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Secondary Phosphine Oxides: Bifunctional Ligands in Catalysis

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Abstract: Metal complexes of secondary phosphine oxides (SPOs) were introduced as homogeneous catalysts in the 1980s for hydroformylation and hydrogenation with platinum as the metal. As neutral species, the ligand properties resemble those of the corresponding tertiary phosphines as was shown in the coordination chemistry developed in the 1970s, but the participation of the OH in bonding and reaction mechanisms provides them with a peculiar additional function. While this was already proposed and recognized in the first publications, it took a while before this found wider appreciation. Meanwhile, SPOs have become popular ligands for homogeneous catalysts, and more recently also for catalysis based on metal nanoparticles. Here we review the relatively small number of publications that pay attention to SPOs as bifunctional ligands.

1. Introduction

Tertiary phosphines and phosphites are undoubtedly the ligands most often used in homogeneous catalysis, but they are experiencing increasing competition of other ligand groups since the 1990s, such as those containing N- or C-atom donor ligands. Replacing one substituent group in tertiary phosphines by OH leads to a new ligand, phosphinous acids. Phosphinous acids **1** are unstable compounds that convert to their stable, tautomeric form secondary phosphine oxides (SPOs) **2**, unless the substituents are strongly electron-withdrawing such as trifluoromethyl groups.[1]

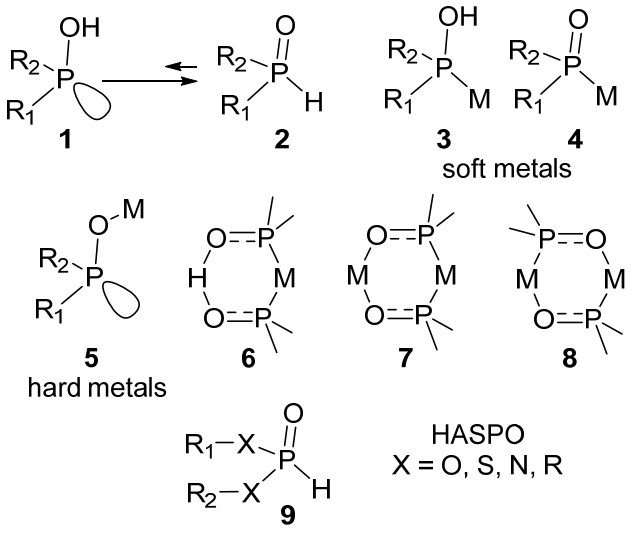
After completing his PhD in the area of coordination chemistry in Leiden, Piet van Leeuwen started with Shell Research Amsterdam in 1968 and worked on organometallic chemistry and homogeneous catalysis. Since 1978 he was head of the section "Fundamental aspects of homogeneous catalysis". In 1990 he founded the homogeneous catalysis group at the University of Amsterdam and moved there full-time in 1994. From 2000 till 2005 he was a part-time professor of industrial homogeneous catalysis in Eindhoven and director of the National-Research-School-Combination-Catalysis. In 2004 he started as a group leader in ICIQ in Tarragona till 2015. He then moved to INSA-Toulouse, where he works in LPCNO. Since 2009 his work focuses on ligand effects in metal nanoparticle catalysis.

As weak acids, phosphinuous acids deprotonate at mild pH. Salts of phosphinous acids are named phosphinites and the anion is referred to as phosphinito group in the literature until 2000, when SPO was introduced.

The coordination chemistry of SPOs is very rich as they can coordinate as a neutral ligand (**3**), in which effectively the equilibrium of SPO has shifted to phosphinous acid, or (upon deprotonation) as P-bound (**4**), or as O-bound (**5**) anions. In **4** the anion is also often called phosphoryl group. The presence of two donor atoms leads to bridged structures as presented in **6**, **7**, and **8**. Structure **6** contains a hydrogen-bonded couple (SPO–H–OPS), formally constituted by one anionic and one neutral ligand. This "supramolecular" arrangement is very stable[2] as the P=O moiety is one of the strongest hydrogen bond acceptors,[3] and particularly favored in complexes as it gives a chelating di-phosphorus mono-anionic ligand.

The electronic properties of SPOs in complexes such as **3**, **6** and **7** resemble those of the tertiary phosphine analogs as had already been derived from the comparison of the ^{31}P NMR data of related diphenylphosphine oxide and triphenylphosphine Pt complexes. Thus, the supramolecular bidentate in **6** can be viewed as an anionic analog of dppe or dppp.[4,5] These preliminary conclusions were corroborated by a more systematic study, which showed in addition that the electronic range for SPOs is slightly more compressed than that of phosphines.[6] The Tolman electronic parameters (TEP, previously called *chi,* χ) were calculated with the method of Gusev[7] by DFT calculations on $Ni(CO)_3L$ complexes. Complexes of type **4** such as $Ni(CO)_3P(O)Ph_2^-$ are anionic and for those complexes gas-phase calculations showed that the phosphoryl anion is a very strong P-donor ligand, but complexation of a Group 1 metal brought this down to normal

values. Since variation of substituents in phosphines has shown enormous effects in the performance of their homogeneous catalysts, one may expect a similar effect of SPOs, but so far exploitation has been modest. HASPO **9** is the name coined for heteroatom-containing SPOs; e.g. dialkyl phosphites belong to this class.[8]



Scheme 1. Coordination modes of SPO ligands

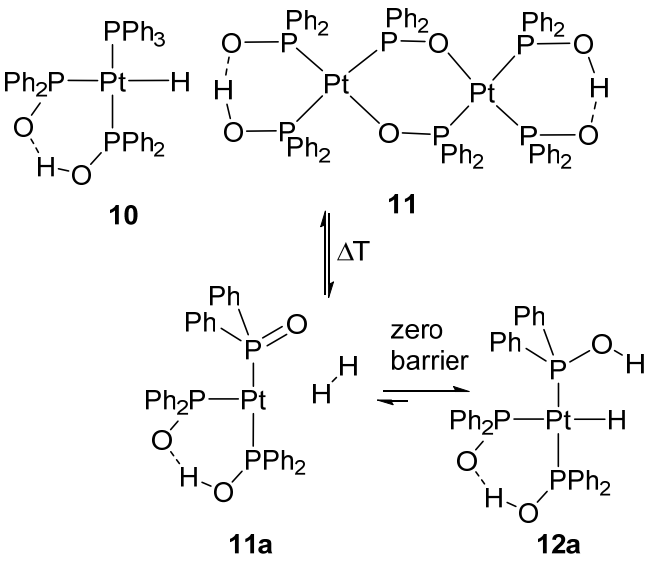
The advantages of SPOs over phosphines are threefold, first they are air and moisture stable, secondly, they can participate in supramolecular bidentate formation, and thirdly, they may act as bifunctional ligands.[9]

The coordination chemistry of SPOs was developed as off the 1970s and has been reviewed a number of times.[5, 10] Coordination chemistry and catalysis of Fe, Ru, Os (group 8) metals has been reviewed more recently.[11] Several reviews on catalysis have appeared[12, 13, 14, 15] and also with focus on enantioselective catalysis.[16,17] In the present review we will focus on metal-ligand cooperation of SPOs,[18,19] in which both O and P donor atoms play a critical role; the phosphorus atom anchors the ligand to the metal and the oxygen atom is available for an active role in the catalytic process, usually as a nucleophile.

2. Hydroformylation and hydrogenation

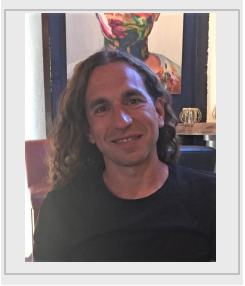
2.1. Homogeneous hydroformylation catalysts

As a pioneering example, platinum complexes **10** and **11** (Scheme 2) containing the bidentate SPO motive (at the time they were called phosphinito complexes)[5,4] were found to catalyse the hydroformylation of alkenes and the hydrogenation of alkenes and aldehydes.[4,20,21,22] Hydroformylation gave aldehydes and alcohols with modest TOFs and a high preference for the desired linear products (>90%). Complex **10** was also converted stepwise in the ethyl complex and the propionyl complex, the putative intermediates of the hydroformylation. Hydrogenation of aldehydes with catalyst **12a** was accelerated by the addition of carboxylic acids, leading to TOFs up to 9000 $mol \cdot h^{-1}$.[23] It was proposed that hydrogen entered the catalytic cycle via a ligand-assisted heterolytic splitting as shown for **11** in Scheme 2. The reaction requires heat to accomplish dissociation, but the actual heterolytic cleavage has a barrier close to zero, as shown later by means of DFT calculations.[24] As an illustration of the bidentate behavior of the hydrogen bonded pair of SPOs, their replacement by dppp on compound **11a** is shown in Scheme 3.[22]

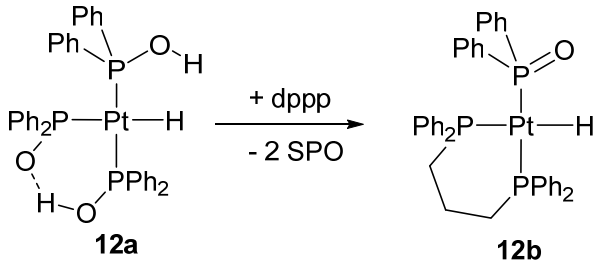


Scheme 2. Catalyst precursors and heterolytic cleavage of H_2.

Israel Cano developed his PhD in the field of homogenous catalysis at University of Huelva. After a short postdoctoral stay at University of Basque Country, he worked as postdoctoral researcher (2012-2016) with Prof. van Leeuwen at ICIQ and INSA (2012-2016). Then, he was awarded with a Marie Sklodowska-Curie fellowship to work with Prof. Jairton Dupont at the University of Nottingham (2016-2019). Since 2019, he is senior researcher in the group of Dr. Rafael Valiente at the University of Cantabria. His interests lie in the development of new materials with catalytic and optical applications: coordination compounds, ionic liquids, metal nanoparticles, and rare-earth metals based nanoparticles.

