

The new coordination modes of bis(1,2,4-diazaphospholy)methane



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ABSTRACT

The coordination behavior of the polydentate ligand bis(1,2,4-diazaphospholy)methane (**Bdapm**) toward group 6 and group 10 metals has been studied. From the reaction with $[\text{W}(\text{CO})_5(\text{NMe}_3)]$, three species with different coordination patterns were isolated and characterized. Thus we proved that the polydentate **Bdapm** ligand could serve as a terminal $\kappa\text{-P}$, bridging $\mu_2\text{-P,P}$ and chelating $\kappa^2\text{-N,N}$ ligand in the complexes $[\text{W}(\text{CO})_5(\kappa\text{-P}\text{-Bdapm})]$, $\{[\text{W}(\text{CO})_5]_2(\mu_2\text{-P,P}\text{-Bdapm})\}$ and $\{\text{W}(\text{CO})_4(\kappa^2\text{-N,N}\text{-Bdapm})\}$, respectively. The $\kappa^2\text{-N,N}$ chelate bonding mode has been also detected in the molybdenum(II) and nickel(II) derivatives $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\kappa^2\text{-N,N}\text{-Bdapm})(\text{CO})_2\text{Cl}]$ and $[\text{Ni}(\text{acac})_2(\kappa^2\text{-N,N}\text{-Bdapm})]$. The reaction of **Bdapm** with $[\text{M}(\text{C,N-Ar})\text{Cl}]$ fragment sources $[\text{Ar} = 2\text{-}(N,N\text{-dimethylaminomethyl})\text{phenyl}$ or $2\text{-}(N,N\text{-dimethylaminomethyl})\text{ferrocenyl}$, $\text{M} = \text{Pd}$ or Pt] gives unstable $\kappa\text{-P}$ bonded species, which are readily converted to the multimetallic complexes $\{[\text{M}(\text{C,N-Ar})\text{Cl}]_2\text{-}\mu_2\text{-P,P}\text{-Bdapm}\}$. The different coordination modes of the **Bdapm** ligand in such compounds were easily distinguished by multinuclear NMR spectroscopy. The crystal structures of five transition metal complexes demonstrating the coordination variability of **Bdapm** are reported. On inspection of the acquired data it is evident that the stability of the studied species increases in the order of the binding modes $\kappa\text{-P} < \mu_2\text{-P,P} < \kappa^2\text{-N,N}$.

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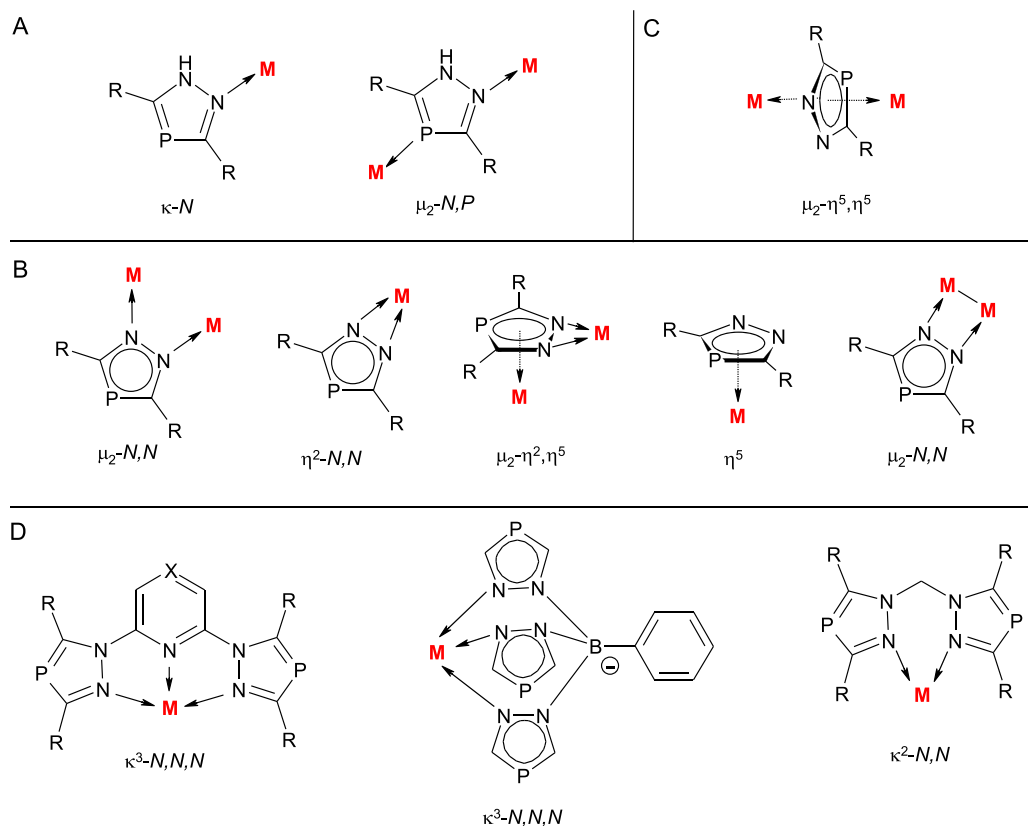
1. Introduction

