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Lithium Salts of 2,4,6-Triaryl-λ⁴-phosphinine Anions – A Comparison Study

CLUSTER ISSUE

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Dedicated to Professor Dr. Lothar Weber on the occasion of his 70th birthday

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The λ³-phosphinine derivatives 2,6-diphenyl-4-(*p*-tolyl)phosphinine and 2-(2′-pyridyl)-4,6-diphenylphosphinine were quantitatively converted into the corresponding λ⁴-phosphinine anions by reaction with phenyllithium. Systematic hydrolysis experiments with H_2O and MeOH show that a subtle interplay between the pK_a values of the generated 1,2-dihydrophosphinine derivatives and the pK_b value of the formed bases, LiOH and $LiOCH_3$, respectively, leads either to the kinetic or thermodynamic product. The coordination chemistry of the λ⁴-phosphinine anions towards Rh^I was further investigated, and the anions based on 2,6-diphenyl-4-(*p*-tolyl)-phosphinine and 2-(2′-pyridyl)-4,6-diphenylphosphinine demonstrate different coordination modes. Whereas the former coordinates in an η⁵ fashion towards the Rh^I atom, the latter acts as a bidentate chelating ligand with an η¹ coordination to the metal center through the phosphorus lone pair.

Introduction

It is well established that the reactivities of pyridine (**A**) and λ³-phosphinine (**B**) are completely opposed as a result of the significant difference in charge distribution in these heterocycles (Figure 1).[1] This effect is due to the lower electronegativity of phosphorus in comparison to those of carbon and nitrogen (Pauling electronegativities: 2.2 for P, 2.5 for C, and 3.0 for N).[2] As a consequence, phosphinines react with organolithium reagents at the electrophilic phosphorus atom to form the corresponding 1-*R* phosphacyclohexadienyl anions, as demonstrated by Märkl and Ashe III (Figure 1).[3,4] For simplicity, these salts are usually defined as species that contain a λ⁴σ³-phosphinine anion (**C**), although they are better described as classical tertiary λ³σ³-phosphanes with a pseudo-ylidic structure (**D**) on the basis of crystallographic data (vide infra).

The coordination chemistry of these interesting λ⁴-phosphinine anions has been studied mainly by Le Floch et al.[5] The ambidentate nature of such anionic ligands allows coordination to a metal center either through the anionic π system (η⁵) or through the lone pair (η¹) of the phosphorus atom. Depending on the substitution pattern at the heterocycle, different coordination modes can thus be adopted. In the absence of additional donor groups, the λ⁴-phosphinine anions coordinate preferentially in an η⁵-fashion (**E**), whereas donor-functionalized 1-*R* phosphacyclohexadienyl anions coordinate through the phosphorus lone pair (**F**).

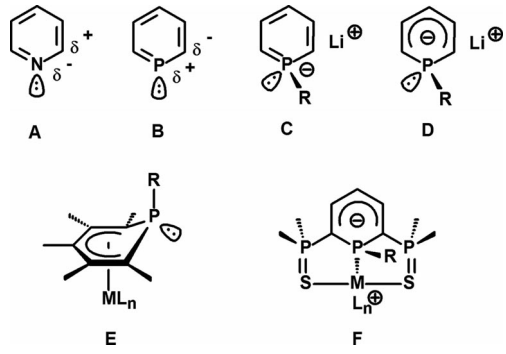

Figure 1. Comparison between pyridine and phosphinine and the coordination modes of anionic λ⁴-phosphinine anions.

We have recently studied in detail the synthesis and coordination chemistry of chiral as well as functionalized 2,4,6-triarylphosphinine derivatives, including phosphorus analogues of 2,2′-bipyridine and terpyridine.[6] Although the reaction of 2,4,6-triphenylphosphinine with organolithium reagents is well documented, the coordination chemistry of 2,4,6-triphenyl-λ⁴-phosphinine anions has hardly been studied, and the few investigated complexes have only been characterized spectroscopically.[3c,5a] We report here on the reaction of 2,6-diphenyl-4-(*p*-tolyl)-phosphinine (**1**) and the structurally related 2-(2′-pyridyl)-4,6-diphenylphosphinine

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(**2**), which are derivatives of 2,4,6-triphenyl-λ^3-phosphinine, with phenyllithium. Moreover, we describe the reactivity of the corresponding lithium salts and the coordination chemistry of the generated 2,4,6-triaryl-λ^4-phosphinine anions towards Rh^I (Figure 2).

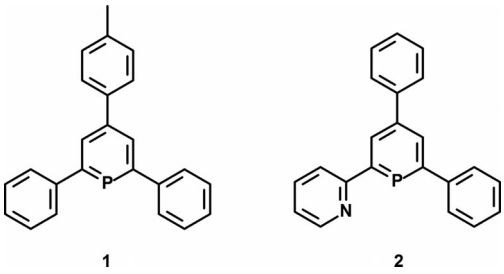
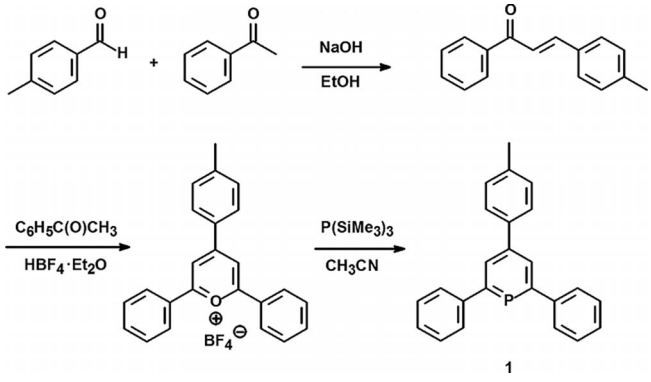


Figure 2. 2,4,6-Triphenylphosphinine derivatives **1** and **2**.

Results and Discussion

During the course of our investigations on functionalized 2,4,6-triaryl-λ^3-phosphinines, we noticed that the unsubstituted 2,4,6-triphenylphosphinine and its coordination compounds are generally difficult to crystallize and consequently difficult to characterize crystallographically. To circumvent this problem, we decided to introduce a $-CH_3$ group in the *para* position of the 4-phenyl group at the phosphorus heterocycle. Compound **1** was obtained in a straightforward manner from *p*-methylbenzaldehyde according to Scheme 1. The new phosphinine was characterized by ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance at δ = 182.6 ppm. In the ^1H NMR spectrum, a doublet at δ = 8.24 ppm ($^3J_{H,P}$ = 5.6 Hz) is observed and is characteristic of the two heteroaromatic protons coupling to the phosphorus atom.



