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Di- and Triazaphospholes as Ligands for Ruthenium(II) and Iridium(III) Complexes

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15 **Di- and Triazaphospholes as Ligands for Ruthenium(II) and**
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18 **Iridium(III) Complexes**
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20 Brigitte Koehler, Susanne Kammerer, Tobias Mayer, Bernd Neumann and Ingo-Peter
21 Lorenz*
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26 Dedicated to Prof. Dr. Ekkehard Lindner on the occasion of his 75th birthday.
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40 **Keywords:** 5-methyl-2-phenyl-1,2,3-diazaphosphole, 2-methyl-2-phenyl-1,2,4,3-
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42 triazaphosphole, *P*-ligand, azaphosphole, ruthenium(II), iridium(III), 1,2-addition.
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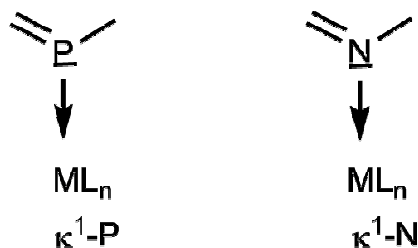
Abstract.

The reaction of the azaphospholes 5-methyl-2-phenyl-1,2,3-diazaphospole (**PDAP**) and 2-methyl-2-phenyl-1,2,4,3-triazaphospole (**PTAP**) with the dimers $[\text{LMCl}_2]_2$ ($\text{LM} = \eta^6\text{-C}_6\text{Me}_6\text{Ru}$, $\eta^5\text{-C}_5\text{Me}_5\text{Ir}$) of ruthenium(II) and iridium(III) only occurs in presence of nucleophiles such as EtOH or H₂O leading to their metal-coordination after cleavage of the dimers. $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ reacts with PDAP and EtOH in the molar ratio 0.5:1:1 to give the *P*-coordinated complex $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2(\text{P-PDAP*EtOH})$ (**1**). In case of $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ the triazaphosphole PTAP was used in the presence of EtOH or H₂O yielding the analogous products $(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2(\text{P-PTAP*EtOH})$ (**2**) or $(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2(\text{P-PTAP*H}_2\text{O})$ (**3**). In **1-3** the former aromatic azaphosphole (σ^2 , $\lambda^3\text{-P}$) has been converted by 1,2 addition of EtOH or H₂O to their *P=C* or *P=N* double bond with the nucleophiles EtO⁻ and OH⁻ bonded to phosphorus (σ^3 , $\lambda^3\text{-P}$). Complexes **1-3** with the piano-stool configuration were characterized by elemental analysis, ³¹P NMR spectroscopy and single crystal X-ray diffraction.

Introduction

Azaphospholes are highly unsaturated five-membered heterocycles containing at least one two-coordinated trivalent phosphorus and one three-coordinated nitrogen atom. Formally azaphospholes are derived from the well known azoles by replacing one =C(*H*)- unit by a σ^2 , $\lambda^3\text{-P}$ atom. Since 1,2-addition reactions destroy the aromatic system, they are not very common. Coordinated to transition metals, however, addition reactions onto azaphospholes might occur. While the synthesis and reactivity of azaphospholes have been investigated

extensively^[1-4], their coordination chemistry has still not received much attention, though they could coordinate via at least two different positions (Scheme 1).



Scheme 1 Possible coordination modes of azaphospholes with transition metals

Literature reports on the coordination behavior of azaphospholes are scarce. One early study by Schmidpeter *et al.* reports on the reaction of azaphospholes with different transition metals. In this study, however, complexes with intact azaphospholes were obtained only with carbonyl complexes, especially of the chromium group.^[5] In case of Pd and Pt complexes the authors only identified intact and unreacted azaphosphole ligands in the ³¹P and ¹⁹⁵Pt NMR spectra.^[6,7] After adding nucleophiles (such as methanol) for addition reactions, the authors obtained single crystals of the reaction products, where the phosphorus atom had been affected by an 1,2-addition and the heterocycle had lost its aromaticity.^[8] The same authors also observed that the five-membered azaphosphole ring can be opened under the formation of a new bidentate ligand, *e.g.* P(=O)(OMe)CH₂CMe=NNH(Me), which can chelate the metal center through the P and the imine N atoms.^[8] When Schmidpeter *et al.* used Me₂AuCl for coordination reactions of azaphospholes two different coordination modes of azaphospholes were observed by ¹H and ³¹P NMR spectroscopy: the κ¹-N and the κ¹-P ligand function (scheme 1).^[9] Cavell *et al.* used Rh complexes as starting materials for their coordination reactions with azaphospholes

