(allyl)(phosphoramidite) complex, **54** (using its crystallographic data), and a model RuCl(*p*-cymene) complex Ru(*p*-cymene)("**49**")$^+$, **58**, depicted in Scheme 8 (bottom right side),[11] where the naphthyl group of the Binol was replaced by the phenyl analogue. Two alternative structures, **54′** and **58′**, with enforced long distances



Scheme 8 DFT optimized structures of complexes **54**, **54′**, **58** and **58′**, emphasizing the shortest M–C contacts with phenyl groups.

between the metal and all phenyl groups, were also optimized. This methodology is similar to that described above for the Cp complexes and all four structures, **54**, **54′**, **58** and **58′** are shown in the scheme.

Given the Binap and MeO-Biphep results discussed above, a third phosphoramidite structural possibility was considered in which the phenyl groups of the amine side-chain were kept far from the metal, and a proximate double bond of the binol naphthyl-fragment allowed to approach either the Ru or Pd centres. Interestingly, no low energy structure with an η^2-olefin could be obtained for this type of interaction, and so this mode of bonding was not pursued further.

Once again, the optimized structure for the Pd complex, **54**, is very close to the experimental one. Specifically, the Pd–C distances to the weakly bound phenyl carbon atoms are calculated to be 2.445 and 2.477 Å, whereas the experimental values are 2.413 and 2.514 Å. The agreement is not quite so good in the Ru complex (calculated: 2.497, 2.477 Å; experimental: 2.386, 2.378 Å), possibly because the model complex chosen is different from the complex for which one has X-ray data.

In the alternative ''non-bonded'' structure containing Pd, **54′**, where no weak η^2-interaction occurs, the shortest Pd–C distance involving the amine phenyl groups is 3.617 Å. For the Ru model complex, **58′**, there is a short contact (3.315 Å) and it involves the biaryl (binol) group of the phosphine. These short contact distances for **54′** and **58′** are too long to be considered covalent bonds.

In order to estimate the strength of the Ru and Pd η^2-interactions, a set of energy decomposition analyses were carried out.[56] These results reveal the strength of the η^2-arene interaction for the Ru complex, **58**, to be 30.13 kcal mol^{-1}. The corresponding value in the Pd complex, **54**, 12.94 kcal mol^{-1}, is closer to the values calculated for $[CpMo(CO)_2(PPh_3)]^+$, 8.58 kcal mol^{-1} and $[CpRu(Binap)]^+$, 13.74 kcal mol^{-1}. A detailed analysis of the data from the calculations reveals that the major difference for **58** involves the ready ability of the amine side-chain to approach the metal, *i.e.*, this fragment does not need to distort in order to complex whereas for $[CpRu(Binap)]^+$, the reorganization energy of the Binap was considerable.

Conclusions

It is clear that a general trend exists: when a potentially reactive, coordinatively unsaturated 14e- or 16e-species is generated, the metal centres attain a more stable structure by attracting the proximate arene electrons from the various atropisomeric chiral auxiliaries. Schemes 2–6 suggest (a) this can be accomplished in several different ways (b) although this discussion has concentrated on Ru and Pd, other metal centres perform similarly and (c) based on both NMR and DFT studies, the energies of these (usually fairly weak) bonds differ considerably. It would be an exaggeration to consider the MOP or phosphoramidite ligands as bidentate (or in the case of Binap and MeO-Biphep, tridentate) donors; however, it seems equally clear that it would be naive to neglect these possibilities. This will be especially true where the coordination chemistry and/or catalytic reactions involve weak ligands and poorly coordinating solvents.

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