Scheme 1. Synthesis of the 2,4,6-triphenylphosphinine derivative **1**.

Colorless crystals of **1** suitable for X-ray diffraction could be obtained by slow crystallization from acetonitrile. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with four independent molecules in the asymmetric unit. The molecular structure is depicted in Figure 3 along with selected bond lengths and angles.

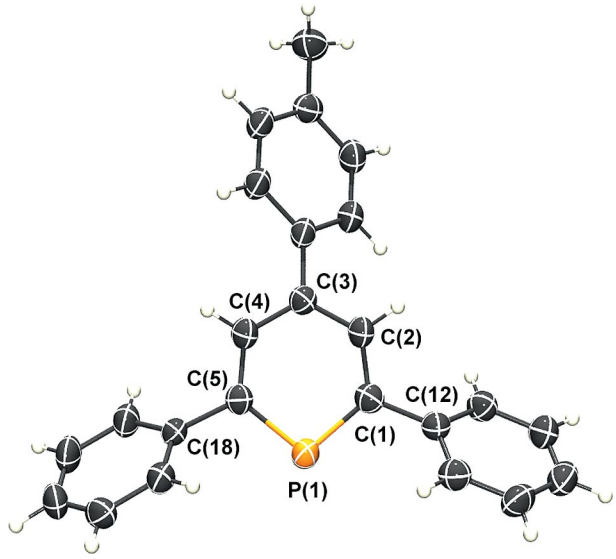
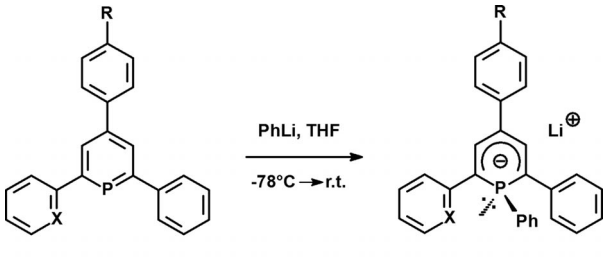


Figure 3. Molecular crystal structure of **1**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.757(3), P(1)–C(5) 1.743(3), C(1)–C(2) 1.391(4), C(2)–C(3) 1.407(4), C(3)–C(4) 1.393(4), C(4)–C(5) 1.384(4), C(1)–C(12) 1.491(4), C(5)–C(18) 1.483(4), C(1)–P(1)–C(5) 101.09(14).

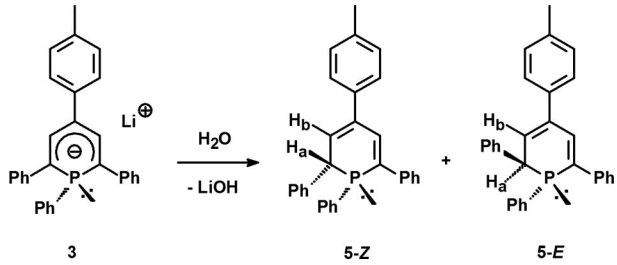
Figure 3 shows one of the very few crystallographically characterized 2,4,6-triarylphosphinine derivatives reported to date. The P heterocycle is essentially planar owing to the aromatic character of the phosphinine ring. The P–C bond lengths are 1.757(3) and 1.743(3) Å, respectively, and the C–P–C angle is 101.09(14)°. The P–C bond lengths thus lie between those of a P–C single bond (PPh_3 1.83 Å[7]) and a P–C double bond [(diphenylmethylene)(mesityl)phosphine, $MesP{=}CPh_2$ 1.704 Å[8]]. As expected for an aromatic system, there is no bond alternation in the carbocyclic part, and the C–C bond lengths are between 1.384(4) and 1.407(4) Å. The tolyl substituent at the *para* position as well as the phenyl groups at the 2- and 6-positions are slightly rotated out of the plane with respect to the phosphorus heterocycle.

The pyridyl-functionalized phosphinine **2** was prepared as recently reported by us.[6a] As anticipated, the $\lambda^3\sigma^2$-phosphinines **1** and **2** can easily be converted into the corresponding $\lambda^4\sigma^3$-phosphinine species **3** and **4** by reaction with stoichiometric amounts of PhLi in tetrahydrofuran (THF) at –78 °C (Scheme 2). Upon addition of the organolithium compound, the solutions change from yellow to dark green and blue, respectively.

Moreover, a large variation in the chemical shifts is observed by $^{31}P\{^1H\}$ NMR spectroscopy between the neutral phosphinines [δ = 182.6 ppm (**1**); δ = 187.4 ppm (**2**)] and the anionic forms [δ = –54.9 ppm (**3**); δ = –58.6 ppm (**4**)]; this indicates that the aromaticity of the ring has been substantially disrupted owing to the presence of a rather basic phosphorus center with a formal sp^3 hybridization (PMe_3: $^{31}P\{^1H\}$ NMR, δ = –60 ppm). Le Floch et al. have isolated and crystallographically characterized lithium salts of λ^4-phosphinine anions and shown that the lithium cation is



Scheme 2. Reactions of **1** and **2** to form the corresponding λ^4-phosphinine anions.



Scheme 3. Reaction of the λ^4-phosphinine anion **3** with H_2O. Enantiomers are not shown.

coordinated in an η^5 fashion and that the phosphorus atom is strongly pyramidalized and points out of the plane defined by the five carbon atoms of the heterocycle.[5c] Taking these findings into consideration, the nucleophilic attack of the organolithium reagent should in principal lead to two different stereoisomers, as depicted in Figure 4.

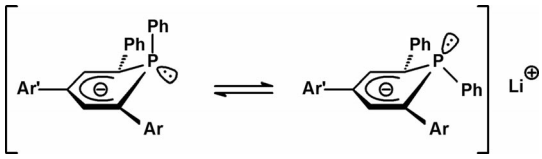


Figure 4. Possible configurations of λ^4-phosphinine anions.

However, it is interesting to note that we found only one sharp signal in the $^{31}P\{^1H\}$ NMR spectra of the 1-*R* phosphahexadienyl salts **3** and **4**, even when the spectra were recorded at –70 °C. Apparently, only one isomer is present in solution, as the barrier for inversion is expected to be high for such trivalent σ^3-coordinated phosphorus species, although the interconversion might be facilitated by an aromatically stabilized $\lambda^4\sigma^3$-intermediate.