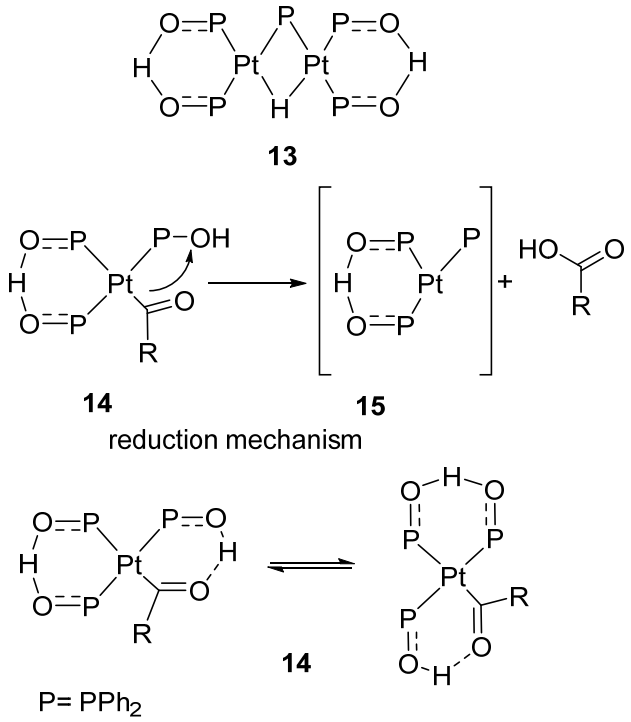


Zoraida Freixa completed her Ph.D. in the area of homogeneous catalysis at the Autonomous University of Barcelona (2000). After a post-doctoral stage at Prof. van Leeuwen's group in Amsterdam (2001–2003) she enrolled as Ramón y Cajal Researcher at the Institute of Chemical Research of Catalonia (ICIQ) as group manager of Prof. van Leeuwen's group (2004–2009). Since 2010, and after a short period as a Lecturer at the University of Barcelona, she holds an Ikerbasque Research Professor position at the University of the Basque Country (UPV-EHU) in San Sebastián, leading a research group focused on homogeneous catalysis and photoswitchable organometallics.



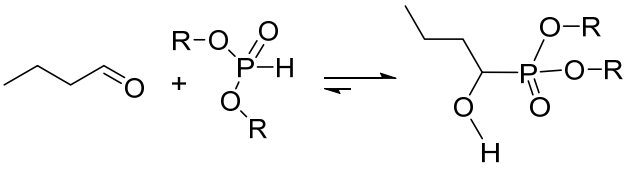
Scheme 3. Ligand substitution on **12a**.

While SPOs were initially selected for their stability, it was soon discovered that they can be highly reactive species. In the Pt catalysed hydroformylation it was found that prolonged reaction times led to the formation of inactive dimeric species **13** containing the SPO-H-OPS bidentates and PPh_2^- and hydrido ligands as the bridges between the two Pt metals. Surprisingly, the phosphide anion stems from the SPO, which is reduced by a Pt-acyl species forming carboxylic acid as a product as well via proposed intermediates of the type **14** and **15** (Scheme 4). The reaction is stoichiometric only but apparently the energy balance allows the reduction of the very strong P=O double bond. An alternative mechanism could have been the known disproportionation of $Ph_2P(H)O$ to give Ph_2PH and Ph_2PO_2H, but this was not the case. Dimer **13** could also be obtained by reaction of **12** and Ac_2O as further proof for its mechanism of formation.



Scheme 4. Decomposition of catalysts **10**–**12**.

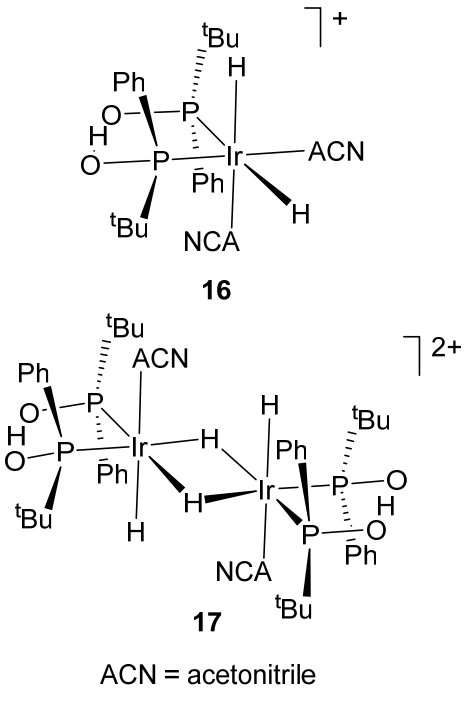
Additionally, free SPOs and HASPOs present in solution during a hydroformylation reaction will add to aldehydes and form α-hydroxyphosphonates (Scheme 5).[25,26] The reaction was used as a temporary storage for SPO ($Ph_2P(H)O$) during the Rh-Ph_3P catalyzed hydroformylation reaction, while when the aldehyde was distilled off, SPO was liberated and could act as stabilizing ligand for the Rh catalyst.[27] Decomposition of the Rh-Ph_3P catalyst upon prolonged heating is well documented and SPO can prevent this.[25]



Scheme 5. HASPO reaction with aldehydes.

2.2. Homogeneous hydrogenation catalysts

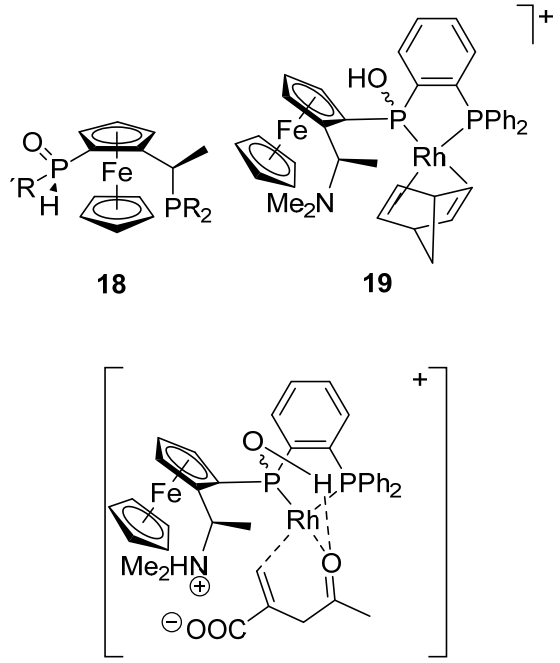
Iridium(III)-SPO systems **16** and **17** (Scheme 6) were investigated as precursors in the hydrogenation of aldehydes. Aldehydes were selectively hydrogenated to the alcohol at 25 °C and with only 5 bar of H_2; cinnamaldehyde was hydrogenated to cinnamyl alcohol with >99% selectivity and TOFs up to 2000 mol·h^{-1}. A ligand-assisted heterolytic hydrogen cleavage was invoked under mild conditions.[28] The racemic mixture of the ligand *t*-BuPhPOH was used and several isomers were identified by ^{1}H and ^{31}P NMR spectroscopy, but all quasi bidentate ligands SPO-H-OPS were homochiral, presumably for steric reasons and the rigidity of the bridge. For complex **17** an X-ray structure was reported.



Scheme 6. Ir hydrogenation catalysts for aldehydes; two of six isomers depicted.

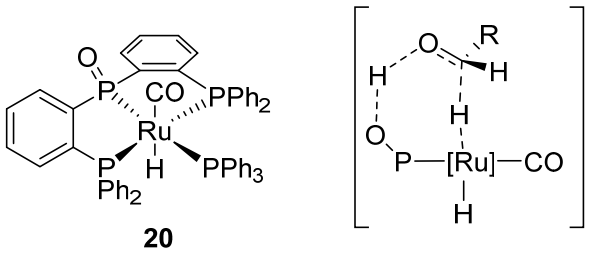
To increase the strength of the ligand coordination to metal centre, and to attain a better-defined chiral pocket for enantioselective processes, an effective strategy is the construction of hybrid chelates phosphine-SPO, as shown by Pfaltz's JoSPOphos ligand (**18**).[29] More recently, this design was exploited further in SPO-Wudaphos complex **19** for Rh hydrogenation of α-

methylene-γ-keto carboxylic acids.[30] According to DFT calculations, the high enantioselectivities obtained (over 99% ee) were attributed to substrate-ligand ion pair and H-bond interactions, mimicking the mode of action of enzymes (Scheme 7).



Scheme 7. Enzyme-inspired SPO-Wudaphos rhodium complex **19** for hydrogenation of α-methylene-γ-keto carboxylic acids and JoSPOphos **18**.

A tridentate pincer phosphine-SPO-phosphine ligand was developed by Chung, Zhang *et al*. The corresponding ruthenium catalyst precursor **20** was highly active in the hydrogenation of α,β-unsaturated aldehydes, with TOFs up to 36,000 mol·h^{-1} and >99% selectivity towards the unsaturated alcohol (at 80 °C and 50 bar H_2).[31] DFT calculations on the reaction mechanism supported a ligand-assisted heterolytic activation of a coordinated H_2 molecule, followed by an outer-sphere transfer mechanism for the aldehyde reduction (Scheme 8), as the one proposed previously for hydrogen transfer mediated by Rh catalysts (Section 3).[32]



Scheme 8. Ru catalyst precursor **20** and DFT derived mechanism for aldehyde hydrogenation catalysis.