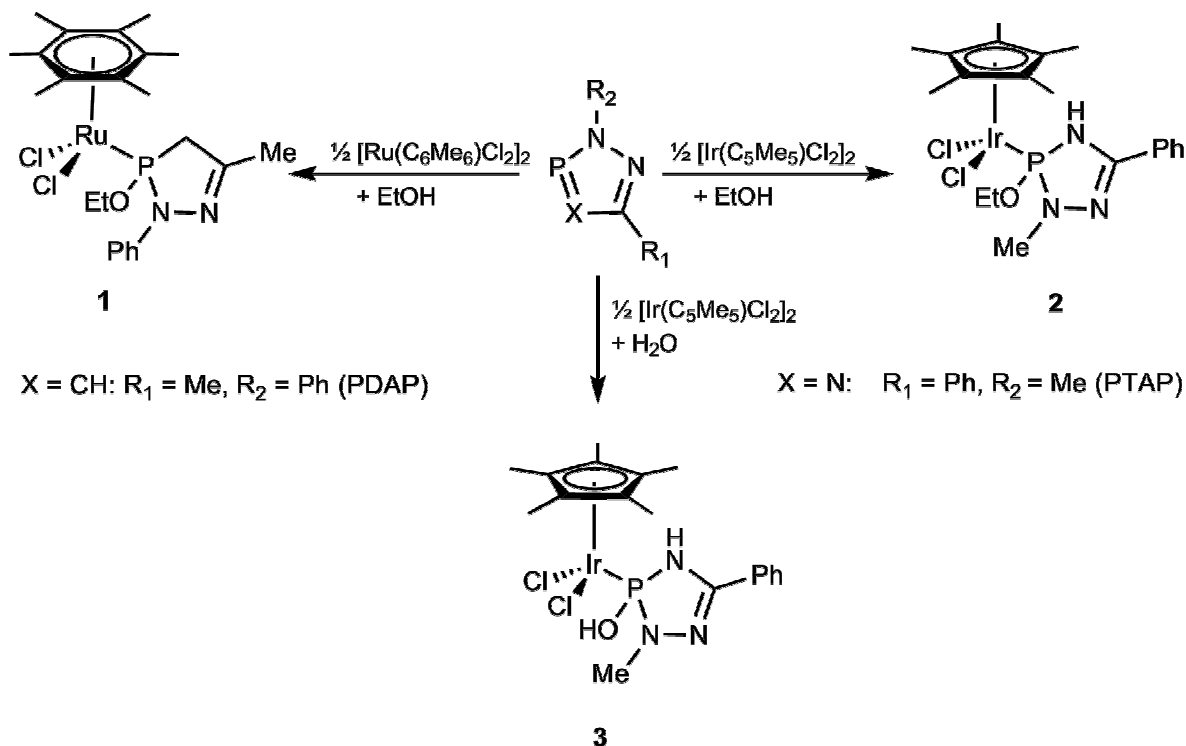
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6 bearing an exocyclic phosphine substituent. In this case, bonding between the ligand and
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8 the metal center exclusively via the phosphine to rhodium was observed.^[10]
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10 11 **Results and Discussion**

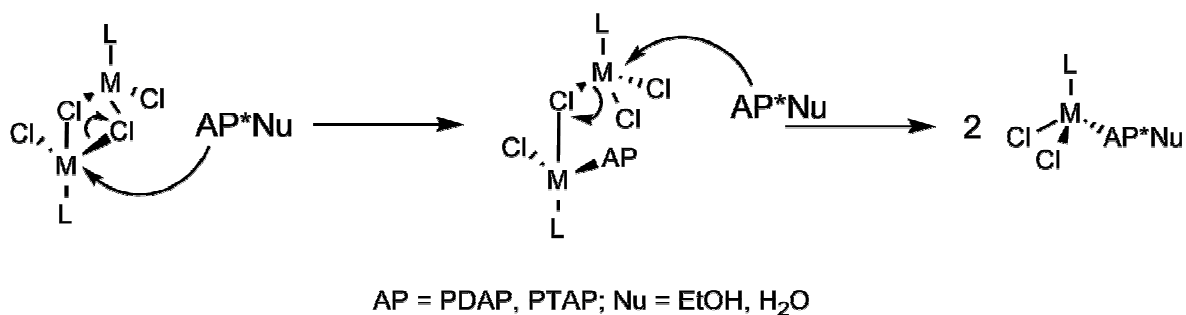
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14 To investigate the coordination behavior and reactivity of azaphospholes towards transition
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16 metal complexes, intact azaphospholes were first reacted with the dimeric Ru(II) and Ir(III)
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18 complexes of the type $[\text{LMCl}_2]_2$ (LM = $\eta^6\text{-C}_6\text{Me}_6\text{Ru}$, $\eta^5\text{-C}_5\text{Me}_5\text{Ir}$). The cleavage of the
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20 dimers to reactive monomers should favor the coordination of one azaphosphole to each
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22 metal. Indeed, in the ^{31}P NMR spectrum of a reaction mixture of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ and
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24 PDAP in addition to the resonance of free azaphosphole (PDAP $\delta = 225.5$ ppm) a new peak
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26 with relatively low intensity was observed shifted to higher field. Both of these resonances
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28 appeared with various relative intensities depending on the reaction conditions. This
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30 indicated that (i) the reaction was not complete and (ii) the reaction was very dependent on
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32 the quality of the solvent (CH_2Cl_2) used, although only freshly distilled solvent was used.
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37 In the first reactions CH_2Cl_2 was used which contained traces of EtOH originating from the
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39 distillation apparatus. Therefore, repeating this reaction with a stoichiometric amount of
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41 EtOH only one signal at 104.8 ppm was detected in the ^{31}P NMR spectrum. Moreover, we
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43 were able to isolate a relatively stable solid reaction product. This was, however, not the
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45 desired complex with the intact azaphosphole, but its 1,2-addition product with EtOH and
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47 this means loss of aromaticity. The former P=C double bond had been changed into a P-C
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49 single bond by adding the ethoxy group to phosphorus and the proton to carbon leading to
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51 the formation of the new complex of the composition $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2(\text{P-PDAP*EtOH})$ (1)
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53 (scheme 2). The analogous reactions were also carried out with $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ and
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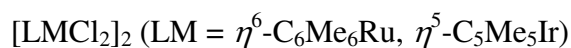
PTAP and stoichiometric amounts of EtOH as well as of H₂O finally yielding the analogous compounds again with the modified azaphospholes, (η^5 -C₅Me₅)IrCl₂(P-PTAP*EtOH) (**2**) or (η^5 -C₅Me₅)IrCl₂(P-PTAP*H₂O) (**3**), respectively (scheme 3).