As demonstrated before by Märkl and Ashe III, the reaction of λ^4-phosphinine anions with H_2O quantitatively and selectively leads to the corresponding 1,2-dihydrophosphinine derivatives.[3d] For 2,4,6-triphenyl-substituted phosphinines such as **3**, the formation of four stereoisomers is consequently expected upon protonation, as a stereogenic center forms at both the phosphorus atom and the carbon atom at the 2-position of the heterocycle. This leads to the presence of the two diastereomeric pairs of enantiomers **5**-*E* and **5**-*Z*, depending on the relative location of the phenyl groups at the 1- and 2-positions with respect to one another (Scheme 3).

On the basis of the sharp melting points of the reaction products formed by protonation of the 2,4,6-triphenyl-λ^4-phosphinine anion with H_2O, it was assumed that only one pair of enantiomers formed predominantly, although the exact nature of the hydrolysis product(s) remained elusive.[3d]

As the hydrogen atoms H_a and H_b (Scheme 3) usually give very characteristic signals in the ^1H NMR spectrum, whereas diastereomers should also be distinguishable by $^{31}P\{^1H\}$ NMR spectroscopy, we also analyzed the protonation of **3** and **4** with H_2O by NMR spectroscopy. Interestingly, the reaction of **3** with H_2O in [D_8]THF leads indeed to the formation of a main product (94% based on integration) with a signal at δ = –50.8 ppm ($^{31}P\{^1H\}$ NMR), whereas a minor species (6%) is detected at δ = –38.0 ppm (Figure 5, a).

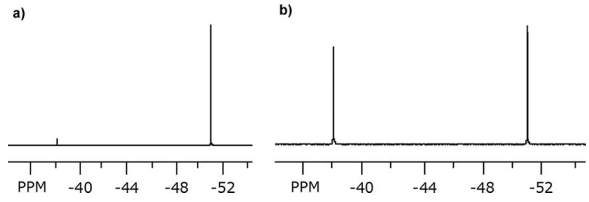


Figure 5. $^{31}P\{^1H\}$ NMR spectra of **5**-*E*/*Z* in [D_8]THF, generated from the hydrolysis of **3** with (**a**) H_2O and (**b**) MeOH.

In the ^1H NMR spectrum of the hydrolysis products (see Figure 5, a), traces of the minor compound can also be next to the characteristic signal of the proton H_b at δ = 5.97 ppm and the proton H_a at δ = 4.23 ppm (Figure 6). An assignment of the exact configuration (*E* or *Z*) of **5** on basis of the size of the coupling constants appeared, however, to be problematic.

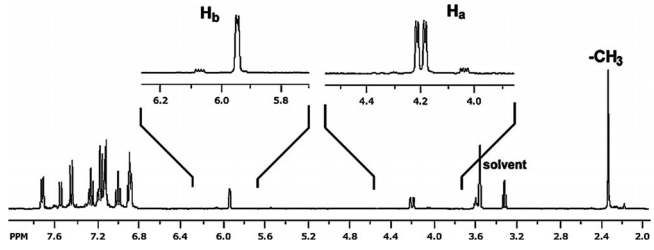


Figure 6. ^1H NMR spectrum of **5**-*E*/*Z* in [D_8]THF.

Therefore, we attempted a crystallographic characterization of the main product. Single crystals of the neutral hydrolysis product, suitable for X-ray diffraction, could indeed be obtained from the main product (as verified by $^{31}P\{^1H\}$ NMR spectroscopy) by slow crystallization from acetonitrile, and the molecular structure is depicted in Figure 7 along with selected bond length and angles.

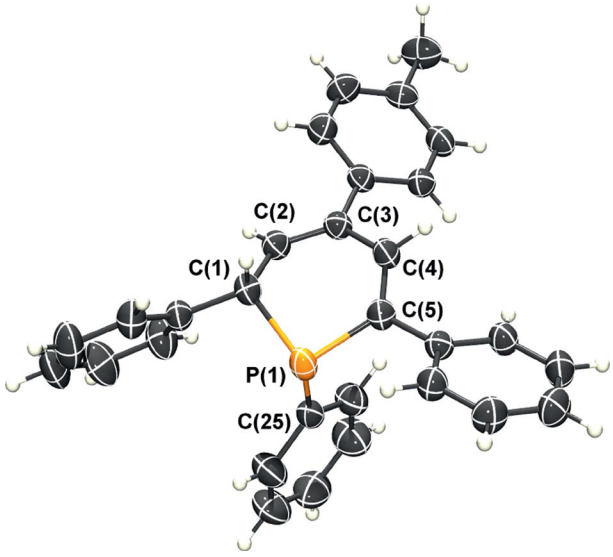


Figure 7. Molecular crystal structure of **5**-*Z*. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.873(2), P(1)–C(5) 1.827(2), C(1)–C(2) 1.497(2), C(2)–C(3) 1.339(2), C(3)–C(4) 1.469(2), C(4)–C(5) 1.343(2), P(1)–C(25) 1.825(2), C(1)–P(1)–C(5) 97.46(8).

The crystallographic characterization reveals that the main product, which is formed by hydrolysis of **3** with H_2O, has the *Z* configuration. The molecular structure of the 1,2-dihydrophosphinine derivative **5**-*Z* can be compared with that of the λ^3-phosphinine **1**. The P–C distances of 1.873(2), 1.827(2), and 1.825(2) Å are much longer than those in **1**, and the phosphorus atom is strongly pyramidalized (Σ_{angles} = 304.5°), as expected for a formally sp^3-hybridized phosphorus atom. Consequently, the C–C bond lengths are consistent with the presence of a C–C single bond [C(1)–C(2)] and a conjugated diene with double bonds between C(2) and C(3) and C(4) and C(5). Therefore, we could identify for the first time the exact nature of the hydrolysis products of the anions derived from λ^4-2,4,6-triphenylphosphinine, and this allows the assignment of the signals observed in the $^{31}P\{^1H\}$ NMR spectra (Figures 5 and 6).

On the other hand, the reaction of the pyridyl-functionalized λ^4-phosphinine anion **4** with H_2O to form the hydrolysis product **6** is more complicated. In addition to protonation of the carbon atom at the 2-position of the heterocycle, the protonation at the carbon atom at the 6-position should also be expected (Figure 8).

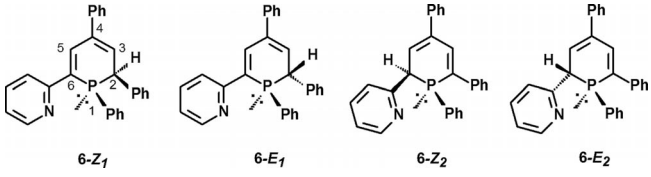


Figure 8. Possible hydrolysis products of **4**. Enantiomers are not shown.