There are several more articles on homogeneous hydrogenation with SPO-based metal complexes as mentioned in the reviews cited above; since these do not comment on a dual role of SPOs we do not include them here.[33]

2.3. General comments on heterolytic cleavage

In sections 2.1 and 2.2 we mentioned heterolytic cleavage of H_2 only briefly and before continuing we present here references that highlight this phenomenon, which is actually older than oxidative addition of H_2 to metal complexes that has dominated during decades our mechanistic thinking. Heterolytic cleavage of H_2 as a 2+2 addition onto a metal-anion pair of Cu(II) carboxylate was already proposed by Halpern in 1959,[34] in part based on much older observations in which quinoline may be the proton acceptor.[35] There may well be examples before the 1980s in which the anion after protonation remains bonded to the metal, as in the present instance of M-SPO. A well-known example of the last kind of a ligand-assisted heterolytic splitting of H_2 across an Ir-amide bond of a P–N–P ligand was proposed by Fryzuk,[36] although later it was reported that H_2 activation occurred in this particular instance by oxidative addition-reductive transfer rather than as a direct heterolytic cleavage of H_2.[37] The reaction may well start with the formation of an η^2-dihydrogen metal complex, while the base will in most cases attack from outer-sphere as was shown for Ru in 1990 by Chinn and Heinekey.[38] The best known examples of intramolecular H_2 cleavage onto M–X are represented by Noyori´s and Shvo's catalysts for hydrogen transfer (see Section 3).[39,40,41] In a recent review the subtle mechanistic details of Noyori's Ru–N bifunctional systems were analyzed.[42] A wide variety of ligand involvement in metal catalytic reactions started with Milstein´s report on pincer complexes, to which we will return in Section 4.[43] ~~We have mentioned the pincer systems here, because there is an interesting coincidence to be discussed in Section 4, which may inspire us to further exploration of SPO ligands.~~ We refer to a range of reviews on metal-pincer catalysis,[44] outer sphere hydrogenation catalysis,[45] pincer-type complexes for catalytic (de)hydrogenation reactions,[46] functional ligands, [47] low MW models for hydrogenases,[48] cooperating ligands,[49] ligand assisted proton transfer,[50,51,52] outer-sphere hydrogen transfer,[53] etc. In particular for the hydrogenation of CO_2, and its reverse, heterolytic, ligand assisted pathways are highly important.[54]

2.4. Nanoparticles as catalysts

Heterolytic cleavage of H_2 on heterogeneous catalysts has been proposed particularly for non-metallic materials that do not easily undergo redox reactions, such as non-noble metal oxides.[55,56] In this early example from 1960, the cleavage of H_2 on α-Cr_2O_3 to carry out the hydrogenation of 1-hexene was named "heterolytic dissociative adsorption at pair sites", and is basically the same mechanism as proposed in homogeneous catalysis. Occasionally, the interface has been invoked for the reaction between H_2 and metal nanoparticles supported on oxides, e.g. Au/TiO_2.[57] However, the dominant mechanism was hydrogen spill-over, i.e. the hydrogen molecule is dissociatively chemisorbed on the metal and hydrogen atoms migrate to the oxide surface, especially when a reducible oxide is involved, *e.g*. TiO_2.[58] On the other hand, for non-reducible oxides migration of hydrides remained unlikely thermodynamically.[59] Recently, however, DFT calculations carried out by Chandler *et al*. showed that H_2 is heterolytically cleaved at the edge of Au NPs supported on TiO_2.[60] We argued that bifunctional ligands coordinated to a metal might provide this mechanism. Phosphine ligand effects in Ru NPs catalysis have been well documented,[61,62] and thus we decided to use SPO ligands to this end (see Figure 1).[63,64] Ligand modified Ru NPs are very active catalysts for arene hydrogenation, with stronger

donors leading to faster catalysts, and good catalysts for ketone hydrogenation.

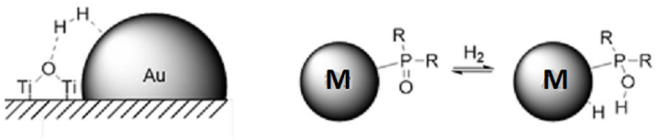
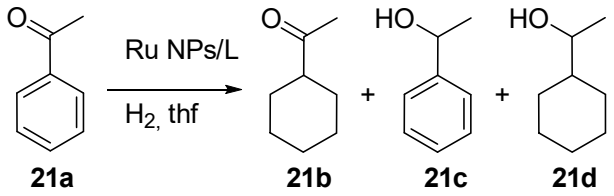


Figure 1. SPO ligands on MNP (right) mimicking metal-support interaction. Reproduced with permission from Ref. 67. Copyright 2014 American Chemical Society.

It was thought that the hydrogenation of **21a**, acetophenone, might be promoted relative to arene hydrogenation through the introduction of an SPO instead of a classic tertiary phosphine thus facilitating the heterolytic cleavage and transfer of H_2 (Scheme 9). Ru NPs were prepared under H_2 from Ru(COT)(COD), which gave NPs of 1.2–1.9 nm in size depending on the ligand and the stoichiometry applied. In general, SPO-ligated Ru NPs were less active hydrogenation catalysts than Ru NPs ligated by phosphines, ketone hydrogenation being less affected than the reduction of the arene. Thus, a relatively large proportion of alcohol **21c** was obtained for SPO Ru NPs, although the effect is modest.[63] Solvents and conditions are also important for the outcome.[65] As an example, Ru NPs stabilized by phosphine-functionalized ionic liquids gave purely **21c**.[66] In addition, long reaction times lead in most cases to complete formation of **21d**.



	selectivity %		
L = $Ph_2P(OH)$ (30 °C, 20 bar)	42	47	6
L = PPh_3 (100 °C, 40 bar)	57	4	39

Scheme 9. Hydrogenation of acetophenone (references 63 and 65 resp.)

Subsequently the research focused on Au NPs, which were prepared from the Au(I)Cl complex containing the [(*tert*-butyl(naphthalen-1-yl)]SPOH adduct by $NaBH_4$ reduction.[67] Small and monodisperse Au NPs (1.24 ± 0.16 nm) were synthetized and characterised in detail. The ligand turned out to be present as the phosphoryl anion, while no phosphinous acid was observed. These anionic ligands are bonded to Au(I) species at the NP surface, as both Au(I) and Au(0) were found in the NPs, and further analysis pointed to an approximate average composition of $Au_{50}SPO_{30}$. Thus, the particles resemble the numerous thiolate Au clusters and NPs but, unlike thiolates, SPOs did not afford precise clusters, so far. These Au NPs were highly selective aldehyde hydrogenation catalysts, not affecting alkene bonds in α,β-unsaturated aldehydes as cinnamaldehyde and acrolein, ketones, alkyne bonds, and cyano and nitro groups, among other groups. A series of control experiments demonstrated a heterolytic H_2 cleavage in which the SPO plays a crucial role and operates cooperatively with a neighbouring gold atom. In a subsequent publication, a ligand effect was reported for a series of alkyl and aryl SPOs.[68] Au NPs ligated by aromatic SPOs contained only phosphoryl anions, displayed a strongly polarised P=O bond and were highly selective in aldehyde hydrogenation. On the other hand, Au NPs ligated by more basic alkyl SPOs contained both phosphoryl groups and phosphinous acids, showed a less polarised P=O bond and they were less selective hydrogenation catalysts. In this vein Lopez et al. conducted a DFT study on acrolein hydrogenation mediated by $Au_{55}(Ph_2PO)_{27}$, which supported a heterolytic cleavage of H_2 and showed outer-sphere hydrogen transfer to acrolein, Figure 2.[69]

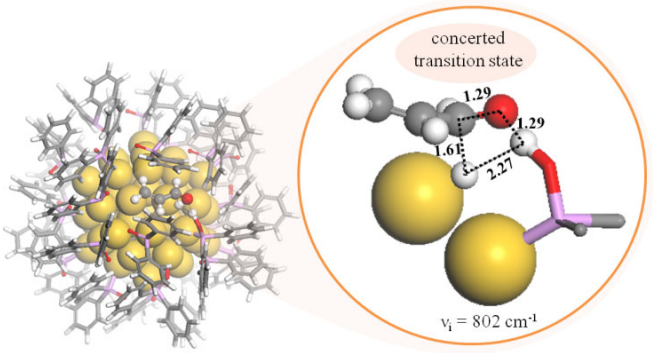
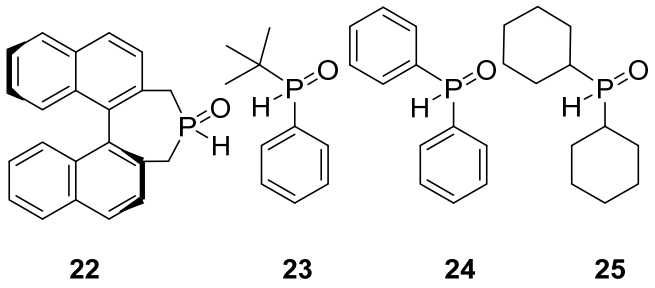


Figure 2. Outer-sphere hydrogen transfer in $Au_{55}SPO_{27}$.[69] Reproduced with permission from Ref. 69. Copyright 2017 American Chemical Society.

