Selective P-4 activation by an organometallic nickel(I) radical: formation of a dinuclear nickel(II) tetraphosphide and related di- and trichalcogenides

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Selective $P_4$ activation by an organometallic nickel(II) radical: formation of a dinuclear nickel(II) tetraphosphide and related di- and trichalcogenides

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The reaction of the 17e nickel(II) radical [CpNi(IDipp)] (1, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) with $P_4$ results in a nickel tetraphosphide [[CpNi(IDipp)]$_2$(μ-$\eta^1$-$\eta^1$-$P_4$)] with a butterfly-$P_4^{2-}$ ligand; related chalcogenides [[CpNi(IDipp)]$_2$(μ-$E_3$)] (E = S, Se, Te) and [[CpNi(IDipp)]$_2$(μ-$E_3$)] (E = S, Se) are formed with $S_8$, $S_{18}$, and $Te_{18}$.

The $P_4$ molecule is the most reactive allotrope of phosphorus; its activation and transformation by transition metal compounds has attracted substantial interest over the years. While many low-valent metal complexes, e.g. transition metal carbynls or anionic metalates, react with $P_4$, it is still challenging to design highly selective transformations.

White phosphorus is able to efficiently trap organic and main group element radicals. Therefore, one potential solution to the selectivity issue is to use a radical pathway in transition metal mediated $P_4$ transformations. While 2nd and 3rd row metal radicals are well-established, nickel(II) radicals have attracted significant attention recently. Importantly, Driess et al. have shown that reactions of β-diketiminato nickel(II) complexes with $P_4$ yield dinuclear complexes [CpNi($\mu$-$\eta^1$-$\eta^1$-$P_4$)]$_2$ with R = Et, iPr. The P-P bond activation in the doubly $\eta^1$-coordinated ligand is reversible and occurs without the reduction of $P_4$ to formally $P_4^{2-}$.

We have been interested in designing new reactive nickel(II) radicals for element–element bond activations. We now report the synthesis of complexes 1–3 featuring an NHC and a cyclopentadienyl ligand, and an initial reactivity study of complex 1 with $P_4$ and related small molecules.

Complexes 1–3 are accessible according to Scheme 1 by the reduction of the appropriate nickel(II) halides with KC$_8$ in THF. $^1$H NMR monitoring shows that 1–3 are formed very selectively; they can be isolated as yellow crystalline solids in modest to high yields. Single X-ray structure analyses (ESI‡) revealed that the nickel centre is surrounded by the carbene carbon and one $\eta^1$-coordinated Cp or Cp* moiety. No further significant interactions between nickel and the diisopropylphenyl groups are apparent. Nonetheless, the cyclopentadienyl ligand is tilted with respect to the nickel carbene bond with an angle C(carbene)–Ni–(C$_5$R$_5$)centroid of 154.3(1), and 2.2(1)°.

Cyclic voltammograms show one electrochemically quasi-reversible wave at $E_{1/2} = -1.02$ and $-1.06$ V vs. Fe/Fe$^+$ for Cp-substituted 1 and 2, respectively, and a reversible wave at $-1.18$ V vs. Fe/Fe$^+$ for the Cp* complex 3 (ESI§). UV/vis-spectroelectrochemistry (see Fig. 1 for 1) confirms that these processes correspond to chemically reversible oxidations of neutral 1–3 to stable cationic nickel(II) complexes, which probably bind THF in the case of 1 and 2. Indeed, the preparative oxidation of 1 with [Cp$_2$Fe]$PF_6$ affords the THF adduct [[C$_8$H$_8$]Ni(IDipp)(THF)]$PF_6$ (1-THF) (ESI‡).

Complexes 1–3 show identical magnetic moments of 3.7, 3.1, and 2.2(1) μ$_B$ in [D$_8$]THF, which indicate the presence of one unpaired electron per molecule. The EPR spectrum of 1 is characteristic for an $S = 1/2$ system and reveals a rhombic g-tensor with significant deviations from g$_{xx}$ pointing to metalloradical character. DFT calculated g$_{xx}$ and g$_{yy}$ values are somewhat smaller than the experimental ones, but show a similar rhombicity (Fig. 1).
Initial reactivity studies of 1 established its behavior as a typical metal-centered radical. The reactions of phenyl disulfide and TEMPO with 1 in THF afforded the known thiolate [(C₅H₅)Ni(SPh)(IDipp)] (4)⁹ and the new TEMPO adduct 5 in quantitative yield (Fig. 2). The molecular structure of 5 shows a side-on η²-coordinated TEMPO ligand and an η¹-coordinated Cp ligand at the distorted square planar nickel(II) atom. The structural parameters agree with presence of a formally anionic TEMPO⁻ ligand.¹⁰ A sharp ¹H NMR singlet at 5.93 ppm is observed for the Cp moiety even at −90 °C presumably due to rapid haptotropic migration.

