

Synthesis and Characterization of η^5 -1,2,4-Diazaphospholide Complexes of Ruthenium[†]

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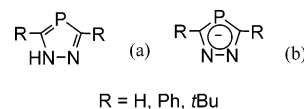
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Summary: Treatment of the 1,2,4-diazaphospholide anions [3,5-*t*Bu₂dp][−] (**1**) and [3,5-Ph₂dp][−] (**2**) with [Cp[∗]RuCl]₄ affords the two complexes [(η^5 -3,5-*t*Bu₂dp)RuCp[∗]] (**3**) and [(η^5 -3,5-Ph₂dp)RuCp[∗]] (**4**) (dp = 1,2,4-diazaphospholide), which are the first examples of sandwich complexes derived from 1,2,4-diazaphospholide ligands. The X-ray crystal structure analysis of **3** reveals that the metal atom is π -bonded to the 1,2,4-diazaphospholide ligand. The bonding was rationalized by DFT calculations.

1H-1,2,4-Diazaphospholes have been known for more than 20 years (Chart 1).^{1–5} As anions with six π electrons, the deprotonated 1H-1,2,4-diazaphospholes exhibit evidence of a certain degree of aromatic delocalization and are the heterocyclic analogues of the cyclopentadienyl ligand (Cp[−]).⁵ The electron distribution within the heterocycle, however, is uneven and presents a charge shift toward the more electronegative nitrogen atoms, on the basis of DFT calculations.⁶ The unique electronic structure as well as the presence of donor lone pairs on the heteroatoms make the 1,2,4-diazaphospholides potentially interesting ligands for the metals across the periodic table. By virtue of the electronic requirements, the resulting complexes of the 1,2,4-diazaphospholides may present coordinations of the types η^1 (N), η^1 (N₁): η^1 (N₂), η^2 (N₁,N₂), η^1 (N₁): η^1 (N₂): η^1 (P), and η^2 (N₁,N₂): η^1 (P) via the nitrogen or/and phosphorus atom(s), of the η^5 type via the π -electron system, or even a combination of the two. In comparison to the cyclopentadienyl ligand, however, the related isoelectronic heterocyclic 1,2,4-diazaphospholide ligands have received much less attention. There is one report by Gudat and co-workers of the lithium complex [(η^1 : η^1 -dp)-(μ -Li)(DME)]₂, bearing a η^1 : η^1 -1,2,4-diazaphospholide ligand (DME = 1,2-dimethoxyethane),⁷ but so far other coordination modes have not been substantiated. As attested to by the number

Chart 1. 1H-1,2,4-Diazaphospholes (a) and 1,2,4-Diazaphospholides (b)



of recent reports on complexes with phosphorus- and nitrogen-containing aromatic heterocyclic ligands as well as the emerging application to molecular materials and catalysis,^{8–11} the use of 1,2,4-diazaphospholide ions as ligands shows promise as an attractive developing area. Therefore, we set out to study metal complexes with 1,2,4-diazaphospholide ligand coordination. Herein, we report the synthesis and characterization of two ruthenium(II) complexes bearing these ligands in η^5 coordination, which are, to the best of our knowledge, the first such complexes with this coordination mode.

Treatment of 3,5-di-*tert*-butyl-1,2,4-diazaphosphole (H[3,5-*t*Bu₂dp])¹ and 3,5-diphenyl-1,2,4-diazaphosphole (H[3,5-Ph₂dp])¹ with metallic potassium in THF (tetrahydrofuran) afforded potassium 3,5-di-*tert*-butyl-1,2,4-diazaphospholide ([3,5-*t*Bu₂dp]K (**1**), 93%) and potassium 3,5-diphenyl-1,2,4-diazaphospholide—THF ([3,5-Ph₂dp]K·0.67THF (**2**), 88%), respectively, as white solids with the evolution of hydrogen. Complex **1** is soluble only in THF, while compound **2** is somewhat soluble in ether. Both complexes were characterized by spectral and analytical methods.¹²

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[†] Dedicated to Professor Alfred Schmidpeter.