Scheme 2 Synthesis of the complexes **1-3** with azaphosphole derivatives



Scheme 3 Proposed mechanism for the reaction of azaphospholes AP*Nu with the dimers



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6 All complexes **1-3** are orange-red solids, soluble in dichloromethane or chloroform and only
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8 stable under an argon or nitrogen atmosphere. Under atmospheric conditions they
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10 decompose within a few hours. The phosphorus signal in the ^{31}P NMR spectrum of each
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12 compound is shifted to higher field ($\delta = 104.8$ (**1**), 70.2 (**2**), 70.3 (**3**) ppm) compared to the
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14 free and intact azaphosphole ligands ($\delta = 225.3$ (**PDAP**), 180.6 (**PTAP**) ppm). Single
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16 crystals of **1-3** suitable for X-ray structure analysis were obtained by diffusion of *n*-pentane
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18 into solutions in CH_2Cl_2 . All compounds crystallize in different crystal systems and space
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20 groups. (**1**: monoclinic $P2_1/n$; **2**: monoclinic $P2_1/c$; **3**: triclinic $P-1$). The molecular
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22 structures of **1-3** are shown in fig. 1-3 together with selected bond lengths and angles.
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27 The ruthenium centre of **1** is octahedrally surrounded by the η^6 -hexamethylbenzene-, two
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29 chlorido-, and one *P*-coordinated PDAP-ligand modified by 1,2-addition of EtOH to the
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31 $\text{P}=\text{C}$ double bond. The phosphole ligand has been changed to a 3-ethoxy-5-methyl-2-
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33 phenyl-3,4-dihydro-2*H*-1,2,3-diazaphosphole completing the piano-stool configuration. The
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35 former σ^2, λ^3 -P atom has been converted into a σ^3, λ^3 -P configuration and is now
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37 tetrahedrally surrounded. The five-membered azaphosphole ring has lost its former planarity
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39 to show now a “very open” envelope conformation with an interplanar angle of only 2° . The
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41 bond length of $\text{P1-C2} = 1.824(3)$ Å indicates a (strong) single bond being 15 pm longer than
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43 a typical $\text{P}=\text{C}$ double bond.^[11] The bond length Ru1-P1 is about 15 pm shorter than both
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45 Ru1-Cl_n ($n = 1, 2$) ($2.404(4)$ Å, $2.414(1)$ Å) bonds. Whereas the bond angles Cl1-Ru1-Cl2
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47 ($87.44(3)^\circ$) and Cl1-Ru1-P1 ($90.66(3)^\circ$) are close to the octahedral one, that of Cl1-Ru1-P1
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49 ($79.46(3)^\circ$) is significantly smaller. The bond lengths from P1 to the main group elements
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51 indicate strong single bonds ($\text{P1-C2} = 1.824(2)$ Å, $\text{P1-N1} = 1.716(5)$ Å, $\text{P1-O1} = 1.599(1)$
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53 Å) and the configuration at P1 is strongly distorted tetrahedral, where the angle N1-P1-C2
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(89.45(2)°) is the smallest, because it is the bite angle within the ring. Ru1-P1-N1 (120.83(1)°) is the largest angle because of the steric demand of the *N*-situated phenyl substituent, which lies nearly parallel to the diazaphosphole ring. The other angles around P1 correspond essentially to tetrahedral values (105° – 116°).

Fig. 1!!!