Cano et al. reported the preparation of Ir nanoparticles by H_2 reduction of $[Ir(OMe)(COD)]_2$ in the presence of a chiral secondary phosphine oxide, (3,5-dihydro-4*H*-dinaphtho[2,1-c:1',2'-e] phosphepine-4-oxide, **22**), Scheme 10.[70] This procedure furnished small, well dispersed and soluble nanoparticles of 1.4 (0.2) nm, which contained both Ir(0) and Ir(I). The synthetic procedure closely resembles that of the homogeneous system mentioned above, but the behavior in catalysis is clearly distinct.[71] A metal:ligand ratio of 1.7 makes that 90% of the surface atoms are ligated by SPO; in addition, 1.3 H atoms were found per surface metal atom on the freshly prepared catalyst. On the basis of IR and ^{31}P NMR studies, it was concluded that the SPO ligands occur as phosphoryl anions. A ligand induced ECD spectrum was observed for the Ir NPs, but no fine structure due to d–d transitions was detected, as the NPs are a mixture of different species. The Ir NPs were found to be active catalysts for the enantioselective hydrogenation of prochiral ketones with an enantiomeric excess up to 56% for 4-methoxyacetophenone. Indeed, a series of experimental tests allowed to prove the role of these Ir NPs as enantioselective catalysts for the asymmetric hydrogenation of ketones and discard the activity of some homogeneous catalyst formed *in situ*. In line with the Au NPs systems, a heterolytic hydrogenation mechanism was proposed.

A detailed characterization study of Ir NPs stabilized by ligands **23**–**25** (Scheme 10) by ^{31}P MAS NMR and IR spectroscopy indicated that an increase in ligand basicity leads to a rise in the amount of phosphinous acid on the surface. It was concluded that, for dicyclohexyl SPO **25**, the ligands occur pairwise as in structure **6**, while *tert*-butyl(phenyl)) and diphenyl SPOs (**23** and **24**,

respectively) are also bound as the phosphoryl anion **4** and the phosphinous acid **3** to the surface of Ir NPs.[72] Hydrogenation of cinnamaldehyde is highly selective to the alcohol, with activities decreasing in the order **23** > **24** > **25.**

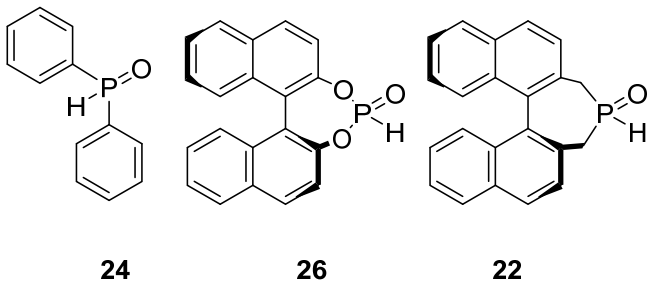


22 **23** **24** **25**

Scheme 10. SPO ligands used for Ir NPs

3. Hydrogen transfer

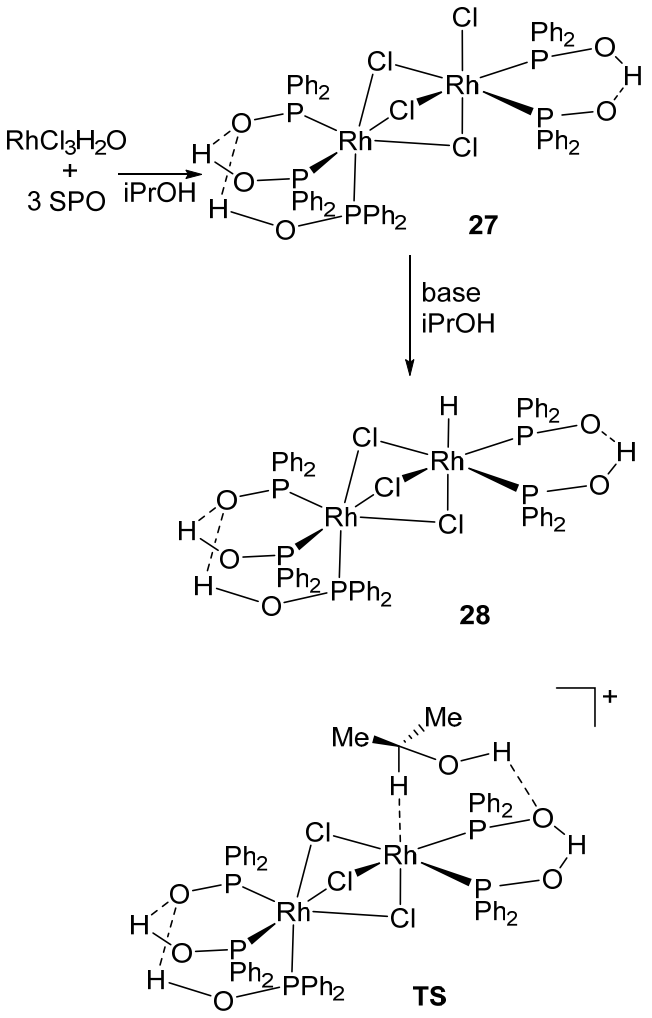
Castro *et al*. found that many transition metal salts in the presence of SPO ligands gave active catalysts for the transfer hydrogenation of alcohols to ketones under the routine conditions.[32] Except Ir, all simple salts became more active when SPOs were added. In particular Rh stood out and thus was studied in more detail. The three ligands used are depicted in Scheme 11. ~~Surprisingly, under the reaction conditions and strong base added~~, In iPrOH mainly one complex was formed, a trichloro bridged dimer, **27**, as confirmed *in situ* NMR spectroscopy and single crystal X-ray structure analysis. Complex **27** was subsequently converted to monohydride **28**, by addition of excess of KOtBu (Scheme 12).



24 **26** **22**

Scheme 11. SPO ligands used for transfer hydrogenation

TOFs up to 1500 mol·h^{-1} were obtained for the reaction of iPrOH and acetophenone (80 °C). In the enantiomeric version with optically pure **22** no ee was observed. **26** gave 89% ee, but this catalyst has a short lifetime in the basic solution. DFT calculations showed that an outer-sphere mechanism for hydrogen transfer was preferred (the lowest transition state is shown in Scheme 12). Ligands **22** and **26** were also used in a 1:1 combination with monodentate phosphines containing a basic or protic function, which led to a broad spectrum of ees and rates demonstrating the supramolecular capabilities of SPOs.



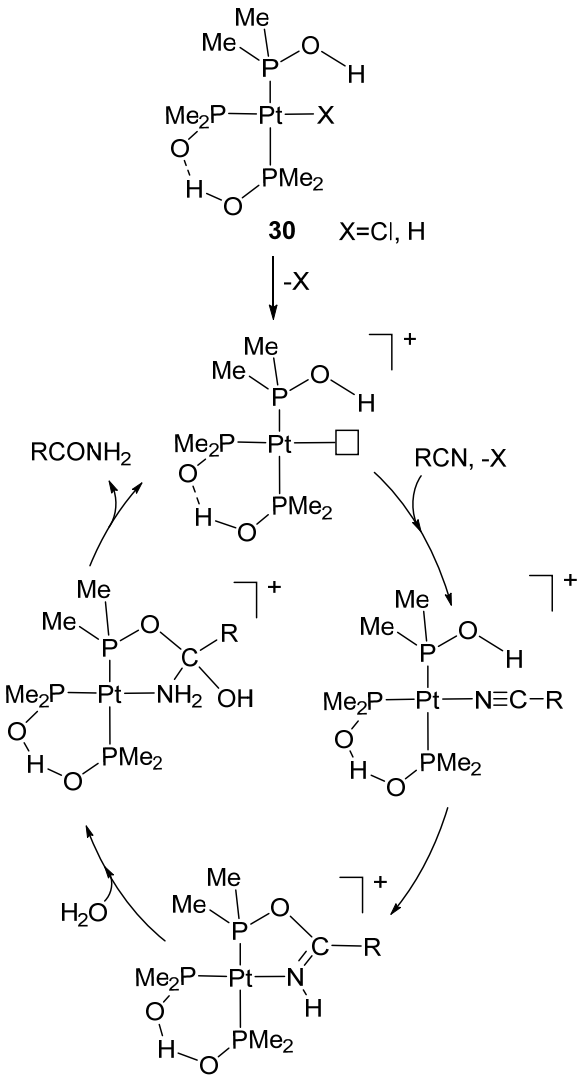
Scheme 12. Preparation of hydrogen transfer catalyst **27** and calculated transition state TS

Pd complex [[(*t*-BuPhPO)$_2$H]$_2$Pd(OAc)]$_2$ **29** was used as oxidative dehydrogenation catalyst for alcohols and a similar outer-sphere mechanism might be operative for this catalyst.[73] Peculiarly, the reduced Pd(0) intermediate can be reoxidized with air without affecting the ligand. In addition, the authors developed a "self-assembling method", which allowed the production of monometallic supramolecular chiral bisphosphinite palladacycles of **29** containing a κ^2-coordinated carboxylate modifiable as desired. As for complexes **10**–**12**[22] a zerovalent metal source was used involving oxidative addition of phosphinous acids to the metal centre.[74] In this instance, interestingly, two hydrogens were transferred to dba forming monohydrogenated dba.

