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

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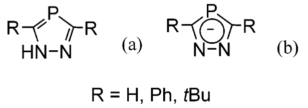
*Summary: Treatment of the 1,2,4-diazaphospholide anions $[3,5\text{-}t\mathrm{Bu_2dp}]^-$ (**1**) and $[3,5\text{-}\mathrm{Ph_2dp}]^-$ (**2**) with $[\mathrm{Cp^*RuCl}]_4$ affords the two complexes $[(\eta^5\text{-}3,5\text{-}t\mathrm{Bu_2dp})\mathrm{RuCp^*}]$ (**3**) and $[(\eta^5\text{-}3,5\text{-}\mathrm{Ph_2dp})\text{-}\mathrm{RuCp^*}]$ (**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.*

1*H*-1,2,4-Diazaphospholes have been known for more than 20 years (Chart 1).[1−5] As anions with six π electrons, the deprotonated 1*H*-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), $\eta^1(\mathrm{N_1})$:$\eta^1(\mathrm{N_2})$, $\eta^2(\mathrm{N_1,N_2})$, $\eta^1(\mathrm{N_1})$:$\eta^1(\mathrm{N_2})$:η^1(P), and $\eta^2(\mathrm{N_1,N_2})$: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 $[(\eta^1\text{:}\eta^1\text{-dp})(\mu\text{-Li})(\mathrm{DME})]_2$, 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 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.

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



Treatment of 3,5-di-*tert*-butyl-1,2,4-diazaphophole (H[3,5-*t*Bu$_2$dp])[1] and 3,5-diphenyl-1,2,4-diazaphosphole (H[3,5-Ph$_2$-dp])[1] with metallic potassium in THF (tetrahydrofuran) afforded potassium 3,5-di-*tert*-butyl-1,2,4-diazaphospholide ([3,5-*t*Bu$_2$-dp]K (**1**), 93%) and potassium 3,5-diphenyl-1,2,4-diazaphospholide−THF ($[3,5\text{-}\mathrm{Ph_2dp}]\mathrm{K}\cdot0.67\mathrm{THF}$ (**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]

[†] Dedicated to Professor Alfred Schmidpeter.

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[‡] Physical Chemistry.

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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 $[3,5\text{-}t\mathrm{Bu_2dp}]^-$ ligand.

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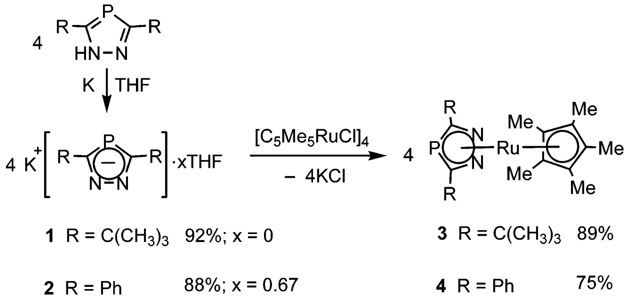
Scheme 1. Synthesis of Compounds 1−4



The reaction of $[\mathrm{Cp^*RuCl}]_4$[13] and **1** and **2** in THF smoothly gave the complexes (η^5-3,5-di-*tert*-butyl-1,2,4-diazaphospholide)(η^5-pentamethylcyclopentadienyl)ruthenium(II) ([(η^5-3,5-$t\mathrm{Bu_2dp}$)RuCp*] (**3**), 89%) and (η^5-3,5-diphenyl-1,2,4-diazaphospholide)(η^5-pentamethylcyclopentadienyl)ruthenium(II) ([(η^5-3,5-$\mathrm{Ph_2dp}$)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, (η^5-1,2,4-diazaphospholide)(η^5-pentamethylcyclopentadienyl)ruthenium(II) ([(η^5-1,2,4-dp)Ru(η^5-$\mathrm{CpMe_5}$)]), 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 $[((\mathrm{CH_3})_2\mathrm{C_3HN_2})\text{-}\mathrm{RuCp^*}]$ (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(η^5-$t\mathrm{Bu_2C_4H_2P}$)][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(η^5-$t\mathrm{Bu_2C_4H_2P}$)] (Ru−P = 2.397(1) Å),[15] [Cp*Ru(η^5-$\mathrm{Me_2Ph(Si}\text{-}i\mathrm{Pr_3)C_4P}$)] (Ru−P = 2.405(1) Å),[17a] [(η^5-$\mathrm{C_5Me_4Et}$)Ru(η^5-$\mathrm{P_5}$)] (2.43 Å (av)),[17b] and [Cp*Ru(η^5-$t\mathrm{Bu_2C_2P_2Sb}$)] (2.419(2), 2.472(2) Å)[17c] and are slightly shorter than ruthenium−nitrogen bond lengths in the sandwich complex [Ru(η^5-$\mathrm{NC_4Me_4}$)$_2$] (Ru−N = 2.1820(13) Å).[18]