The molecular structures **2** and **3** are very similar and also closely resemble that of **1**. They possess the analogous piano-stool configuration, formed by the η^5 -pentamethylcyclopentadienyl-, two chloride- and the PTAP-ligand again modified by 1,2 addition of EtOH (**2**) or H₂O (**3**). In both cases the nucleophiles have again attacked the phosphorus atom with the consequence of loss of aromaticity and formation of a “very open” envelope conformation. (interplanar angles: 3° (**2**) and 4° (**3**)). Additionally, the bonds P1-N are elongated indicating a P-N(H) single bond (**2**: P1-N3 = 1.680(2) Å; **3**: P1-N3 = 1.667(1) Å). All other bond lengths and angles of **2** and **3** are also very similar and in the expected range, *e.g.* Ir-Cl ~2.41 Å, P1-O1 ~1.6 Å, bite angle N-P-N ~ 87°).

Fig. 2 and Fig. 3!!!

Experimental Section

General Considerations

All reactions and manipulations were carried out under dry argon atmosphere using Schlenk line techniques. The azaphospholes, $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ were prepared according to the literature methods.^[12-15] All solvents were purified by standard methods [25]; dichloromethane was distilled from calcium hydride, and *n*-pentane was distilled from sodium. ¹H, ¹³C and ³¹P NMR spectra were measured using a Jeol Eclipse

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6 270, Jeol Eclipse 400 and Jeol EX400 spectrometer; the shifts are given relative to the
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8 external standards (TMS and 85% H₃PO₄). Mass spectra were recorded with a Jeol Mstation
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10 JMS 700 and IR spectra were recorded using Nicolet 520 FT-IR and Perkin Elmer Spectrum
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12 One FT-IR-Spektrometer in the range of 4000-400 cm⁻¹. Elemental analyses were
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14 performed by the Microanalytical Laboratory of the Department of Chemistry and
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16 Biochemistry, LMU Munich using a Heraeus Elementar Vario El.
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19 20 *X-ray Crystallography*

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22 Single crystal X-ray diffraction data were collected on an Nonius Kappa CCD
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24 diffractometer, using graphite-monochromated Mo-K_α radiation. Single crystal X-ray
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26 structure analyses were performed by direct methods using the SHELXS software and
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28 refined on *F*² by full matrix least-square with SHELXL-97 using anisotropic displacement
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30 parameters.^[16]
31
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33 34 *Syntheses of the complexes 1-3*

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36 **General procedure:** The **ligand** (0.2 mmol) was dissolved in 4 mL freshly distilled
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38 dichloromethane and a solution of [**LMCl**]₂ (0.1 mmol) in 4 mL dichloromethane was
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40 added. After 2 h 0.2 mmol of the **nucleophile** were added dropwise. The solution was
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42 stirred for 24 h at r.t.. The solvent was removed from the colored solution in vacuo and the
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44 resulting residue was purified by stirring with dry *n*-hexane. The solvent was then discarded
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46 and the solid dried in vacuo. Single crystals of **1-3** suitable for X-ray structure analysis were
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48 obtained by diffusion of *n*-pentane into the solutions of **1-3** in CH₂Cl₂.
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53 **C₂₃H₃₃N₂OPRuCl₂ (1): ligand:** PDAP (35.2 mg); [**LMCl**]₂: [(η⁶-C₆Me₆)RuCl₂]₂ (66.8
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55 mg); **nucleophile:** EtOH (116.6 μL), red crystals; yield = 22%. ³¹P{¹H} NMR (CD₂Cl₂,
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6 161.997 MHz) δ = 104.8 ppm. **MS** (DEI) m/z = **556** (M, 25%), 521 (M-Cl, 87%), 486 (M-
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8 2Cl, 20%).

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10 **C₂₀H₂₉N₃OPIrCl₂ (2): ligand:** PTAP (35.4 mg); **[LMCl₂]₂:** [η^5 -C₅Me₅)IrCl₂]₂ (79.6 mg);
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12 **nucleophile:** EtOH (116.6 μ L); red crystals; yield = 89%. **IR** (KBr)/cm⁻¹: 3823 w, 3385 w,
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14 3047 w, 2989 w, 2977 w, 2963 w, 2944 w, 2922 w, 2891 w, 2801 w, 1963 w, 1711 w, 1599
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16 w, 1590 w, 1554 w, 1500 w, 1462 w, 1444 m, 1389 s, 1312 m, 1263 s, 1196 m, 1153 w,
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18 1103 m, 1016 s, 975 m, 942 s, 841 m, 807 m, 774 m, 768 m, 717 s, 695 m, 664 w, 656 w,
19
20 619 m, 601 m. **MS** (DEI) m/z = **622** (M, 5%), 587 (M-Cl, 58%), 552 (M-2Cl, 18%). **¹H**
21
22 **NMR** (C₆D₆): δ = 8.21 (d, ⁵J_{PH} = 9.9 Hz, H_{3/7}), 7.65 (m, 3H, H^{arom.}), 3.81 (d, ³J_{PH} = 6.6 Hz,
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24 3H, H^{Me}), 1.43 (15H, H^{Cp*}) ppm. **¹³C NMR** (C₆D₆): δ = 169.3, 166.7 (d, ²J_{PC} = 14.4 Hz, C₁),
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26 134.6 (d, ³J_{PC} = 5.6 Hz, C₂), 130.2 (s, C^{arom.}), 129.1 (s, C^{arom.}), 128.4 (s, C^{arom.}), 126.9 (s,
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28 C^{arom.}), 40.7 (d, ²J_{PC} = 10.0 Hz, C_{Me}), 8.67 (Cp*) ppm. **³¹P{¹H} NMR** (CD₂Cl₂, 161.997
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30 MHz) δ = 70.2. **³¹P NMR** (CD₂Cl₂, 161.997 MHz) δ = 70.2 (d, ²J_{PH} = 19.3 Hz) ppm.