The first routes to substituted 1,2,4-diazaphospholes (*dap*), reported in 1984, were based on the [3+2] cycloaddition of phosphalkynes or their precursors to diazoalkanes [1,2]. At the same time Schmidpeter and Willhalm presented the reaction of the Vilsmeier reagent, $\text{P}(\text{SiMe}_3)_3$, and hydrazine which yielded the unsubstituted 1*H*-1,2,4-diazaphosphole [3]. After more than 30 years, *dap* chemistry has undergone a renaissance due to large-scale availability of $\text{P}(\text{SiMe}_3)_3$ [4,5], a versatile source of phosphorus in heterocycle syntheses, and due to the development of a general route to various 1*H*-1,2,4-diazaphospholes [6]. As *dap* contains both hard (N) and soft (P) donor atoms, it is a unique representative of hybrid ligands. The first report dealing with *dap* coordination behavior described its reaction with group 6 carbonyl derivatives [7]. In the resulting adducts the *dap* ligand serves as a terminal $\kappa\text{-P}$ or bridging $\mu_2\text{-N,P}$ ligand, see Scheme 1A. The 1*H*-1,2,4-diazaphosphole molecule could be easily deprotonated to give stable heteroaromatic systems resembling the cyclopentadienyl ligand. The diazaphospholide anion shows multiple binding modes and various complexes with $\kappa\text{-N}$, $\mu_2\text{-N,N}$, $\eta^2\text{-N,N}$ and η^5 -bonded *dap* anions have been described (1B) [7–9].

In particular cases the *dap* anion is able to enforce a very short metal–metal bond by $\mu_2\text{-N,N}$ coordination in paddlewheel shaped dibismuthanes [10]. Diazaphospholide complexes, where a five-membered heterocycle connects two metals in the $\mu_2\text{-}\eta^2,\eta^5$ or $\mu_2\text{-}\eta^2,\eta^4$ mode, have been reported very recently [9,11,12]. The *dap* ligand and its derivatives undergo a two-electron reduction giving a stable radical dianion which, after coordination toward two potassium cations, yields an unusual “inverse sandwich” structure (1C) [13]. Recent studies demonstrated that the *dap* anion is a useful synthon for building larger molecules behaving as polydentate ligands. Those comprise *dap*-substituted pyridines or pyrazines, [14] bis(diazaphospholy)methanes (**Bdapm**) [15] and tris(diazaphospholy)borates (**PhTdap**) [16]. These ligands are able to coordinate transition and non-transition metals, but exclusively as nitrogen donors (1D). It should be noted that from more than fifty structures deposited in the Cambridge Structural Database only in a single molecule, $\{[\text{Cr}(\text{CO})_5]_2(\mu_2\text{-N,P}\text{-C}_2\text{H}_3\text{N}_2\text{P})\}$, has a dative phosphorus–metal bond been detected [7]. Our previous work demonstrated that the phosphorus atom of the aromatic diazaphospholide ring in the **PhTdap** ligand is inert and does not tend to coordinate transition metals. However in the case of the complex $[\text{Pd}(\text{C,N-dmba})(\kappa^2\text{-N,N}\text{-PhTdap})]$ [*dmba* = 2-(*N,N*-dimethylaminomethyl)phenyl], bearing a pendant *dap* ring with significant diene character, interaction with nickel(0) species was detected by ^{31}P CP/MAS NMR [16]. On inspection of these data, it