We next investigated the reactivity of 1 with the heavier chalcogens. The reaction with S₈ (1/8 equivalents) gave the blue disulfide 6-S and the purple trisulfide 7-S (Fig. 3) in a 7:3 ratio according to ¹H NMR analysis. 6-S is soluble in n-hexane and diethyl ether and can thus be separated from 7-S by extraction and subsequent crystallisation (ESI‡). Disulfide-bridged dinuclear complexes with an M–S–S–M motif are well-known,¹¹ while complexes with an unsupported μ-S₃²⁻ bridge are still rather scarce.¹¹a,b,12 The structure of 7-S shows a similar S₁–S₂–S₃ angle and S–S bond lengths as the structure of [(C₅H₅)Fe(CO)₂]₂(μ-S₃).¹¹a Diselenide 6-Se (31% isolated) is the major reaction product of 1 with one equivalent of elemental selenium. A ¹H NMR spectrum of the reaction mixture (THF, room temperature) shows that 6-Se is formed in more than 80% yield whereas the triselenide 7-Se is a minor by-product. Ditelluride 6-Te was the only product to be detected after stirring 1 with one equivalent of grey tellurium for seven days. It was isolated as a dark brown crystalline solid in 31% yield. The molecular structures of 6-Se, 6-Te and 7-Se are analogous to the corresponding sulfides 6-S and 7-S (ESI‡).

Considering that a mixture of at least two products is formed with sulfur and selenium, it was gratifying to discover that complex 1 reacts with P₄ in a highly selective fashion in THF at room temperature, giving tetraphosphide 8 as the sole product. The reaction is instantaneous, and compound 8 can be isolated as an analytically pure, dark purple powder in quantitative yield simply by removing the solvent. Its molecular structure (Fig. 3)
shows an exo/exo configuration for the two \([\text{C}_{5} \text{H}_{5}]_{2} \text{Ni(IDipp)}\) units. The P-P bond lengths (2.2111(7)–2.2334(7) Å) are very similar to those in P$_4$ (P–P 2.21 Å). The $^{31}$P{1H} NMR spectrum shows two triplets at $\delta = -307.4$ and $-45.8$ ppm with $^{1}J_{P-P} = -190.5$ Hz. These values are similar to those of \([\text{Cp}^*\text{NiFe(CO)}_{3}]_{2} \mu_{\eta^{1}}\eta^{1}-\text{P}_4\] and \([\text{Cp}^*\text{Cr(CO)}_{3}]_{2} \mu_{\eta^{1}}\eta^{1}-\text{P}_4\] as well as a tetraphosphate-1.0-bicyclooctane framework.\(^1\)

In conclusion, we have prepared rare mononuclear cyclopentadienyl nickel(i) complexes 1–3 with significant metallo-radical character.\(^6\)^\(^7\) This feature was successfully utilized for the high-yield synthesis of the novel tetraphosphido complex \([\text{C}_{5} \text{H}_{5}]_{2} \text{Ni(IDipp)}\) \(\mu_{\eta^{1}}\eta^{1}-\text{P}_4\] (8), which features an uncommon $\mu_{\eta^{1}}\eta^{1}$-bridging $\text{P}_4^{2-}$ ligand.\(^1\)\(^4\) Further reactivity studies of 1–3 and 8 are in progress; the results will be reported in due course.

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Notes and references
§ During the preparation of this manuscript, Hazari et al. reported the synthesis and characterization of 1, 1-THF and closely related mono- and dinuclear species by a different synthetic route.\(^7\) Based on DFT calculations, the bending of the $\text{C}_{5} \text{H}_{5}$-Ni-$\text{C}_{5} \text{H}_{5}$ centroid angle in the structure of 1 was attributed to the asymmetric spin density distribution.
¶ The hydride complex \([\text{C}_{5} \text{H}_{5}]_{2} \text{Ni(IDipp)}\) (1-H) was identified as a minor by-product (<5%) of the synthesis of 1. Compound 1-H was prepared independently and features a distinct molecular structure from 1; see the ESF for details.

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