4. Hydration of nitriles

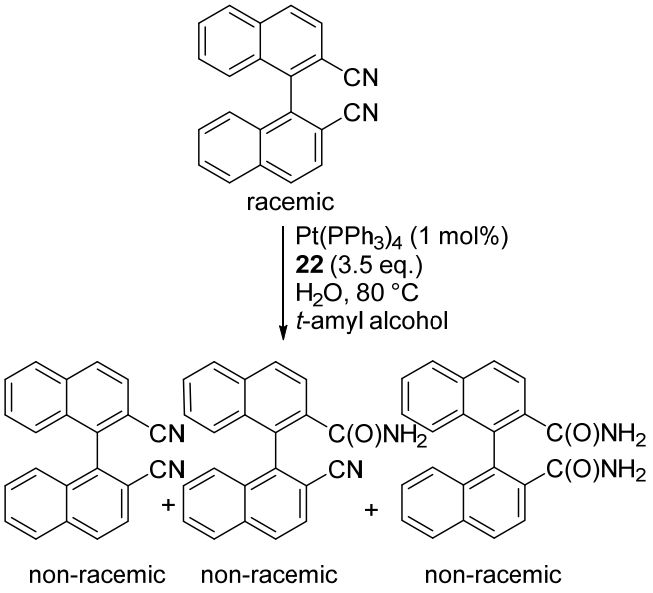
It took more than 10 years after the first reports on hydrogenation and hydroformylation[20] before Ghaffar and Parkins (1995) published their findings on a completely different reaction with Pt-SPO complexes, *viz*. the hydration of nitriles to amides.[75] Platinum complex **30** (Scheme 13) was an active and highly selective hydration catalyst with TOFs ~500 mol·h^{-1} for several nitriles at reflux temperature and 1500 mol·h^{-1} for acrylonitrile, and TONs up to 50,000 (77,000).[76] Notably, there is no tendency

towards further hydrolysis to the acid. Even more interesting, in the present context, is the proposed mechanism outlined in Scheme 13. The nitrile coordinates to the Lewis acidic metal via its nitrogen donor atom and the SPO oxygen atom does a nucleophilic attack at the nitrile C-atom. Water attacks the intermediate formed and the amide is liberated. More common mechanisms were collected by Knapp *et al.*, but in their work on the ethyl analog of **30** they could not find further proof for a mechanism.[77] The scope of the reaction has been enlarged to both more sensitive and less reactive substrates by De Vries et al.[78] An attempt to asymmetric catalysis failed due to racemization of the product.



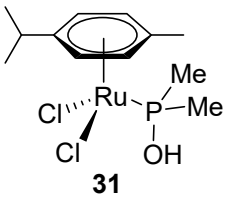
Scheme 13. Hydrolysis reaction of nitriles proposed by Parkins

Recently, Virgil, Grubbs, *et al*. replaced the SPO-H-OPS in **30,** as shown in Scheme 3 for **12**, by a large number of diphosphine ligands in a high-throughput screening and in this way obtained cationic complexes that were far more active than **30**.[79] Catalysts based on dppf were active even at room temperature and also cyanohydrins could now be used. Gulyàs and co-workers developed an enantiomeric version of Parkins' Pt catalyst using ligand **22**.[80] For simple substrates no resolution could be obtained, as mentioned above, probably due to racemization under the conditions. Instead, binaphthyl dinitriles (Scheme 14) and the derived products did not racemize and they gave an approximate rate difference of 4–5 between the two enantiomers for the conversion of the first nitrile to amide. As a result, at 45% conversion the diamide product could be obtained in low yield (15%) at >99% ee, and at high conversion the remaining starting dinitrile material (17%) showed an ee of 96 %; an interesting result, but the ees and yields are too low to be of practical value.

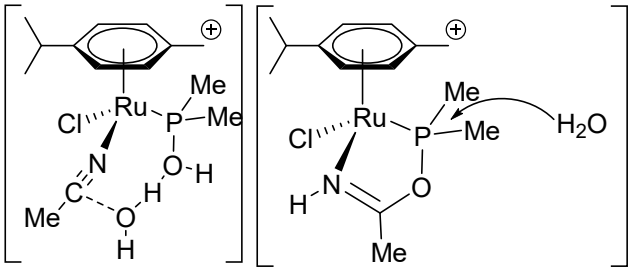


Scheme 14. Asymmetric addition of water to nitriles

Tyler and co-workers discovered that Ru complexes of SPO ligands are also active catalysts for the hydration of nitriles.[81] Thus, (η^6-*p*-cymene)$RuCl_2$(Me_2POH) **31** catalysed addition of water to acetonitrile at 100 °C with a TOF >32 mol·h^{-1} (measured at full conversion). The catalyst precursor **31** and the intermediate initially proposed **32a** are depicted in Scheme 15. According to this reaction scheme, the ligand "tugs" the water molecule via hydrogen bonding, directing the nucleophilic attack at the nitrile C-atom, as has been proposed for several bifunctional ligands.[82,83]



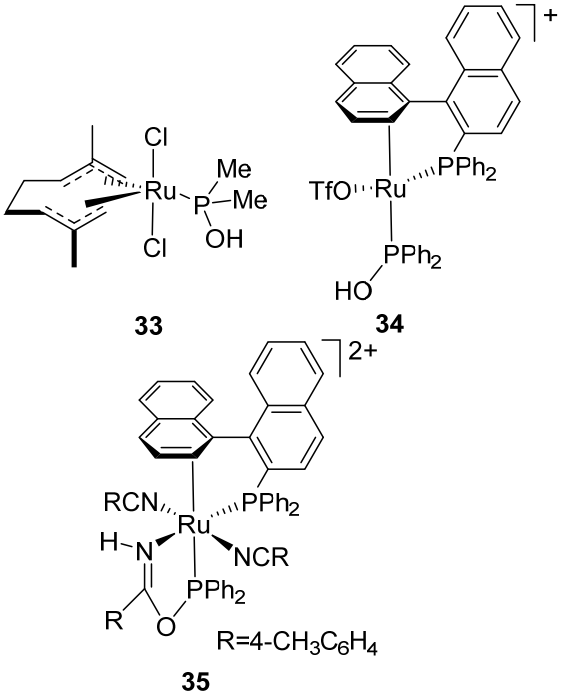
31



32a **32b**

Scheme 15. Ru-SPO catalysts **31** and proposed intermediates for the addition of water to nitriles.

A related catalyst **33** with Ru(IV) as the central metal atom was reported by Cadierno *et al.*, which was much faster than **31** as it showed TOFs up to 1200 mol·h^{-1} at 60 °C.[84] The same hydrogen bonding assisted mechanism was proposed. Notably, it can be used in water and in case the amide crystallises, separation is easy. Soon thereafter, a potential intermediate for Ru-SPO catalysed nitrile hydration was proposed by the same group for a different ligand system, **34**, a complex synthesised by Pregosin via P–C cleavage of BINAP by water (Scheme 16).[85,86] Both, **34** and the putative Parkins' intermediate **35**, also isolated by Pregosin, function as catalysts, albeit **35** at lower rates. In addition, **35** was shown to hydrolyse to give the amide product. Thus, there is now clear evidence for Parkins' intermediate proving the bifunctional action of SPOs on Ru.

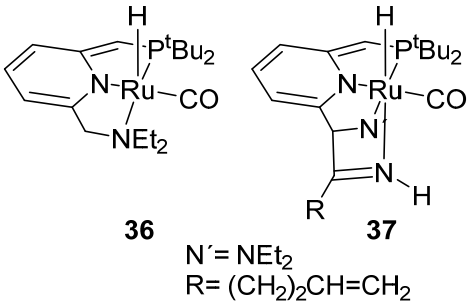


Scheme 16. Ru-SPO catalysts **33–35.**

Later, DFT analysis on the reaction mechanism of nitriles hydration using arene-ruthenium(II) complexes containing SPO ligands showed that the lowest energy pathway for the attack of water is an attack on the more electrophilic P-atom of the metallacycle of the Tyler type catalyst (**32b** in Scheme 15), rather than at the acetamidate C-atom as drawn by Parkins.**[87]** Instead of **31** one could also use the analogous complex with Ar_2PCl as precursor.[88]

Cadierno, Lopez, et al. studied the osmium analogue of **31** and this turned out to be the fastest Os catalyst to date for the hydration of nitriles with TOFs at 80 °C up to 200 mol·h^{-1}.[89] The Os catalyst is faster than the Ru one in the hydration of less-reactive aliphatic nitriles. The catalyst works in water. DFT calculations are in support of the metallacyclic mechanism.

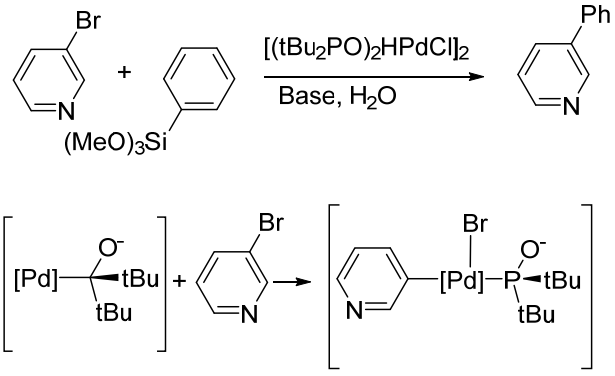
Interestingly, another type of nitrile hydration Ru catalyst was discovered by Otten and De Vries, *viz.* the P-N-N pyridine dearomatized pincer system **36** mentioned above under hydrogenation.[90,91] In this catalyst also an anionic function of the ligand, C-based in this instance, adds onto the electrophilic C-atom of the nitrile and **37** was identified as intermediate (Scheme 17). This is the second system showing analogies between the two bifunctional ligands, a dearomatized pincer and an SPO.