Indeed, the reaction of **4** with H_2O in THF is much less selective than the reaction of **3** with H_2O. Four signals are detected in the $^{31}P\{^1H\}$ NMR spectrum at δ = –40.9 (1.2% by integration), –43.4 (28.9%), –49.6 (32.7%), and –52.6 ppm (37.2%; Figure 9, a). By comparing the chemical shift and intensity of the signals of these data with those obtained for **5**-*E*/*Z* (Figure 5, a), we propose that the resonances at δ = –40.9 and –49.6 ppm correspond to **6**-E_1/Z_1, generated by protonation of the carbon atom at the 2-position (Figure 8). By comparison of the $^{31}P\{^1H\}$ NMR spectroscopic data and the crystallographic results for **5**-*Z* described above, the signal at δ = –49.6 ppm most likely corresponds to the isomer **6**-Z_1, whereas the signal at δ = –40.9 ppm can be assigned to the **6**-E_1 isomer, although no exact proof can be provided here. The signals at δ = –43.4 and –52.6 ppm consequently belong to **6**-E_2/Z_2, generated from the protonation of the carbon atom at the 6-position, which is next to the pyridine ring (Figure 9, a). If these assumptions are correct, the protonation at the carbon atom next to the pyridine ring is much less selective than the protonation of the carbon atom at the 2-position of the heterocycle, as **6**-E_2/Z_2 are formed in a ratio of approximately 40:60, in contrast to **6**-E_1/Z_1, which are formed in a ratio of 4:96 (Figure 9, a), similar to the situation observed for **5**-*E*/*Z* in the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 5.

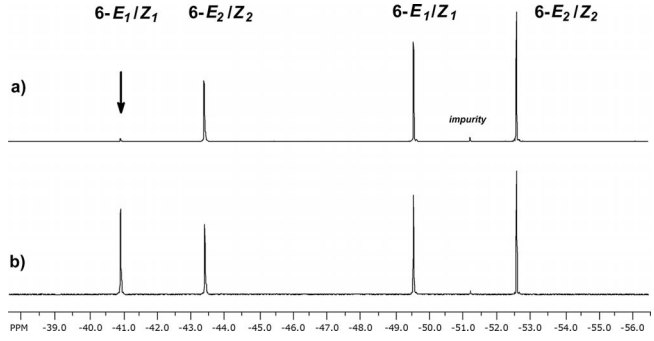


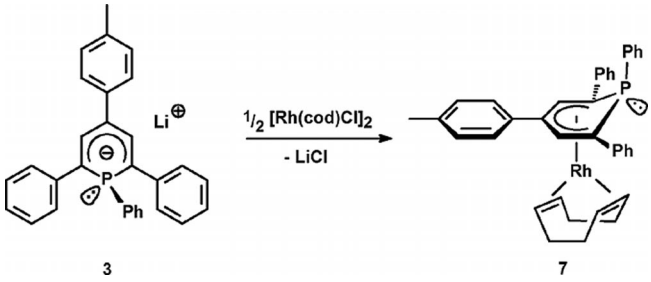
Figure 9. $^{31}P\{^1H\}$ NMR spectra of the species formed by protonation of the λ^4-phosphinine anion **4** with (**a**) H_2O or (**b**) MeOH.

As LiOH is formed upon protonation of the λ^4-phosphinine anion with H_2O, this difference in reactivity and selectivity might be attributed to a small, but significant, difference in the pK_a values of **5**-*E*/*Z* and **6**-$E_1/Z_1/E_2/Z_2$, as the protonation at the 2- or 6-position is reversible.

As $LiOCH_3$ is a slightly stronger base than LiOH, we decided to quench solutions of **3** and **4** with MeOH to form the corresponding 1,2-dihydrophosphinines and $LiOCH_3$. Interestingly, the protonation of the λ^4-phosphinine anions **3** and **4** with methanol leads indeed to a dramatic change in selectivity. The relative amounts of **5**-*E*/*Z*, after quenching **3** with MeOH, change from 6:94 to approximately 50:50 (based on the integrals in the $^{31}P\{^1H\}$ NMR spectra shown in Figure 5, b). On the other hand, the product composition observed when **4** is quenched with methanol changes significantly only for the species that were formally assigned as **6**-E_1/Z_1 and generated from the protonation of the carbon atom at the 2-position (Figure 8). Despite the presence of the pyridyl group at the 6-position, **6**-E_1/Z_1 is very similar to **5**-*E*/*Z* and should consequently result in similar NMR spectroscopic data (Scheme 3, Figure 5). Indeed, the ratio

again changes from 6:94 to approximately 50:50, whereas the ratio of the formally assigned **6**-E_2/Z_2 species remains unchanged at 40:60 (Figure 9, b). These results nicely indicate that the assignment according to Figure 8 is most likely correct. Moreover, they show that the quenching of solutions of λ^4-phosphinine anions is more complex than previously assumed and that there is a subtle interplay between the pK_a values of the generated 1,2-dihydrophosphinine species and the pK_b values of the formed bases. Although quenching of the Li salts with H_2O leads preferentially to the kinetic product (**5**-*Z* in the case of **3**), the presence of the stronger base $LiOCH_3$ clearly leads ultimately to the thermodynamic product **5**-*E*. It can also be concluded that the 1,2-dihydrophosphinine **6**-E_2/Z_2 is apparently slightly more acidic than the 1,2-dihydrophosphinine **6**-E_1/Z_1, as the thermodynamic equilibrium is already reached with LiOH as a base.

After the investigation of the reactivity of **3** and **4** towards H_2O and MeOH, we became interested in the coordination chemistry of the λ^4-phosphinine anions towards Rh^I. The reaction of **3** with 0.5 equiv. of the rhodium(I) dimer $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) leads quantitatively to the new species **7**, which shows a doublet in the $^{31}P\{^1H\}$ NMR spectrum at δ = –58.6 ppm. The small $J_{P,Rh}$ coupling constant of 11.1 Hz is indicative of η^5 coordination of the phosphorus heterocycle to the metal center, as an η^1 coordination through the phosphorus lone pair should result in a much larger coupling constant (Scheme 4).[1e,5d] It is interesting to note, again from the $^{31}P\{^1H\}$ NMR spectroscopic data, that only one isomer of the Rh^I complex has been formed, as the lone pair could in principle be oriented either in an axial or equatorial position of the heterocycle.



Scheme 4. Reaction of **3** with the Rh^I complex $[Rh(cod)Cl]_2$.