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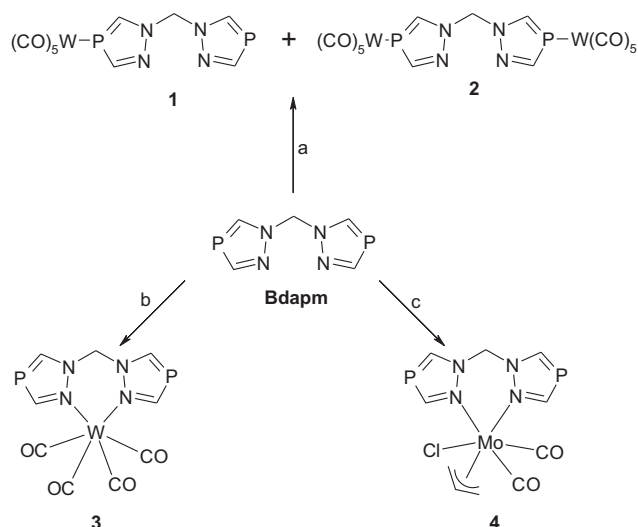
Scheme 1. Coordination modes known for *dap* based ligands: (A) neutral 1*H*-1,2,4-diazaphosphole, (B) diazaphospholide anion, (C) diazaphospholide radical dianion, (D) molecules bearing more than one *dap* ring (*X* = N or CH).

is evident that anionic diazaphospholides prefer bonding *via* the nitrogen atoms or through the heteroaromatic π -system, whereas the corresponding neutral heterocyclic diene could also serve as a phosphorus donor toward certain transition metals. Therefore, we set to study the coordination properties of the neutral **Bdapm** ligand, with the view to prepare metal complexes in which the *dap* ring is bonded *via* the phosphorus atom. Herein we report the synthesis, spectroscopic and structural characterization of group 6 and group 10 metal species coordinated with the **Bdapm** ligand.

2. Results and discussion

Pure **Bdapm** was prepared in high yield from 1*H*-1,2,4- λ^3 -diazaphosphole and dichloromethane following the procedure known for the synthesis of bis(pyrazolyl)methane [17]. The melting point and NMR spectra are identical to those reported previously [15]. Its characteristic IR and Raman bands are due to aromatic (strong band at $\sim 3064\text{ cm}^{-1}$) and aliphatic (medium band at 2971 cm^{-1}) CH stretching modes. The most intense Raman absorption at 901 cm^{-1} (IR: 896 cm^{-1}) was assigned to an out-of-plane CH deformation, a band typical for the presence of an isolated CH moiety in various heterocycles and polysubstituted benzenes [18]. The electronic spectrum in the UV–Vis region showed two bands at 258 and 228 nm, attributable to π – π^* transitions of the *dap* rings.

The reaction of **Bdapm** with $[\text{W}(\text{CO})_5(\text{NMe}_3)]$ gives a mixture of products separable by column chromatography, see Scheme 2. The major product ($\sim 70\%$) has been identified as the complex $\{[\text{W}(\text{CO})_5]_2(\mu_2\text{-}P,P\text{-Bdapm})\}$ (2) with the bridging ligand coordinated toward two $\text{W}(\text{CO})_5$ fragments *via* phosphorus atoms. The second compound ($\sim 10\%$) obtained from this reaction was



Scheme 2. The preparation of group 6 compounds. (a) $[\text{W}(\text{CO})_5(\text{NMe}_3)]$, (b) $[\text{W}(\text{CO})_4(1,5\text{-cod})]$, (c) $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{MeCN})_2(\text{CO})_2\text{Cl}]$.

$[\text{W}(\text{CO})_5(\kappa\text{-}P\text{-Bdapm})]$ (1), containing one *P*-bound $\text{W}(\text{CO})_5$ group. We have also isolated small amounts ($<2\%$) of a third complex, $\{[\text{W}(\text{CO})_4(\kappa^2\text{-}N,N\text{-Bdapm})]\}$ (3), where **Bdapm** acts as an *N,N*-chelator. The yield of each complex could be modified by the reaction conditions. Using hexane at ambient temperature and a 1:1 ligand-to-metal stoichiometry affords 1 in yields up to 60%, whereas the reaction in boiling MeCN almost exclusively gives complex 3. Chelate 3 is also accessible by the reaction of **Bdapm** with $[\text{W}(\text{CO})_4(1,5\text{-cod})]$. Both 1 and 2 are solids dissolvable in

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