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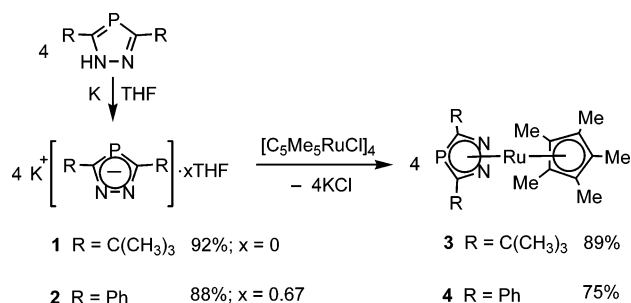
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(6) Our DFT calculations followed by natural bond orbital (NBO) population analysis on the charge distribution of the 3,5-di-*tert*-butyl-1,2,4-diazaphospholide anion indicated that two nitrogen atoms gain more weight (N (−0.37), P (0.17)); see the Supporting Information for the calculations on [3,5-*t*Bu₂dp][−] ligand.

Scheme 1. Synthesis of Compounds 1–4



The reaction of [Cp*RuCl]₄¹³ and 1 and 2 in THF smoothly gave the complexes (η⁵-3,5-di-*tert*-butyl-1,2,4-diazaphospholide)(η⁵-pentamethylcyclopentadienyl)ruthenium(II) ([η⁵-3,5-*t*Bu₂dp)RuCp*] (3), 89%) and (η⁵-3,5-diphenyl-1,2,4-diazaphospholide)(η⁵-pentamethylcyclopentadienyl)ruthenium(II) ([η⁵-3,5-Ph₂dp)RuCp*] (4), 75%), respectively, as orange crystals (Scheme 1).¹² Both compounds are soluble in common organic solvents and could be readily sublimed under high vacuum. They may be handled briefly (2–5 min) in air in the solid state. Attempts to prepare an analogous complex, (η⁵-1,2,4-diazaphospholide)(η⁵-pentamethylcyclopentadienyl)ruthenium(II) ([η⁵-1,2,4-dp)Ru(η⁵-CpMe₅)], using the 1,2,4-diazaphospholide ligand in a similar manner were unsuccessful.

An X-ray crystal structure determination of complex 3 was carried out. The molecule has a sandwich structure with two π-bonded ligands (Figure 1).¹² The ligands appear to be essentially coplanar with a centroid–ruthenium–centroid angle of 176.3(3)° as well as a dihedral angle of 5.73(14)° between the two five-membered rings. The latter is larger than that observed in the pseudo-ruthenocene complex [(CH₃)₂C₃HN₂)RuCp*] (2.6(4)°).¹⁴ Interestingly, the cross-orientation of the two cyclic ligands is a close to eclipsed conformation, the corresponding torsion angles for C(12)–Ru–C(1)–C(7) and P(1)–Ru–C(11)–C(16) being –5.4(3) and 2.9(3)°, respectively. This orientation is consistent with that found in the related species [Cp*Ru(η⁵-*t*Bu₂C₄H₂P)]¹⁵ and decamethylruthenocene.¹⁶ The metal-to-ring distances ruthenium–pentamethylcyclopentadienyl (centroid, 1.817(3) Å) and ruthenium–1,2,4-diazaphospholide (centroid, 1.823(3) Å) demonstrate the π-bonding of ruthenium to the two ligands. Within the 1,2,4-diazaphospholide ligand, the ruthenium–phosphorus bond length is 2.4309(7) Å, while the ruthenium–nitrogen distances are 2.165(2) and 2.166(2) Å, respectively, which fall in the expected range of ruthenium–phosphorus distances associated with the sandwich complexes [Cp*Ru(η⁵-*t*Bu₂C₄H₂P)] (Ru–P = 2.397(1) Å),¹⁵ [Cp*Ru(η⁵-Me₂Ph(Si-*i*Pr₃)C₄P)] (Ru–P = 2.405(1) Å),^{17a} [(η⁵-C₅Me₄Et)Ru(η⁵-P₅)] (2.43 Å (av)),^{17b} and [Cp*Ru(η⁵-*t*Bu₂C₂P₂Sb)] (2.419(2), 2.472(2) Å)^{17c} and are slightly shorter than ruthenium–nitrogen bond lengths in the sandwich complex [Ru(η⁵-NC₄Me₄)₂] (Ru–N = 2.1820(13) Å).¹⁸