After removal of LiCl, crystals of **7** suitable for X-ray diffraction could be obtained after recrystallization from diethyl ether. Figure 10 shows the molecular crystal structure of **7**, along with selected bond lengths, distances, and angles. The graphical representation of **7** indeed confirms that the phosphorus heterocycle coordinates in an η^5 fashion to the Rh^I atom with the phenyl group in axial position. The phosphorus atom is clearly located above the plane of the five carbon atoms (Figure 10, b) and is strongly pyramidalized, as expected for a formally sp^3-hybridized phosphorus atom (Σ_{angles} = 301.4°). A comparison can also be

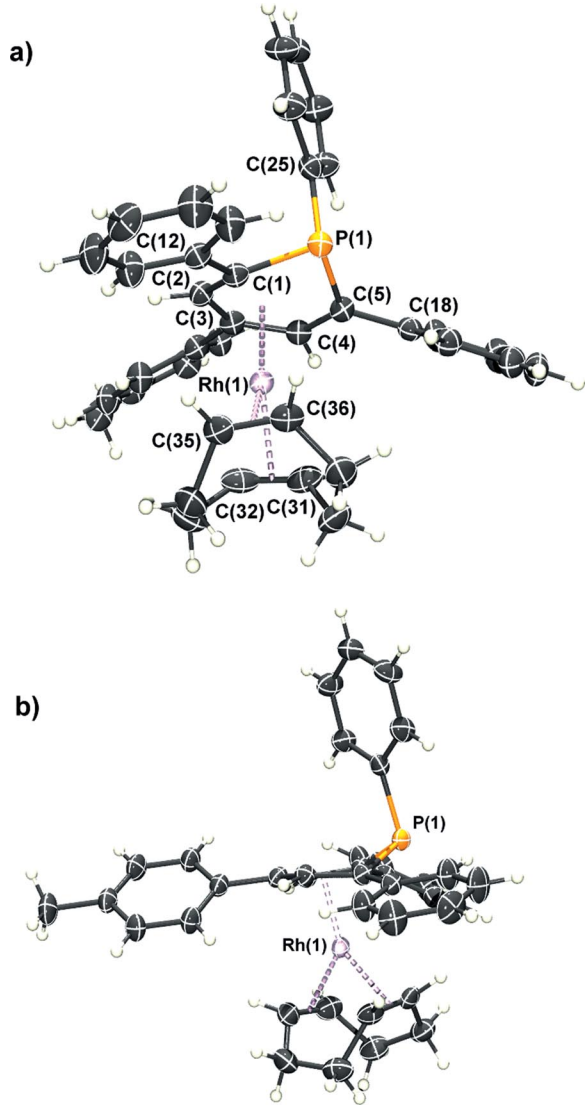
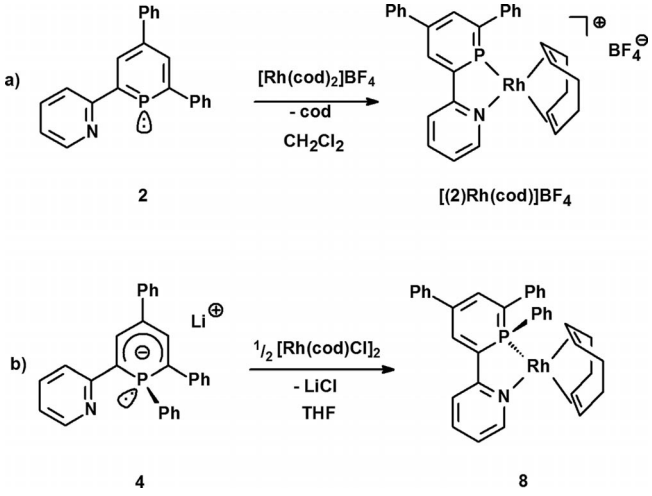


Figure 10. Molecular crystal structure of **7**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å], distances [Å], and angles [°]: P(1)–C(1) 1.842(3), P(1)–C(5) 1.822(3), C(1)–C(2) 1.434(3), C(2)–C(3) 1.409(3), C(3)–C(4) 1.440(4), C(4)–C(5) 1.392(4), P(1)–C(25) 1.848(3), C(1)–C(12) 1.499(3), C(5)–C(18) 1.493(4), Rh(1)–C(31) 2.164(3), Rh(1)–C(32) 2.159(3), Rh(1)–C(35) 2.115(3), Rh(1)–C(36) 2.114(3), C(1)–P(1)–C(5) 94.70(11).

made between the bond lengths in the complexed anionic λ^4-phosphinine **3** in compound **7**, and the structurally related neutral λ^3-phosphinine **1** (see Figure 3). The C–C bond lengths in the carbocyclic part of **1** as well as in the coordination compound **7** are very similar with 1.384(4)–1.407(4) Å in (**1**) and 1.392(4)–1.440(4) Å in (**7**). On the other hand, significant lengthening of the P(1)–C(1) and the P(1)–C(5) bonds is observed in **7**. The corresponding values increase from the neutral λ^3-phosphinine [P(1)–C(1) 1.757(3), P(1)–C(5) 1.743(3) Å] to the complexed anionic λ^4-phosphinine [P(1)–C(1) 1.842(3), P(1)–C(5) 1.822(3) Å] and reflect the transition of a C(sp^2)–P(sp^2) to a C(sp^2)–P(sp^3) system upon reaction with PhLi and subsequent co-

ordination. It should be mentioned here that a few related Rh^I complexes containing substituted η^5-coordinated λ^4-phosphinines anions have been structurally characterized by Le Floch et al.[5d]

We were further interested in the coordination chemistry of the pyridyl-functionalized λ^4-phosphinine anion **4** towards the Rh^I precursor $[Rh(cod)Cl]_2$, as we recently reported on the reaction of the neutral pyridyl-functionalized phosphinine **2** (Figure 1) with $[Rh(cod)_2]BF_4$ to form the cationic Rh^I complex $[(\mathbf{2})Rh(cod)]BF_4$. In this case, the P,N-hybrid ligand coordinates in a bidentate chelating fashion to the metal center (Scheme 5, a).[1e]



Scheme 5. Comparison between the neutral P,N-hybrid ligand **2** and the corresponding λ^4-phosphinine anion **4** with respect to its coordination chemistry towards Rh^I.