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36 **C₁₈H₂₅N₃OPIrCl₂ (3): ligand:** PTAP (35.4 mg); **[LMCl₂]₂:** [η^5 -C₅Me₅)IrCl₂]₂ (79.6 mg);
37
38 **nucleophile:** H₂O (36.4 μ L); red crystals; yield = 30%. **³¹P{¹H} NMR** (CD₂Cl₂, 161.997
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40 MHz) δ = 70.3 ppm. **MS** (DEI) m/z = **594** (M, 13%), 559 (M-Cl, 46%), 524 (M-2Cl, 23%).
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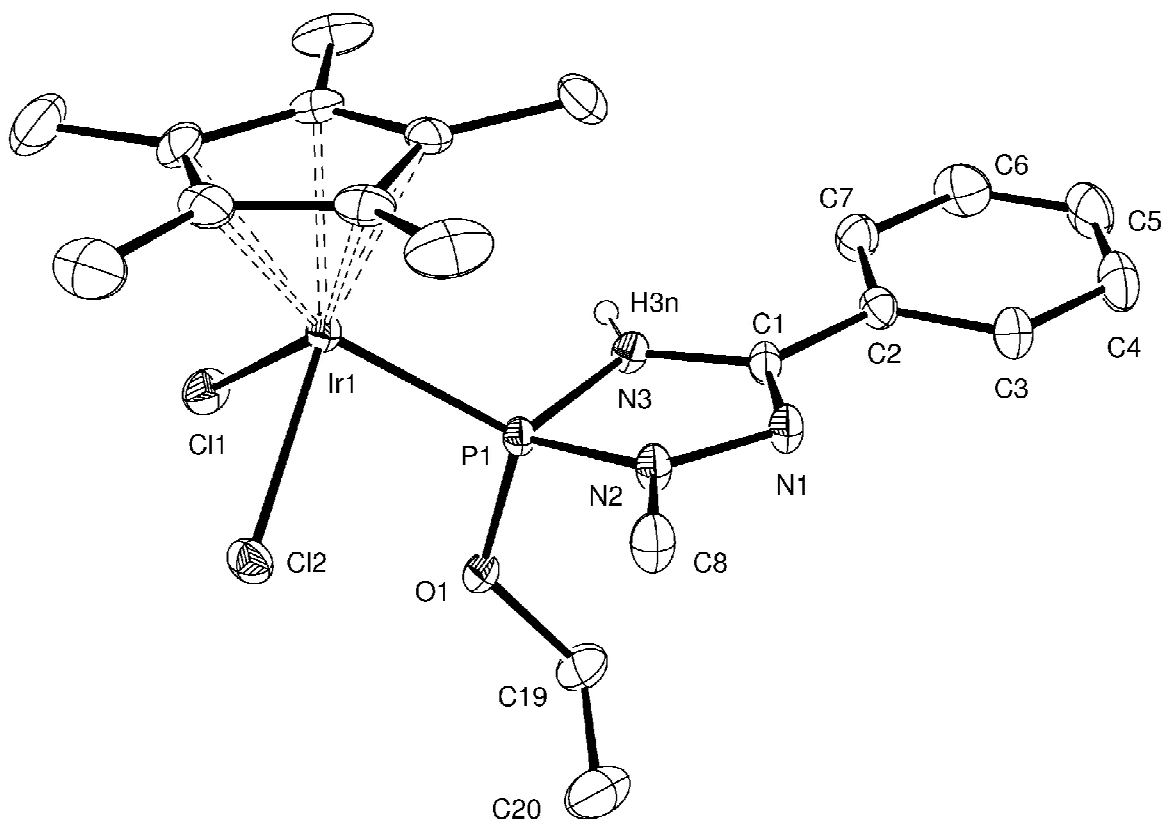