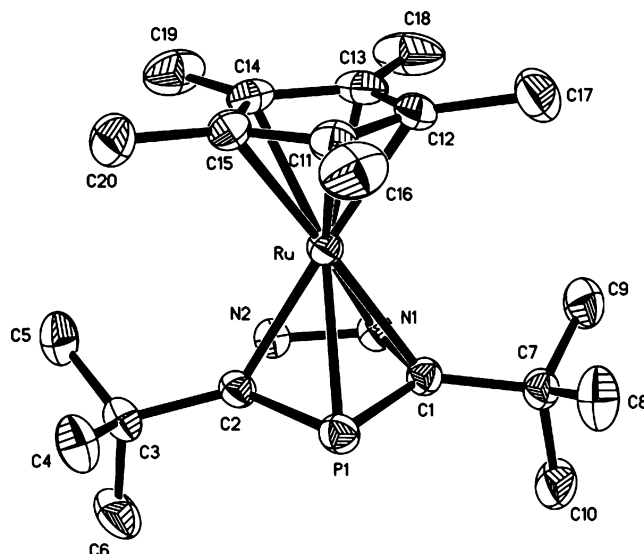


Figure 1. Molecular structure of 3 with thermal ellipsoids at the 50% probability level, as determined by a single-crystal X-ray diffraction study. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru–N(1) = 2.165(2), Ru–N(2) = 2.166(2), Ru–C(1) = 2.213(3), Ru–C(2) = 2.225(2), Ru–C(11) = 2.170(3), Ru–P(1) = 2.4309(7), C(1)–P(1) = 1.777(3), C(2)–P(1) = 1.780(3), C(1)–N(1) = 1.372(3), C(2)–N(2) = 1.368(3), N(1)–N(2) = 1.395(3); N(1)–Ru–N(2) = 37.59(8), N(1)–Ru–C(1) = 36.50(8), C(1)–Ru–P = 44.68(7), C(1)–P(1)–C(2) = 85.77(12), C(1)–N(1)–N(2) = 112.0(2), N(1)–C(1)–P(1) = 115.09(18); N(2)–N(1)–C(1)–P(1) = –0.9(3), C(2)–P(1)–C(1)–N(1) = 1.6(2), C(12)–Ru–C(1)–C(7) = –5.4(3), P(1)–Ru–C(11)–C(16) = 2.9(3).

The elemental analysis results are in complete agreement with the formulas of compounds 3 and 4.¹² The mass spectra of both complexes exhibit molecular ion peaks with the correct isotopic distributions ([M⁺] at *m/z* 434 for 3 and *m/z* 474 for 4). The ¹H NMR (C₆D₆, 23 °C) spectrum of complex 3 displays two sharp resonances at δ 1.34 for the *t*Bu groups in addition to δ 1.73 for the C₅Me₅ group, attributable to a rotation of the two ligand rings about their metal–ring centroid axes at room temperature.¹⁹ The ³¹P{¹H} NMR resonance (C₆D₆, 23 °C) is observed at –61.89 ppm, which is drastically shifted upfield relative to the corresponding signals of the free heterocyclic ligand H[3,5-*t*Bu₂dp] (³¹P δ +65.4 ppm) and the potassium salt 1 (³¹P δ +50.65 ppm).^{1,12} The observed significant upfield shift resonance upon ligation of the anion to transition metals in the ³¹P{¹H} NMR spectrum is generally diagnostic for the π-bonding of metals to a phosphorus atom.^{15,20} The ¹³C{¹H} NMR spectrum (C₆D₆, 23 °C) displays resonances at δ 31.75 (s), 34.823 (d, ²J_{CP} = 30.0 Hz, CCH₃), and 148.280 (d, ¹J_{CP} = 273.0 Hz, PCN) for the 1,2,4-diazaphospholide ligand of complex 3. At δ 31.75, however, the coupling constant (³J_{CP}(Me)) is too small to be observed (the ³J_{CP}(Me) coupling constant (26.8 Hz) is observed for 1).^{12,21} Surprisingly, a coupled resonance at δ 89.06 (d, J_{CP} = 26.0 Hz) for the carbon atoms of the pentamethylcyclopentadienyl ring is observed in complex 3,

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presumably due to the closer distance between the interacting nuclei. The resonance at δ -58.55 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 23°C) strongly supports the π -bonding of ruthenium to the 1,2,4-diazaphospholide in complex **4** (vs ^{31}P δ $+67.19$ ppm for **2**).¹²