Inspired by these results, we wondered whether a related neutral Rh^I complex could be formed by reaction of **4** with the abovementioned Rh^I dimer $[Rh(cod)Cl]_2$. The addition of a solution of **4** in THF to 0.5 equiv. of $[Rh(cod)Cl]_2$ indeed leads instantaneously to the new species **8**, which shows a single doublet at δ = 13.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum with a $J_{P,Rh}$ coupling constant of 152.2 Hz. This value is typical for phosphinine–Rh^I complexes, in which the ligand is bound in an η^1 fashion through the phosphorus lone pair to the metal center. It should be noted here that the $^1J_{P,Rh}$ coupling constant in $[(\mathbf{2})Rh(cod)]BF_4$ has a value of 188.6 Hz. Moreover, the typical signals for cod-containing metal complexes could be detected in the ^1H NMR spectrum of **8**. These results are in agreement with previous findings that donor-functionalized λ^4-phosphinine anions preferentially coordinate through the phosphorus lone pair in an η^1 fashion towards a metal center (Figure 1).[5d] However, we were so far unable to confirm the exact nature of **8** by single-crystal X-ray diffraction. Nevertheless, the NMR spectroscopic data are quite evident that the proposed schematic structure of **8**, in which the phosphinine derivatives acts as a bidentate ligand, is correct.

Conclusions

We have presented a detailed comparison study between 2,6-diphenyl-4-(*p*-tolyl)phosphinine and the structurally related 2-(2′-pyridyl)-4,6-diphenylphosphinine and could demonstrate that the neutral 2,4,6-triphenyl-λ^3-phosphinine derivatives can quantitatively be converted into the corresponding λ^4-phosphinine anions by reaction with phenyllithium. The lithium salts are very sensitive towards hydrolysis, which leads to the corresponding 1,2-dihydrophosphinine derivatives. The systematic protonation of the λ^4-phosphinine anions with either H_2O and MeOH showed that there is a subtle interplay between the pK_a values of the generated 1,2-dihydrophosphinines and the pK_b value of the base formed LiOH or LiOMe; this leads either to the kinetic or thermodynamic hydrolysis product as confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. For hydrolysis of the λ^4-2,6-diphenyl-4-(*p*-tolyl)phosphinine anion, the main product could be characterized crystallographically, and the *Z* isomer was revealed as the major species and kinetic product. We could further show that the phosphinine derivatives differ in their coordination chemistry towards Rh^I, as different coordination modes were observed for the anions based on 2,6-diphenyl-4-(*p*-tolyl)phosphinine and the donor-functionalized 2-(2′-pyridyl)-4,6-diphenylphosphinine. Whereas the former one coordinates in an η^5 fashion towards the Rh^I atom, the latter one acts as a bidentate, chelating ligand with an η^1 coordination through the phosphorus lone pair to the metal center.

Experimental Section

General: All reactions were performed under argon by using Schlenk techniques. All glassware was dried prior to use. Dry solvents were prepared by using custom-made solvent purification columns filled with Al_2O_3 from Braun Solvent systems. THF was distilled under argon from potassium/benzophenone prior to use. All common solvents and chemicals were commercially available. NMR spectra were recorded with a JEOL LAMBADA 400 NMR Spectrometer (^1H NMR 399.74 MHz, $^{13}C\{^1H\}$ NMR 100.51 MHz, $^{31}P\{^1H\}$ NMR 161.82 MHz); the ^{13}C and ^{31}P spectra were ^1H decoupled. The ^1H and ^{13}C chemical shifts are given relative to tetramethylsilane (TMS), and the residual solvent peaks were used as the reference signal; the ^{31}P chemical shifts are referenced to an 85% aqueous solution of H_3PO_4. Compound **2** was prepared according to literature procedures.[6a]

2,6-Diphenyl-4-(*p*-tolyl)-λ^3-phosphinine (1): Compound **1** was synthesized according to the pyrylium salt route from acetophenone and *p*-methylbenzaldehyde.[6a] The obtained pyrylium salt (3.00 g, 7.31 mmol) was dissolved in acetonitrile (20 mL), and tris(trimethylsilyl)phosphine (4.26 mL, 14.6 mmol) was added dropwise. The resulting dark red reaction mixture was heated under reflux for six hours and then cooled to room temperature. After removal of the solvent under high vacuum, the residue was purified by flash column chromatography under inert conditions (SiO_2, petroleum ether/ethyl acetate 1:0, 19:1). After removal of the solvent under high vacuum, a pale yellow solid was obtained (1.70 g, 5.02 mmol, 69%). ^1H NMR (399.74 MHz, [D$_8$]THF, 25 °C): δ = 2.39 (s, 3 H, CH_3), 7.31 (d, $J_{H,H}$ = 8.4 Hz, 2 H, H_{ar}), 7.38 (t, $J_{H,H}$ = 6.8 Hz, 2 H, H_{ar}), 7.46 (t, $J_{H,H}$ = 7.7 Hz, 4 H, H_{ar}), 7.69 (d, $J_{H,H}$ = 8.1 Hz,

2 H, H_{ar}), 7.76 (d, $J_{H,H}$ = 7.1 Hz, 4 H, H_{ar}), 8.24 (d, $J_{P,H}$ = 5.6 Hz, 2 H, H_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.51 MHz, [D$_8$]THF, 25 °C): δ = 21.3 (s), 128.6 (d, $J_{C,P}$ = 1.7 Hz), 128.6 (d, $J_{C,P}$ = 12.7 Hz), 128.9 (d, $J_{C,P}$ = 1.9 Hz), 129.8 (s), 130.6 (s), 132.4 (d, $J_{C,P}$ = 12.2 Hz), 138.9 (d, $J_{C,P}$ = 0.9 Hz), 140.3 (d, $J_{C,P}$ = 3.3 Hz), 144.7 (d, $J_{C,P}$ = 24.3 Hz), 145.3 (d, $J_{C,P}$ = 13.7 Hz), 173.1 (d, $J_{C,P}$ = 51.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = 182.6 (s) ppm.