Scheme 17. Ru-pincer catalyst for the addition of water to nitriles

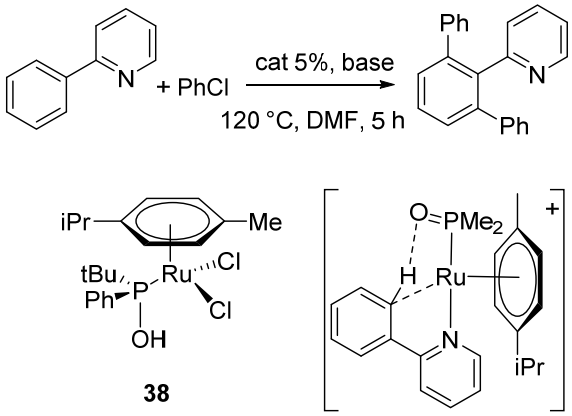
5. C–H Arylation, Cross coupling

For reactive substrates, high catalyst concentrations, and high temperatures, any Pd source will work in C–C coupling reactions (Heck, Suzuki, Negishi) and so do Pd-SPO complexes. Bedford and co-workers showed that phosphite and phosphinito complexes of Pd yielded TONs up to 500,000 in the Suzuki reaction, and noted that a variety of precursors and ligands may give similar results.[92] Earlier, palladacycles were found to be extremely efficient catalysts and these may well be precursors to SPO complexes.[93] It was suggested that probably anionic ligand motives **4** were involved, creating an electron rich intermediate accelerating the oxidative addition. In his review on cross coupling reactions with SPO complexes, Hong concluded that, generally speaking, SPO complexed transition metal catalysts exhibit comparable efficiencies to those shown by tri-substituted phosphines and no specific role for SPO[14] or HASPO[8] was indicated in most instances. Thus, we will not review them here. HASPO Pd complexes are efficient catalysts for Kumada–Corriu cross-couplings of (hetero)aryl or alkenyl tosylates, but no special role of the ligand was proposed.[94,95] See for example the mechanism proposed by Wolf and Lerebours in Scheme 18 for the precursor $[(tBu_2PO)_2HPdCl]_2$, in which the very electron-rich tBu_2PO^- anion accelerates the oxidative addition in a Pd catalysed Sonogashira reaction and Hiyama coupling in water, both with 3-bromopyridine.[96,97]



Scheme 18. Activation of Pd by tBu_2PO^-

There are, however, several interesting exceptions in which bifunctionality plays a role or may play a role. C–H arylation with Rh, Ru, and Pd catalysts, and more recently 3d metals, has received an enormous amount of attention in the last three decades as one of the most successful applications of C–H functionalization.[98, 99] Most popular is the arylation/vinylation/alkylation of aryl molecules containing an (*ortho*) directing polar group, 2-phenylpyridine being the typical example. In addition to this directing group, the catalyst often uses a basic group assisting in the concerted proton transfer/metalation, which can be as simple as a carboxylate.[100] Inspired by the successful use of Ru–PPh_2 complexes by Sames in C–H arylation,[101] Ackermann *et al*. introduced Ru–SPO complexes to this end ($[RuCl_2(cymene)]_2$ and 4 SPOH mixed *in situ* giving **38**), and this catalyst arylated successfully 2-phenylpyridine.[102] In a subsequent publication, which concerned actually carboxylate complexes (which were slightly better!), they proposed a mechanism for SPO shown in Scheme 19, according to which a phosphoryl anion assists in the concerted, cooperative metalation–deprotonation of the aryl group.[103] In a later study, Gelman, Ackermann, et al. reported interesting applications of this reaction and supported the mechanistic proposals with DFT studies.[104]

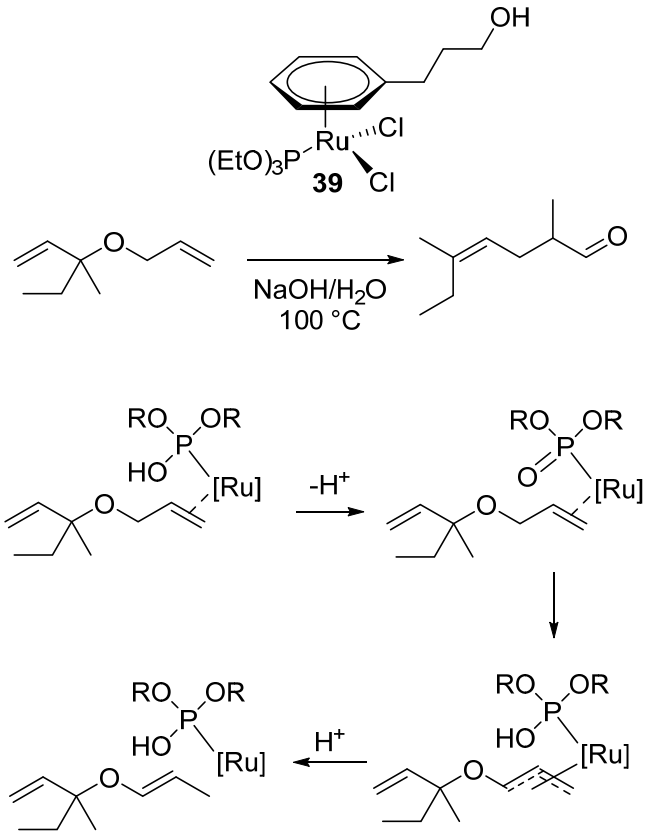


Scheme 19. C–H arylation by the cooperative metalation-deprotonation mechanism

Simultaneously, the reaction was studied in more detail with isolated complexes and several SPO ligands by Clavier et al.[105] Excess chloride has a detrimental effect on the reaction and the SPO should not be too bulky. Their DFT studies also showed that the concerted pathway depicted in Scheme 11 is indeed the one with the lowest barrier.

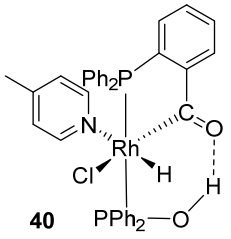
6. Other reactions

The Ru half sandwich complexes **38** discussed in the previous section were used as isomerization catalyst by Cadierno *et al*.[106] Thus, **39** was used for the tandem isomerization/Claisen rearrangement of diallyl ethers in water as shown in Scheme 20. Triethyl phosphite is *in situ* hydrolysed to the HASPO diethyl phosphite. A proton transfer to the coordinated SPO was proposed as the way that leads to the Ru(allyl) intermediate, and *vice versa*. More recently, complex **38** was shown to be a catalyst for allylbenzene isomerization and the C–H arylation described above.[107]



Scheme 20. Ruthenium pre-catalyst **39** for the tandem isomerization/Claisen rearrangement of diallyl ethers in water

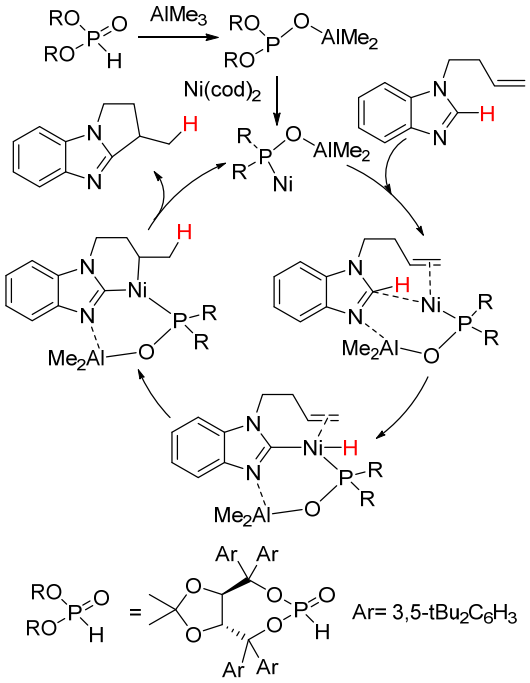
Garralda *et al*. showed that the Rh-acyl moiety derived from *o*-(diphenylphosphino)benzaldehyde and SPOs forms a strong O---H---O intramolecular hydrogen bond in Rh complexes of the type **40**, as shown above for Pt in **14**. The ligand system can be described as a pseudo P–C–P pincer ligand in a meridional arrangement (Scheme 21). Rhodium complex **40** was evaluated as precatalyst for the hydrolytic release of hydrogen from ammonia- or *t*-butylamine- and dimethylamine-borane substrates.[108] The kinetics were rather complex. No special role was assigned to the hydrogen bonded SPO, but the presence of protic and hydridic hydrogen atoms on both the precatalyst and the substrate suggests an active role of the ligand in the process.



Scheme 21. Catalyst **40** for amine-borane hydrolysis

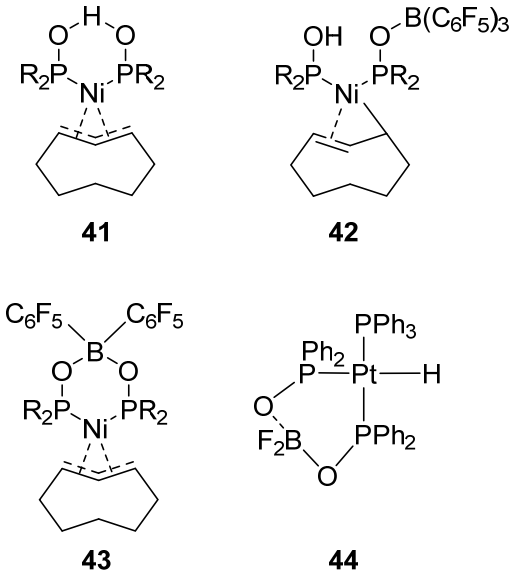
Wang and Ye reviewed the C–C bond formation, mostly cyclizations of alkenyl heterocycles, with Ni-Al catalysts.[109] In

several instances the Ni and Al metals were connected with an SPO, including chiral ones.[110] The Al cation (introduced synthetically as $AlMe_3$) functions as a Lewis acid while Ni activates a C–H bond, undergoes migratory insertion and gives reductive elimination. The reaction was developed by Hiyama et al.[111] and the initial discovery of SPO's action in this field by Cramer[110] was further explored subsequently. Scheme 22 shows an example for a chiral SPO complex by Ye *et al*.[112] In this chemistry, SPOs connect the soft metal centre and the Lewis acid catalyst in a way similar to the other mechanisms involving bifunctional activity, with the difference that, in this instance, the electrophile does not form part of the substrate but of the catalyst; for more reactions we refer to Ye's review.[109]



Scheme 22. Enantioselective Ni-Al bimetallic catalysed exo-selective C-H cyclization of imidazoles with alkenes

Breuil *et al*. studied SPO Ni complexes **41** and those modified by Lewis acid $B(C_6F_5)_3$ **42**, **43** in ethene oligomerisation (Scheme 23).[113] Complexes **41** gave side products of ethene and the ligands but no oligomers. However, complexes **42** are active. Several aryl groups as substituents were investigated and electron donors (*p*-MeO) gave only traces, while the other ligands gave up to 15,000 turnovers in 90 min. Interestingly, **43** is inactive, which reminds us of Pt complex **44**, the BF_2 analogue of **10**, which was also inactive in hydroformylation and only gave the Pt acyl intermediate.[22] In the present instance no hydrogen activation needs to be invoked, but perhaps asymmetry or flexibility can explain the different behaviour.