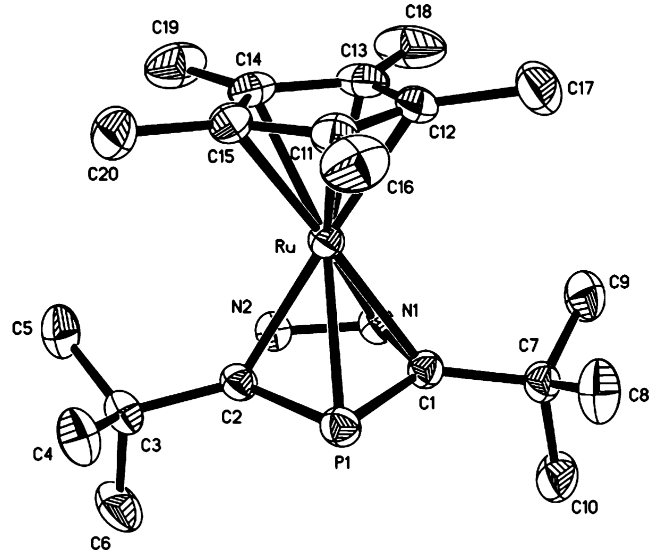


Figure 1. Molecular structure of **3** with thermal ellipsoids at the 50% probability level, as determined by a single-crystal X-ray diffraction study. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru−N(1) = 2.165(2), Ru−N(2) = 2.166(2), Ru−C(1) = 2.213(3), Ru−C(2) = 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 ^{1}H NMR ($\mathrm{C_6D_6}$, 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 $\mathrm{C_5Me_5}$ group, attributable to a rotation of the two ligand rings about their metal−ring centroid axes at room temperature.[19] The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR resonance ($\mathrm{C_6D_6}$, 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-$t\mathrm{Bu_2dp}$] (^{31}P δ +65.4 ppm) and the potassium salt **1** (^{31}P δ +50.65 ppm).[1,12] The observed significant upfield shift resonance upon ligation of the anion to transition metals in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum is generally diagnostic for the π-bonding of metals to a phosphorus atom.[15,20] The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum ($\mathrm{C_6D_6}$, 23 °C) displays resonances at δ 31.75 (s), 34.823 (d, $^2J_{\mathrm{CP}} = 30.0$ Hz, *C*CH$_3$), and 148.280 (d, $^1J_{\mathrm{CP}} = 273.0$ Hz, P*C*N) for the 1,2,4-diazaphospholide ligand of complex **3**. At δ 31.75, however, the coupling constant ($^3J_{\mathrm{CP}}$(Me)) is too small to be observed (the $^3J_{\mathrm{CP}}$(Me) coupling constant (26.8 Hz) is observed for **1**).[12,21] Surprisingly, a coupled resonance at δ 89.06 (d, $J_{\mathrm{CP}} = 26.0$ Hz) for the carbon atoms of the pentamethylcyclopentadienyl ring is observed in complex **3**,

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(12) Synthetic procedures, analytical and spectroscopic data for **1**−**4**, crystallographic data for **3**, and details of the calculations for both the [3,5-$t\mathrm{Bu_2dp}$]$^-$ ligand and **3** are contained in the Supporting Information.

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(21) The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra for H[3,5-$t\mathrm{Bu_2dp}$] and H[3,5-$\mathrm{Ph_2dp}$] have been studied, and the $^3J_{\mathrm{CP}}$(Me) coupling was reported for the former: Claramunt, R. M.; López, C.; Schmidpeter, A.; Willhalm, A.; Elguero, J.; Alkorta, I. *Spectroscopy* **2001**, *15*, 27.

presumably due to the closer distance between the interacting nuclei. The resonance at δ −58.55 in the $^{31}P\{^{1}H\}$ 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 pyrroyl and phospholyl ligands over σ-coordination.[15,17a,22] In addition, the steric and electronic effects of the fragment [Cp*Ru^{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-diazaphosphole 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** displays the populations [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]

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

	P	N1	N2	Ru	ref
[3,5-tBu$_2$dp]$^-$ (**1**)	0.167	−0.372	−0.372		*a*
[(3,5-tBu$_2$dp)RuCp*] (**3**)	0.544	−0.311	−0.310	0.24	*a*
Cp$_2$Ru				0.25	24c
CpRu(P$_5$)				−0.08	24c
Ru(P$_5$)$_2$				−0.88	24c

[a] This work.

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.

Acknowledgment. We are grateful to the National Natural Science Foundation of China (NSFC) (Grant No. 20571017) for the support of this research.

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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