1,2,6-Triphenyl-4-(*p*-tolyl)cyclophosphahexadienyllithium (3): Phosphinine **1** (30.4 mg, 0.09 mmol) was dissolved in THF (2 mL), and the solution was cooled to –78 °C. Phenyllithium (1.8 M in OBu$_2$, 0.05 mL, 0.09 mmol) was added and the obtained dark green mixture was warmed to room temperature. The solvent was removed under vacuum, and a red viscous oil was obtained. This oil led again to a dark green solution when it was dissolved. The product was quantitatively formed according to ^{31}P NMR spectroscopy. ^1H NMR (399.74 MHz, [D$_8$]THF, 25 °C): δ = 2.18 (s, 3 H, CH_3), 6.64 (tt, $J_{H,H}$ = 7.2, 1.1 Hz, 2 H, H_{ar}), 6.74–6.79 (m, 1 H, H_{ar}), 6.80–6.88 (m, 4 H, H_{ar}), 7.02 (t, $J_{H,H}$ = 7.7 Hz, 4 H, H_{ar}), 7.19–7.26 (m, 3 H, H_{ar}), 7.28–7.33 (m, 1 H, H_{ar}), 7.59 (d, $J_{H,H}$ = 7.0 Hz, 2 H, H_{ar}), 7.74–7.81 (m, 4 H, H_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.51 MHz, [D$_8$]THF, 25 °C): δ = 21.1 (s), 98.5 (d, $J_{C,P}$ = 6.5 Hz), 113.7 (s), 120.1 (s), 122.7 (s), 124.7 (d, $J_{C,P}$ = 18.8 Hz), 125.2 (s), 127.1 (d, $J_{C,P}$ = 2.9 Hz), 128.3 (s), 128.4 (d, $J_{C,P}$ = 8.6 Hz), 129.2 (s), 131.0 (d, $J_{C,P}$ = 2.9 Hz), 131.1 (d, $J_{C,P}$ = 6.8 Hz), 144.7 (s), 149.5 (d, $J_{C,P}$ = 30.6 Hz), 152.5 (d, $J_{C,P}$ = 37.4 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = –54.9 (s) ppm.

1,4,6-Triphenyl-2-(2-pyridyl)-cyclophosphahexadienyllithium (4): Phosphinine **2** (29.5 mg, 0.09 mmol) was dissolved in THF (2 mL), and the solution was cooled to –78 °C. Phenyllithium (1.8 M in OBu$_2$, 0.05 mL, 0.09 mmol) was added, and the obtained deep blue mixture was warmed to room temperature. The solvent was removed, and a red sticky solid was obtained. This oil led again to a dark blue solution when it was dissolved. The product was quantitatively formed according to ^{31}P NMR spectroscopy. ^1H NMR (399.74 MHz, [D$_8$]THF, 25 °C): δ = 6.82–6.75 (m, 2 H, H_{ar}), 6.96–6.88 (m, 4 H, H_{ar}), 7.05 (t, $J_{H,H}$ = 8 Hz, 2 H, H_{ar}), 7.24–7.14 (m, 4 H, H_{ar}), 7.33–7.31 (m, 2 H, H_{ar}), 7.51 (d, $J_{H,H}$ = 8 Hz, 1 H, H_{ar}), 7.72–7.63 (m, 4 H, H_{ar}), 7.85–7.83 (m, 2 H, H_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.51 MHz, [D$_8$]THF, 25 °C): δ = 90.6 (d, $J_{C,P}$ = 23.4 Hz), 103.7 (d, $J_{C,P}$ = 23.4 Hz), 112.3 (d, $J_{C,P}$ = 1.0 Hz), 116.7 (d, $J_{C,P}$ = 8.1 Hz), 117.3 (d, $J_{C,P}$ = 3.0 Hz), 121.4 (s), 122.3 (d, $J_{C,P}$ = 1.2 Hz), 123.2 (s), 123.8 (s), 124.8 (d, $J_{C,P}$ = 15.2 Hz), 125.6 (s), 126.7 (d, $J_{C,P}$ = 5.1 Hz), 127.5 (s), 127.5 (d, $J_{C,P}$ = 1.0 Hz), 128.0 (s), 129.3 (d, $J_{C,P}$ = 15.2 Hz), 130.9 (d, $J_{C,P}$ = 15.2 Hz), 133.4 (d, $J_{C,P}$ = 2.0 Hz), 133.8 (s), 135.5 (d, $J_{C,P}$ = 2.0 Hz), 143.0 (s), 145.2 (s), 145.9 (s), 146.1 (s), 146.1 (s), 146.2 (s), 146.8 (d, $J_{C,P}$ = 2.0 Hz), 166.0 (d, $J_{C,P}$ = 25.4 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = –58.6 (s) ppm.

1,2,6-Triphenyl-4-(*p*-tolyl)-1,2-dihydrophosphinine (5): Compound **3** (14.6 mg, 0.045 mmol) was redissolved in THF, and water or methanol (0.045 mmol) was added. The solvent was removed, and a pale red powder was obtained. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = –38.0 (s, *E* isomer), –50.8 (s, *Z* isomer) ppm.

1,4,6-Triphenyl-2-(2-pyridyl)-1,2-dihydrophosphinine (6): Compound **4** (14.6 mg, 0.045 mmol) was redissolved in THF, and water or methanol (0.045 mmol) was added. The solvent was removed, and a dark red powder was obtained. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = –40.9, –43.4, –49.6, –52.6 ppm.

[(cod)Rh(η^5-3)] (7): A THF solution of **1** (60.9 mg, 0.18 mmol) and [Rh(cod)Cl]$_2$ (44.4 mg, 0.09 mmol) was cooled to –78 °C, and phenyllithium was added dropwise (0.05 mL, 0.09 mmol). The mixture was warmed to room temperature, and the solvent was evaporated under vacuum. Dichloromethane was added, and the solution was filtered through Celite. The solvent was removed under vacuum, and a dark red powder was obtained. The product was quantitatively formed according to ^{31}P NMR spectroscopy. Crystals suitable for X-ray diffraction were obtained after several days by recrystallization from ether. ^1H NMR (399.74 MHz, [D$_8$]THF, 25 °C): δ = 1.77–1.87 (m, 4 H, H_{cod}), 1.90–2.01 (m, 4 H, H_{cod}), 2.31 (s, 3 H, CH_3), 3.21–3.29 (m, 4 H, H_{cod}), 6.57 (d, $J_{H,H}$ = 3.0 Hz, 2 H, H_{ar}), 6.93–7.00 (m, 5 H, H_{ar}), 7.11 (t, $J_{H,H}$ = 7.3 Hz, 2 H, H_{ar}), 7.19 (d, $J_{H,H}$ = 8.0 Hz, 2 H, H_{ar}), 7.28 (t, $J_{H,H}$ = 7.7 Hz, 4 H, H_{ar}), 7.62 (d, $J_{P,H}$ = 8.1 Hz, 2 H, H_{ar}), 7.93–7.99 (m, 4 H, H_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.51 MHz, [D$_8$]THF, 25 °C): δ = 26.5 (s), 32.2 (s), 79.1 (d, $J_{C,P}$ = 12.5 Hz), 100.5 (dd, $J_{C,P}$ = 6.6, 2.8 Hz), 107.5 (dd, $J_{C,Rh}$ = 7.7, $J_{C,P}$ = 4.6 Hz), 126.4 (d, $J_{C,P}$ = 1.9 Hz), 127.7 (d, $J_{C,P}$ = 16.9 Hz), 128.0 (s), 128.2 (s), 128.5 (d, $J_{C,P}$ = 3.8 Hz), 129.4 (s), 129.4 (s), 129.6 (s), 130.3 (s), 137.6 (d, $J_{C,P}$ = 0.8 Hz), 138.2 (s, $J_{C,P}$ = 63.1 Hz), 143.9 (d, $J_{C,P}$ = 25.5 Hz), 148.0 (d, $J_{C,P}$ = 44.0 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.82 MHz, [D$_8$]THF, 25 °C): δ = –49.9 (d, $J_{P,Rh}$ = 11.3 Hz) ppm.