The observation of an η^5 -1,2,4-diazaphospholide coordination mode in the phenyl- and *tert*-butyl-substituted 1,2,4-diazaphospholide complexes is significant, in view of the fact that no such coordination mode has been previously authenticated. Apparently, steric protection due to the *tert*-butyl and phenyl groups plays a critical role in the successful preparation of complexes **3** and **4**, where the substituents of the heterocyclic ligands likely block the heteroatom lone pairs (N, N, P) and prevent ruthenium from σ -coordination. This is consistent with the notion that bulky substituents in the 2- and 5-positions of the pyrrolyl and phospholyl ligands generally favor η^5 coordination of the transition metal to pyrrolyl and phospholyl ligands over σ -coordination.^{15,17a,22} In addition, the steric and electronic effects of the fragment $[\text{Cp}^*\text{Ru}^{\text{II}}]$ is the likely reason for the η^5 -1,2,4-diazaphospholide coordination, as it is known to have an extraordinary ability to form η^5 complexes with five-membered aromatic heterocycles.²³ It is interesting to note that several transition-metal complexes with 1*H*-1,2,4-diazaphospholide ligands are known, in which the metals are exclusively σ -bonding to the neutral ligands via heteroatoms.⁷

To gain a better understanding of the bonding, we have performed a series of DFT calculations followed by natural bond orbital (NBO) population analyses on the 3,5-di-*tert*-butyl-1,2,4-diazaphospholide ion as well as on complex **3**.^{12,24a,b} The calculation on the former reveals that the HOMO and HOMO-2, which differ in energy by 0.49 eV, are both π -bonding orbitals. Such characteristics are thus in favor of participating in π -bonding with orbitals of the proper symmetry from the metal and the pentamethylcyclopentadienyl ligand to form the HOMO-3 and HOMO-4 in **3**, indicating the π -orbital characteristic of bonding to ruthenium.¹² The NBO analysis of **3**

Table 1. Natural Charge Distributions of Several Ruthenium Species (NPA)

	P	N1	N2	Ru	ref
$[\text{3,5-tBu}_2\text{dp}]^-$ (1)	0.167	-0.372	-0.372		<i>a</i>
$[(\text{3,5-tBu}_2\text{dp})\text{RuCp}^*]$ (3)	0.544	-0.311	-0.310	0.24	<i>a</i>
Cp_2Ru				0.25	24c
$\text{CpRu}(\text{P}_5)$				-0.08	24c
$\text{Ru}(\text{P}_5)_2$				-0.88	24c

^a This work.

displays the populations $[\text{Kr}]5s^{0.16}4d^{7.58}5p^{0.04}$ on the ruthenium center, a negative charge of -0.31 on the 1,2,4-diazaphospholide, and a positive charge of 0.07 on the pentamethylcyclopentadienyl ligand, where a significant difference is revealed in the charge distribution between the two ligands. The more negative charge on the 1,2,4-diazaphospholide in compound **3** may therefore represent an electron-withdrawing characteristic relative to the pentamethylcyclopentadienyl ligand. With respect to the charge distribution on the metal, however, the value ($+0.24$) is very close to that ($+0.25$) in ruthenocene obtained in previous calculations.^{24c} This result may suggest that the heterocyclic ligand in **3** is a poorer donor relative to the cyclopentadienyl ligand (Table 1). Additionally, the NBO analysis results suggest that the heteroatom lone pairs rarely participate in bonding to ruthenium center.¹²

In conclusion, we present here an easy, high-yield synthetic procedure and full characterization of the first sandwich ruthenium complexes with η^5 coordination of 1,2,4-diazaphospholide ligands, whose π -coordination characteristics are demonstrated by both experimental findings and DFT calculations. The results of DFT calculations also indicated that the 3,5-di-*tert*-butyl-1,2,4-diazaphospholide ligand is a poorer electron donor relative to the pentamethylcyclopentadienyl ligand, evidenced by the longer distances of ruthenium to the 1,2,4-diazaphospholide compared to those of ruthenium to the pentamethylcyclopentadienyl ligand in **3**. Our work in this paper suggests that the η^5 -1,2,4-diazaphospholide coordination is easily accessible only with bulky groups on the heterocyclic ligands. The results of the present study therefore argue that η^5 -1,2,4-diazaphospholide ligand coordination with bulky substituents may be possible in other low-valent transition-metal complexes. We are currently exploring such 1,2,4-diazaphospholide chemistry with metals.

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Supporting Information Available: Text, tables, and figures giving synthetic procedures, analytical and spectroscopic data for **1–4**, and details of the molecular orbital calculations for the 1,2,4-diazaphospholide and **3** and a CIF file giving X-ray crystallographic data for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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