Scheme 23. Ni complexes investigated for oligomerisation and comparison with Pt complex

Summary and Outlook

We have shown that SPO ligands participate in a variety of metal catalysed reactions playing a dual role, as a modifying ligand utilising its soft phosphorus atom for coordination to transition metals, and as functional ligand employing the oxygen atom as a nucleophile for harder entities. The fragment M–P–O can be considered as an FLP (frustrated Lewis pair),[69] ready to react in a heterolytic fashion with suitable substrates. What is more, they play these roles not only in coordination complexes but also in MNPs. Through H-bonding, SPOs can also take part in supramolecular combinations; homo-combinations give monoanionic bidentate ligands, but they also form combinations with other ligands having proton acceptors or donors,[32] which is relatively under-explored. We have seen that many similarities exist with other bifunctional ligand systems used in hydrogenation and hydration reactions, and reactions of CO_2. We expect that this refocus on SPO will stimulate further inventions of this generally stable and easy to synthesize ligand group.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis • HASPO • phosphinito • phosphoryl • SPO

[1] B. Hoge, S. Neufeind, S. Hettel, W. Wiebe, C. Thoesen, *J. Organomet. Chem.* **2005**, *690,* 2382–2387.
[2] Y. A. Ustynyuk, Y. V. Babin, V. G. Savchenko, E. M. Myshakin, A. V. Gavrikov, *Russ. Chem. Bull.* **2010**, *59*, 686–694.
[3] C. A. Hunter, *Angew. Chem. Int. Ed.* **2004**, *43*, 5310.
[4] P. W. N. M. van Leeuwen, C. F. Roobeek, J. H. G. Frijns, A. G. Orpen, *Organometallics* **1990**, *9*, 1211–1222.
[5] D. M. Roundhill, R. P. Sperline, W. B. Beaulieu, *Coord. Chem. Rev.* **1978**, *26*, 263–279.
[6] D. Martin, D. Moraleda, T. Achard, L. Giordano, G. Buono, *Chem. Eur. J.* **2011**, *17*, 12729–12740.
[7] D. G. Gusev, *Organometallics* **2009**, *28*, 763–770.
[8] L. Ackermann, *Isr. J. Chem.* **2010**, *50*, 652–663.
[9] P. W. N. M. van Leeuwen, Z. Freixa in *Supramolecular Catalysis*, (Ed.: P. W. N. M. van Leeuwen) Wiley-VCH, Weinheim, **2009**, pp. 258–263.
[10] P. Sutra, A. Igau, *Coord. Chem. Rev.* **2016**, *308*, 97–116.
[11] J. Francos, D. Elorriaga, P. Crochet, V. Cadierno, *Coord. Chem. Rev.* **2019**, *387*, 199–234.
[12] L. Ackermann, *Synthesis* **2006**, *10*, 1557–1571.
[13] A. W. Parkins, *Platin. Met. Rev.* **1996**, *40*, 169–174.
[14] T. M. Shaikh, C.-M. Weng, F.-E. Hong, *Coord. Chem. Rev.* **2012**, *256*, 771–803.
[15] A. Gallen, A. Riera, X. Verdaguer, A. Grabulosa, *Catal. Sci. Technol.* **2019**, *920*, 5504–5561.
[16] N. V. Dubrovina, A. Boerner, *Angew. Chem. Int. Ed.* **2004**, *43*, 5883–5886.
[17] H. Clavier, G. Buono, *Chem. Rec.* **2017**, *17*, 399–414.
[18] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236–12273.
[19] V. T. Annibale, D. Song, *RSC Adv.* **2013**, *329*, 11432–11449.
[20] P. W. N. M. van Leeuwen, C. F. Roobeek, *Eur. Pat. Appl. EP 82-201634*, **1983**. Priority: GB 81-38734 (*Chem. Abstr.*, 1983, **99**, 121813).
[21] P. W. N. M. van Leeuwen, C. F. Roobeek, R. L. Wife, J. H. G. Frijns, *J. Chem. Soc., Chem. Commun.* **1986**, 31–33.
[22] P. W. N. M. van Leeuwen, C. F. Roobeek, *New J. Chem.* **1990**, *14*, 487–493.
[23] P. W. N. M. van Leeuwen, C. F. Roobeek, *Advances in Chemistry Series* **1992**, Vol. 230 (Homogeneous Transition Met. Catal. React.), pp. 367–376.
[24] E. Santos, C. Bo, *unpublished*.
[25] P. W. N. M. van Leeuwen, J. C. Chadwick, *Homogeneous Catalysts,* Wiley/VCH, Weinheim, **2011**, pp. 227–234.
[26] A. Christiansen, D. Selent, A. Spannenberg, M. Koeckerling, H. Reinke, W. Baumann, H. Jiao, R. Franke, A. Boerner, *Chem. Eur. J.* **2011**, *17*, 2120–2129.
[27] M. Matsumoto, M. Tamura, *J. Mol. Catal.* **1983,** *19, 365–316.*
[28] I. Cano, L. M. Martinez-Prieto, L. Vendier, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2018**, *8*, 221–228.
[29] H. Landert, F. Spindler, A. Wyss, H.-U. Blaser, B. Pugin, Y. Ribourduoille, B. Gschwend, B. Ramalingam, A. Pfaltz, *Angew. Chem. Int. Ed.* **2010**, *49*, 6873–6876.
[30] C. Chen, Z. Zhang, S. Jin, X. Fan, M. Geng, Y. Zhou, S. Wen, X. Wang, L. W. Chung, X.-Q. Dong, X. Zhang, *Angew. Chem. Int. Ed.* **2017**, *56*, 6808–6812.
[31] X. Tan, W. Zeng, X. Zhang, L. W. Chung, X. Zhang, *Chem. Commun.* **2018**, *54*, 535–538.
[32] P. M. Castro, H. Gulyás, J. Benet-Buchholz, C. Bo, Z. Freixa, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2011**, *1*, 401–407.
[33] X.-b. Jiang, A. J. Minnaard, B. Hessen, B. L. Feringa, A. L. L. Duchateau, J. G. O. Andrien, J. A. F. Boogers, J. G. de Vries, *Org. Lett.* **2003**, *5*, 1503–1506.
[34] J. Halpern, *J. Phys. Chem.* **1959**, *63,* 398–403.
[35] M. Calvin, *Trans. Faraday Soc.* **1938**, *34*, 1181–1191.
[36] M. D. Fryzuk, P. A. MacNeil, *Organometallics* **1983**, *2*, 682–684.
[37] M. D. Fryzuk, P. A. MacNeil, S. J. Rettig, *Organometallics* **1985**, *4,* 1145–1147.
[38] M. S. Chinn, D. M. Heinekey, *J. Am. Chem. Soc.* **1990**, *112,* 5166–5175.
[39] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997,** *30*, 97–102.
[40] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 2675–2676.
[41] Y. Blum, D. Czarkie, Y. Rahami, Y. Shvo, *Organometallics* **1985**, *4*, 1459–1461.
[42] P. A. Dub, J. C. Gordon, *Nat. Rev. Chem.* **2018**, *2*, 396–408.
[43] C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792.
[44] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236–12273.
[45] O. Eisenstein, R. H. Crabtree, *New J. Chem.* **2013**, *37*, 21–27.
[46] S. Werkmeister, J. Neumann, K. Junge, M. Beller, *Chem. Eur. J.* **2015**, *21*, 12226–12250.
[47] B. Askevold, H. W. Roesky, S. Schneider, *ChemCatChem* **2012**, *4*, 307–320.
[48] F. Gloaguen, T. B. Rauchfuss, *Chem. Soc. Rev.* **2009**, *38*, 100−108.
[49] H. Gruezmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 1814–1818.
[50] S. Kuwata, T. Ikariya, *Chem. Eur. J.* **2014**, *20*, 9539–9542.
[51] N. E. Smith, W. H. Bernskoetter, N. Hazari, *J. Am. Chem. Soc.* **2019**, *141*, 17350−17360.
[52] D. B. Grotjahn, *Chem. Eur. J.* **2005**, *11*, 7146 –7153.
[53] L. V. A. Hale, N. K. Szymczak, *ACS Catal.* **2018**, *8*, 6446−6461.
[54] N. Onishi, G. Laurenczy, M. Beller, Y. Himeda, *Coord. Chem. Rev.* **2018**, *373*, 317–332.
[55] R. L. Burwell, A. B. Littlewood, M. Cardew, G. Pass, C. T. H. Stoddart, *J. Am. Chem. Soc.* **1960**, *82*, 6272–6280.
[56] R. L. Burwell Jr., J. F. Read, K. C. Taylor, G. L. Haller, *Z. Phys. Chem. Neue Fol.* **1969**, *64*, 18–25.
[57] D. Ren, L. He, L. Yu, R.-S. Ding, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *J. Am. Chem. Soc.* **2012**, *134*, 17592−17598.
[58] M. Boudart, M. A. Vannice, J. E. Benson, *Z. Phys. Chem. Neue Fol.* ***1969***, *64*, 171–177.
[59] R. Prins, *Chem. Rev.* **2012**, *112*, 2714−2738.
[60] T. Whittaker, K. B. S. Kumar, C. Peterson, M. N. Pollock, L. C. Grabow, B. D. Chandler, *J. Am. Chem. Soc.* **2018**, *140*, 16469−16487.
[61] D. González-Gálvez, P. Nolis, K. Philippot, B. Chaudret, P. W. N. M. van Leeuwen, *ACS Catal.* **2012**, *2*, 317–321.
[62] L. M. Martínez-Prieto, B. Chaudret, *Acc. Chem. Res.* **2018**, *51*, 376–384.
[63] E. Rafter, T. Gutmann, F. Low, G. Buntkowsky, K. Philippot, B. Chaudret, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2013**, *3*, 595–599.
[64] Rossi *et al.* introduced piperazine ligands for this purpose; one nitrogen connects the ligand to the metal surface, the other one abstracts a proton from H_2: J. L. Fiorio, N. López, L. M. Rossi, *ACS Catal.* **2017**, *7*, 2973−2980.
[65] J. Llop Castelbou, E. Breso-Femenia, P. Blondeau, B. Chaudret, S. Castillon, C. Claver, C. Godard, *ChemCatChem* **2014**, *6*, 3160–3168.
[66] H.-y. Jiang, X.-x. Zheng, *Catal. Sci. Technol.,* **2015**, *5*, 3728–3734.
[67] I. Cano, A. M. Chapman, A. Urakawa, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2014**, *136*, 2520–2528.
[68] I. Cano, M. A. Huertos, A. M. Chapman, G. Buntkowsky, T. Gutmann, P. B. Groszewicz, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2015**, *137*, 7718–7727.
[69] N. Almora-Barrios, I. Cano, P. W. N. M. van Leeuwen, N. Lopez, *ACS Catal.* **2017**, *7*, 3949–3954.
[70] I. Cano, M. J.-L. Tschan, L. M. Martinez-Prieto, K. Philippot, B. Chaudret, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2016**, *6*, 3758–3766.
[71] I. Cano, L. M. Martinez-Prieto, B. Chaudret, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2017**, *23*, 1444–1450.
[72] I. Cano, L. M. Martinez-Prieto, P. F. Fazzini, Y. Coppel, B. Chaudret, P. W. N. M. van Leeuwen, *Phys. Chem. Chem. Phys.* **2017**, *19*, 21655–21662.
[73] A. Vasseur, R. Membrat, D. Gatineau, A. Tenaglia, D. Nuel, L. Giordano, *ChemCatChem* **2017**, *9*, 728–732.