[(cod)Rh(η^1-4)] (8): Compound **4** (58.5 mg, 0.18 mmol) was dissolved in THF, and the solution was cooled to –78 °C. A THF solution of [Rh(cod)Cl]$_2$ (44.38 mg, 0.09 mmol) was added dropwise. The mixture was warmed to room temperature, and the solvent was evaporated. Dichloromethane was added, and the solution was filtered through Celite. The solvent was evaporated, and a black shiny powder was obtained. The product formed quantitatively according to ^{31}P NMR spectroscopy. ^1H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 1.73 (br. s, 4 H, H_{cod}), 2.33 (br. s, 4 H, H_{cod}), 4.03 (br. s, 4 H, H_{cod}), 6.88 (tt, d, $J_{H,H}$ = 7.3, $J_{H,H}$ = 1.2 Hz, 1 H, H_{ar}), 7.01–7.15 (m, 10 H, H_{ar}), 7.26–7.33 (m, 8 H, H_{ar}), 8.08–8.13 (m, 2 H, H_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.51 MHz, [D$_8$]THF, 25 °C): δ = 26.2 (s), 31.6 (s), 76.9 (br. s), 114.0 (s), 118.8 (d, $J_{C,P}$ = 11.5 Hz), 123.5 (s), 124.2 (s), 126.2 (d, $J_{C,P}$ = 0.9 Hz), 127.5 (s), 127.8 (d, $J_{C,P}$ = 5.9 Hz), 128.4 (s), 128.5 (d, $J_{C,P}$ = 22.7 Hz), 128.9 (d, $J_{C,P}$ = 2.4 Hz), 129.0 (s), 129.2 (d, $J_{C,P}$ = 2.6 Hz), 129.31 (s), 130.1 (d, $J_{C,P}$ = 2.3 Hz), 132.4 (d, $J_{C,P}$ = 13.66 Hz), 136.8 (s), 140.6 (s), 144.5 (s), 144.7 (d, $J_{C,P}$ = 3.0 Hz), 144.5 (s) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_8$]THF, 25 °C): δ = –13.0 (d, $J_{Rh,P}$ = 152.2 Hz) ppm.

X-ray Crystal Structure Determination of 1: Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of **1** in acetonitrile.

Crystallographic data: $C_{24}H_{19}P$; *Fw* = 338.4; 0.40 × 0.20 × 0.05 mm; colorless platelet, monoclinic; $P2_1/c$; a = 11.6267(13), b = 20.773(3), c = 7.3953(9) Å; α = 90, β = 91.777(10), γ = 90°; V = 1785.2(4) Å^3; Z = 4; $D_{calcd.}$ = 1.259 g cm^{-3}; μ = 1.56 mm^{-1}. 12005 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (Mo-K_α radiation; λ = 0.71073 Å) to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.69 Å^{-1} at a temperature of 200 K. 4791 reflections were unique (R_{int} = 0.079). The structures were solved with SHELXS-97[9] by using direct methods and refined on F^2 for all reflections with SHELXL-97.[9] Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 227 parameters were refined without restraints. R_1 = 0.063 for 2022 reflections with $I > 2\sigma(I)$, and wR_2 = 0.160 for 4791 reflections, S = 0.815, the residual electron density was between –0.37 and 0.96 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[10]

X-ray Crystal Structure Determination of 5-*Z*: Crystals suitable for X-ray diffraction could be obtained after the mixture was stirred with water for only 10 min, the solvent was evaporated, and acetonitrile was added for removal of the LiOH by filtration over Celite.

The Solvent was again removed, and the yellow powder obtained was recrystallized from acetonitrile.

Crystallographic data: $C_{30}H_{25}P$; *Fw* = 416.51; 0.43 × 0.3 × 0.21 mm; colorless block, triclinic; $P\bar{1}$; a = 10.347(2), b = 11.003(2), c = 11.191(2) Å; α = 97.92(3), β = 94.78(3), γ = 112.51(3)°; V = 1152.7(5) Å^3; Z = 2; $D_{calcd.}$ = 1.1999 g cm^{-3}; μ = 0.134 mm^{-1}. 12916 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (Mo-K_α radiation; λ = 0.71073 Å) to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.69 Å^{-1} at a temperature of 210 K. 6163 reflections were unique (R_{int} = 0.055). The structures were solved with SHELXS-97[9] by using direct methods and refined on F^2 for all reflections with SHELXL-97.[9] Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 284 parameters were refined without restraints. R_1 = 0.046 for 6163 reflections with $I > 2\sigma(I)$, and wR_2 = 0.100 for 6163 reflections, S = 0.837, the residual electron density was between –0.58 and 0.42 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[10]

X-Ray Crystal Structure Determination of 7: Crystals suitable for X-ray diffraction were obtained after several days by cooling a saturated solution of **7** in dry diethyl ether.

Crystallographic data: $C_{38}H_{36}PRh$; *Fw* = 626.6; 0.20 × 0.19 × 0.18 mm^3; orange block, triclinic; $P\bar{1}$; a = 11.4403(8), b = 11.7642(9), c = 12.3651(10) Å; α = 72.295(6), β = 69.699(6), γ = 70.685(6)°; V = 1438.8(2) Å^3; Z = 2; $D_{calcd.}$ = 1.446 g cm^{-3}; μ = 6.75 mm^{-1}. 14088 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (Mo-K_α radiation; λ = 0.71073 Å) to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.69 Å^{-1} at a temperature of 200 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.85–0.93 correction range).[11] 7725 reflections were unique (R_{int} = 0.062). The structures were solved with SHELXS-97[9] by using direct methods and refined on F^2 for all reflections with SHELXL-97.[9] Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 363 parameters were refined without restraints. R_1 = 0.038 for 5844 reflections with $I > 2\sigma(I)$, and wR_2 = 0.096 for 7725 reflections, S = 0.915, the residual electron density was between –1.06 and 0.77 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[10]

CCDC-962497 (for **1**), -962499 (for **5**-*Z*), and -962498 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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