Fig. 2: ORTEP plot of **2** with thermal ellipsoids at probability 30% level; H-atoms of C-H bonds are omitted for clarity; selected bond lengths [Å], and angles [°]: Ir1-P1 2.243(2), Ir1-Cl1 2.412(3), Ir1-Cl2 2.403(5), Ir1-Cp* ~ 2.198, P1-O1 1.584(1), P1-N3 1.680(2), P1-N2 1.671(1), N1-N2 1.396(2), N1-C1 1.296(6), C1-N3 1.387(2); Cl1-Ir1-Cl2 88.86(4), Cl1-Ir1-P1 91.56(4), Cl2-Ir1-P1 87.98(4), Ir1-P1-O1 110.73(1), Ir1-P1-N3 121.38(1), Ir1-P1-N2 117.57(1), O1-P1-N3 107.27(2), O1-P1-N2 109.42(2), N3-P1-N2 87.72(2), P1-N2-N1 115.82(3), N2-N1-C1 108.42(3), N1-C1-N3 114.89(4), C1-N3-P1 112.43(3); torsion angle (°): P1-N2-N1-C1 7.27(4), P1-N3-C1-N1 -4.31(5), N3-C1-C2-C7 3.34(6), N3-C1-C2-C3 -175.82(4).

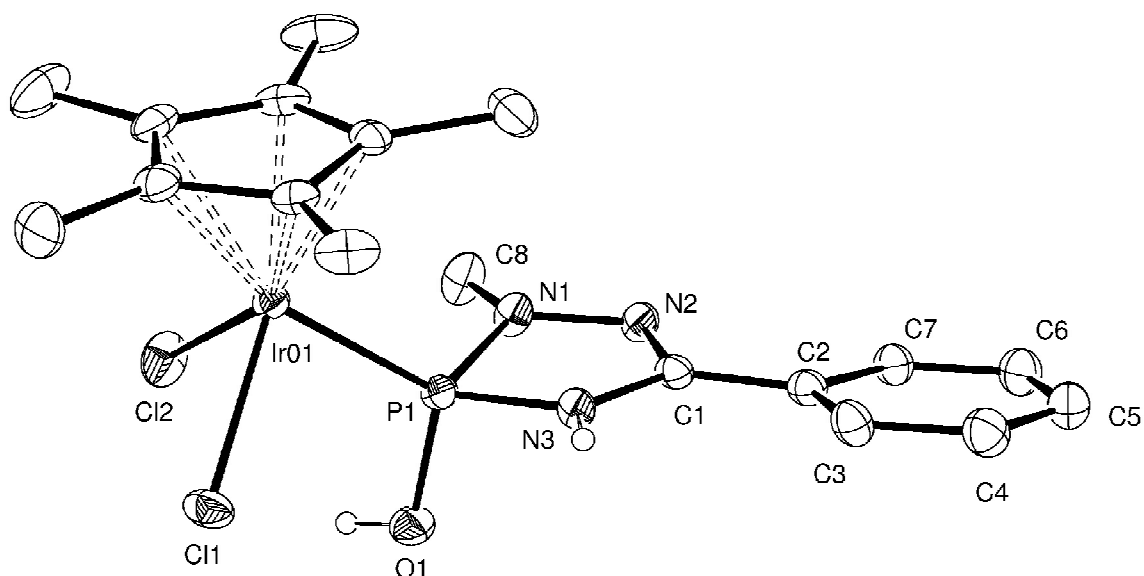
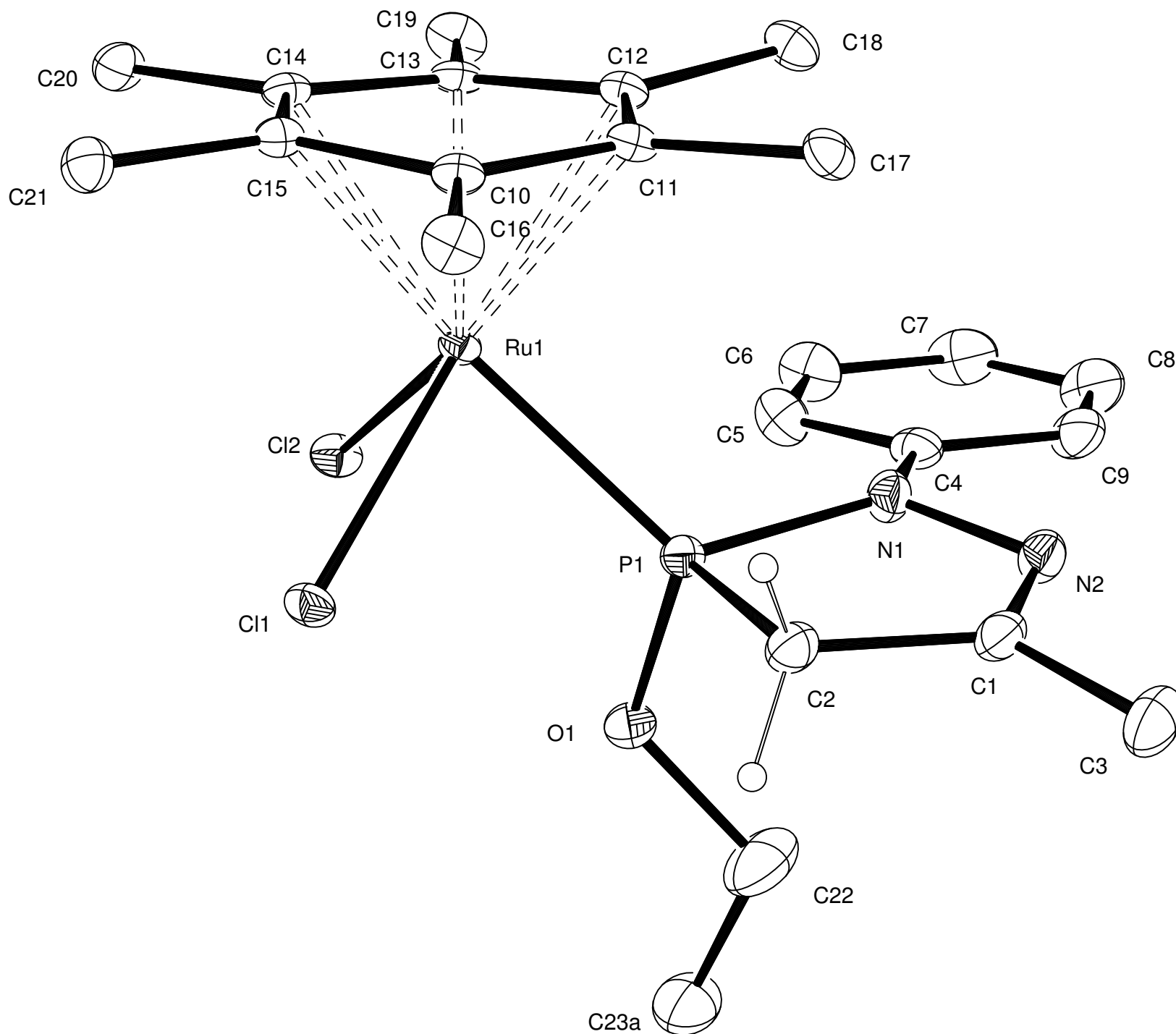