[74] A. Vasseur, R. Membrat, D. Palpacelli, M. Giorgi, D. Nuel, L. Giordano, A. Martinez, *Chem. Commun.* **2018**, *54*, 10132–10135.
[75] T. Ghaffar, A. W. Parkins, *Tetrahedron Lett.* **1995**, *36*, 8657–8660.
[76] T. Ghaffar, A. W. Parkins, *J. Mol. Catal. A: Chem.* **2000,** *160*, 249–261.
[77] S. M. M. Knapp, T. J. Sherbow, T. J. Ahmed, I. Thiel, L. N. Zakharov, J. J. Juliette, D. R. Tyler, *J. Inorg. Organomet. Polym.* **2014**, *24*, 145–156.
[78] X.-b. Jiang, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *J. Org. Chem.* **2004**, *69*, 2327–2331.
[79] X. Xing, C. Xu, B. Chen, C. Li, S. C. Virgil, R. H. Grubbs, *J. Am. Chem. Soc.* **2018**, *140*, 17782−17789.
[80] H. Gulyàs, I. Rivilla, S. Curreli, Z. Freixa, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2015**, *5*, 3822–3828.
[81] S. M. M. Knapp, T. J. Sherbow, R. B. Yelle, J. J. Juliette, D. R. Tyler, *Organometallics* **2013**, *32*, 3744–3752.
[82] T. Smejkal, B. Breit, *Organometallics* **2007**, *26,* 2461–2464.
[83] T. J. Ahmed, S. M. M. Knapp, D. R. Tyler, *Coord. Chem. Rev.* **2011**, *255,* 949–974.
[84] E. Tomas-Mendivil, F. J. Suarez, J. Diez, V. Cadierno, *Chem. Commun.* **2014**, *50*, 9661–9664.
[85] T. J. Geldbach, D. Drago, P. S. Pregosin, *J. Organomet. Chem.* **2002**, *643–644*, 214–222.
[86] E. Tomas-Mendivil, L. Menendez-Rodriguez, J. Francos, P. Crochet, V. Cadierno, *RSC Adv.* **2014**, *4*, 63466–63474.
[87] E. Tomas-Mendivil, V. Cadierno, L. Menendez-Rodriguez, R. Lopez, *Chem. Eur. J.* **2015**, *21*, 16874–16886.
[88] R. González-Fernández, P. J. González-Liste, J. Borge, P. Crochet, V. Cadierno, *Catal. Sci. Technol.* **2016**, *6*, 4398–4409.
[89] R. González-Fernández, P. Crochet, V. Cadierno, M. I. Menéndez, R. López, *Chem. Eur. J.* **2017**, *23,* 15210–15221.
[90] L. E. Eijsink, S. C. P. Perdriau, J. G. de Vries, E. Otten, *Dalton Trans.* **2016**, *45*, 16033–16039.
[91] B. Guo, J. G. de Vries, E. Otten, *Chem. Sci.* **2019**, *10*, 10647–10652.
[92] R. B. Bedford, S. L. Hazelwood, M. E. Limmert, J. M. Brown, S. Ramdeehul, A. R. Cowley, S. J. Coles, M. B. Hursthouse, *Organometallics* **2003,** *22,* 1364–1371 and references therein.
[93] R. B. Bedford, S. L. Hazelwood (née Welch), M. E. Limmert, *Chem. Commun.* **2002**, 2610–2611.
[94] L. Ackermann, A. R. Kapdi, S. Fenner, C. Kornhaaß, C. Schulzke, *Chem. Eur. J.* **2011**, *17*, 2965–2971.
[95] H. Xu, K. Ekoue-Kovi, C. Wolf, *J. Org. Chem.* **2008**, *73*, 7638–7650.
[96] C. Wolf, R. Lerebours, *Org. Biomol. Chem.* **2004**, *2,* 2161–2164.
[97] C. Wolf, R. Lerebours, *Org. Lett.* **2004**, *6*, 1147–1150.
[98] *Modern arylation methods* (Ed.: L. Ackermann), Wiley-VCH, Weinheim, **2009**.
[99] P. Gandeepan, T. Mueller, D. Zell, G. Cera, S. Warratz, L. Ackermann, *Chem. Rev.* **2019**, *119*, 2192–2452.
[100] The peculiar role of carboxylates for palladium catalyzed reactions with aromatic C–H bonds and C–C bond formation was already recognized long before anything was known about the mechanisms: R. van Helden, G. Verberg, *Recl. Trav. Chim. Pays-Bas* **1965,** *84*, 1263–1273.
[101] K. Godula, B. Sezen, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 3648-3649.
[102] L. Ackermann, *Org. Lett.* **2005**, *7*, 3123–3125.
[103] L. Ackermann, R. Vicente, A. Althammer, *Org. Lett.* **2008**, *10*, 2299–2305.
[104] D. Zell, S. Warratz, D. Gelman, S. J. Garden, L. Ackermann, *Chem. Eur. J.* **2016,** *22,* 1248–1252.
[105] L. V. Graux, M. Giorgi, G. Buono, H. Clavier, *Dalton Trans.* **2016**, *45*, 6491–6502.
[106] B. Lastra-Barreira, J. Francos, P. Crochet, V. Cadierno, *Organometallics* **2018**, *37*, 3465–3474.
[107] R. Gonzalez-Fernandez, P. Crochet, V. Cadierno, *Organometallics* **2019**, *38,* 3696–3706.
[108] V. San Nacianceno, L. Ibarlucea, C. Mendicute-Fierro, A. Rodríguez-Diéguez, J. M. Seco, I. Zumeta, C. Ubide, M. A. Garralda, *Organometallics* **2014**, *33,* 6044–6052.
[109] Y.-X. Wang, M. Ye, *Sci. China: Chem.* **2018**, *61*, 1004–1013.
[110] P. A. Donets, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 11772–11775.
[111] A. Yada, S. Ebata, H. Idei, D. Zhang, Y. Nakao, T. Hiyama, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1170–1184.
[112] Y.-X. Wang, S.-L. Qi, Y.-X. Luan, X.-W. Han, S. Wang, H. Chen, M. Ye, *J. Am. Chem. Soc.* **2018**, *140*, 5360–5364.
[113] R. Lhermet, E. Moser, E. Jeanneau, H. Olivier-Bourbigou, P.-A. R. Breuil, *Chem. Eur. J.* **2017**, *23*, 7433–7437.

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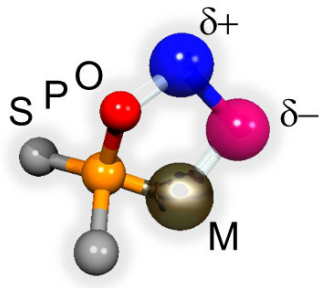

The participation in catalysis of the unit M–PR_2–O as part of coordination complexes and metal nanoparticles is highlighted. The enforced separation of the soft metal Lewis acid and the hard oxygen base shows exciting reactivities towards various substrates in catalysis, often reminiscent of other bifunctional catalysts. In this mini-review one can read more about this simple metal-ligand combination with such a rich catalytic performance, yet leaving space for many new developments.