Fig. 3: ORTEP plot of **3** with thermal ellipsoids at probability 30% level; H-atoms of C-H bonds and one dichloromethane are omitted for clarity; selected bond lengths [\AA], and angles [$^\circ$]: Ir1-P1 2.240(8), Ir1-Cl1 2.415(11), Ir1-Cl2 2.399(36), Ir1-Cp* ~ 2.198, P1-O1 1.598(3), P1-N3 1.667(1), P1-N1 1.668(2), N1-N2 1.404(2), N2-C1 1.297(3), C1-N3 1.390(2); Cl1-Ir1-Cl2 87.69(5), Cl1-Ir1-P1 88.96(4), Cl2-Ir1-P1 87.40(4), Ir1-P1-O1 113.76(1), Ir1-P1-N3 121.24(1), Ir1-P1-N1 118.27(1), O1-P1-N3 104.53(2), O1-P1-N1 107.68(2), N3-P1-N1 87.94(2), P1-N1-N2 115.04(3), N1-N2-C1 108.08(3), N2-C1-N3 114.96(3), C1-N3-P1 112.31(3); torsion angle ($^\circ$): P1-N1-N2-C1 -11.69(4), P1-N3-C1-N2 7.23(47), N3-C1-C2-C7 10.70(2), N3-C1-C2-C3 171.28(1).

Table 1 Crystallographic data of **1-3**

Compound	1	2	3
Empirical formula	C ₂₃ H ₃₃ Cl ₂ N ₂ OPRu	C ₂₀ H ₂₉ Cl ₂ IrN ₃ OP	C ₁₉ H ₂₇ Cl ₄ IrN ₃ O
Formula weight [g mol ⁻¹]	556.47	621.560	678.439
Temperature [K]	200(2)	200(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P-1</i>
a [Å]	8.2762(17)	7.8270(16)	9.5340(2)
b [Å]	38.055(8)	13.745(3)	11.6880(2)
c [Å]	8.4072(17)	21.263(4)	11.9552(2)
α [°]	90	90	76.2240(10)
β [°]	115.55(3)	95.3852(11)	85.6880(10)
γ [°]	90	90	72.4740(10)
Volume [Å ³]	2388.8(8)	2277.42(7)	1233.82(4)
Z	4	4	2
Density (calculated) [mg/m ³]	1.5473(5)	1.81282(6)	1.8262(6)
Absorption coefficient [mm ⁻¹]	0.965	6.183	5.924
F(000)	1144	1216	660
Crystal size [mm ³]	0.26 x 0.19 x 0.03	0.20 x 0.11 x 0.08	0.18 x 0.07 x 0.06
Reflections collected	9646	10129	10211
Independent reflections	5403 [R(int) = 0.0210]	4956 [R(int) = 0.0245]	5360 [R(int) = 0.0321]
Compl. to θ = 27.47°	98.5	99.8	99.6
Data/restraints/parameters	5403/0/288	4956/0/262	5360/0/268
Goodness-of-fit on F ²	1.166	1.046	1.065
Final R indices [I>2σ(I)]	<i>RI</i> = 0.0378	<i>RI</i> = 0.0574	<i>RI</i> = 0.0289
	<i>wR2</i> = 0.0764	<i>wR2</i> = 0.0619	<i>wR2</i> = 0.0697
R indices (all data)	<i>RI</i> = 0.0490	<i>RI</i> = 0.0371	<i>RI</i> = 0.0322
	<i>wR2</i> = 0.0798	<i>wR2</i> = 0.0616	<i>wR2</i> = 0.0712
Largest diff. Peak/hole [e.Å ⁻³]	0.445 and -0.522	1.502 and -1.295	2.102 and -1.491
CCDC	727144	727145	727146

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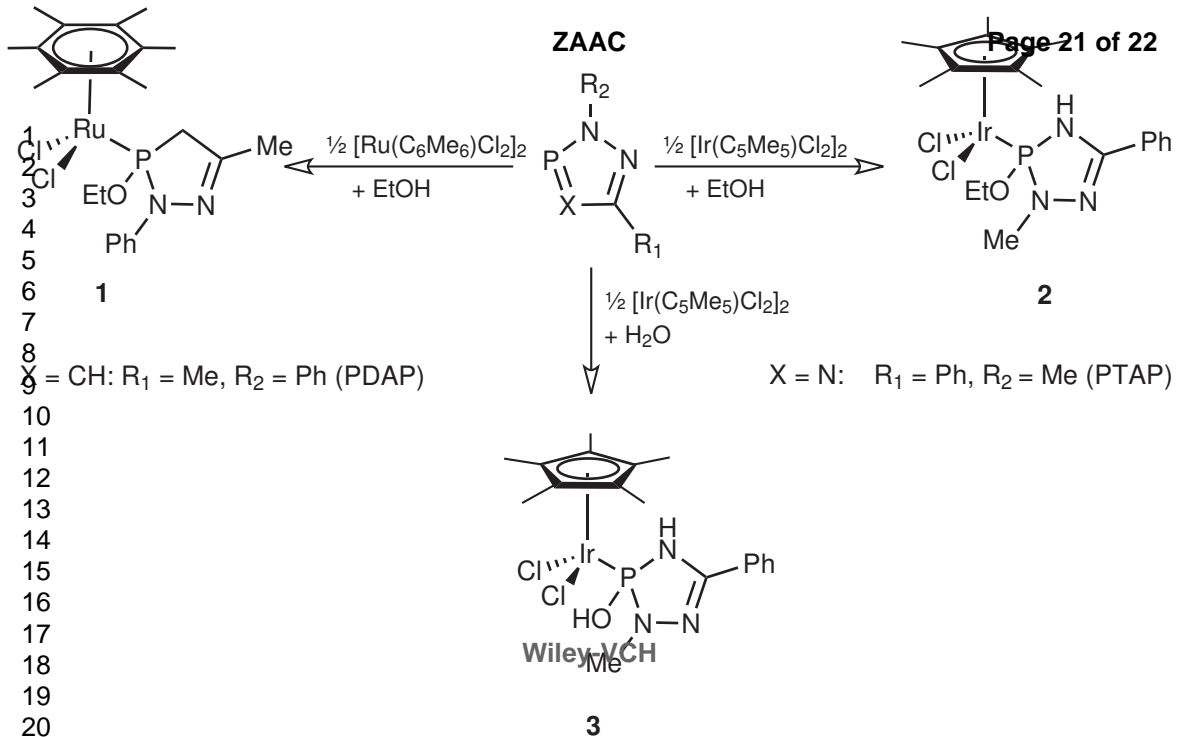
Wiley-VCH

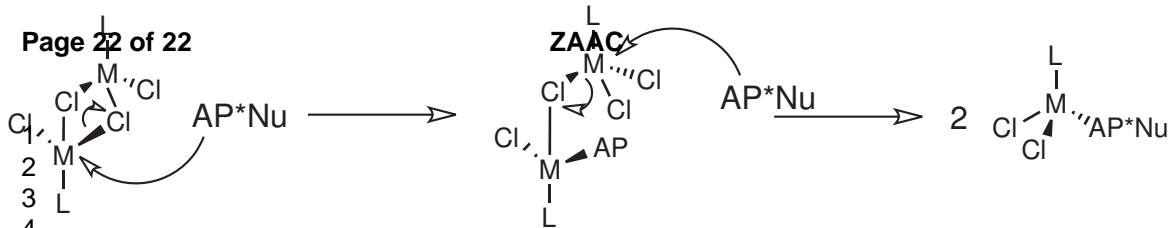
1 ML_n
2 κ^1-P
3

N



ML_n
 κ^1-N





AP = PDAP, PTAP; Nu = EtOH, H₂O

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