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

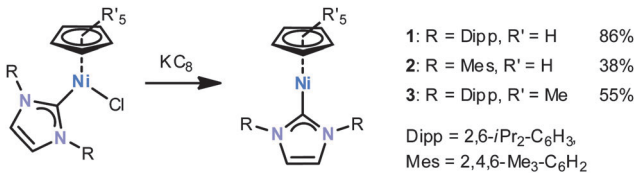
Stefan Pelties,[a] Dirk Herrmann,[a] Bas de Bruin,[b] František Hartl[c] and Robert Wolf*[a]

The reaction of the 17*e* nickel(I) radical [CpNi(IDipp)] (1, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) with P_4 results in a nickel tetraphosphide $[\{CpNi(IDipp)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ with a butterfly-P_4^{2-} ligand; related chalcogenides $[\{CpNi(IDipp)\}_2(\mu\text{-}E_2)]$ (E = S, Se, Te) and $[\{CpNi(IDipp)\}_2(\mu\text{-}E_3)]$ (E = S, Se) are formed with S_8, Se_∞ and Te_∞.

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.[1] While many low-valent metal complexes, *e.g.* transition metal carbonyls or anionic metalates, react with P_4, it is still challenging to design highly selective transformations.[2,3]

White phosphorus is able to efficiently trap organic and main group element radicals.[4] 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 metalloradicals are well-established,[5] nickel(I) radicals have attracted significant attention recently.[6,7] Importantly, Driess *et al.* have shown that reactions of β-diketiminato nickel(I) complexes with P_4 yield dinuclear complexes $[(L^RNi)_2(\mu\text{-}\eta^3{:}\eta^3\text{-}P_4)]$ (L^R = HC[CMeN(2,6-$R_2C_6H_3$)]$_2$ with R = Et, iPr).[8] The P–P bond activation in the doubly η^3-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(I) 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.



Scheme 1 Synthesis of nickel(I) complexes **1**–**3**.

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 η^5-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–$(C_5R_5)_{centroid}$ of 154.3(1)° for **1**, 151.9(1)° for **2** and 164.6(1)° for **3**.§

Cyclic voltammograms show one electrochemically quasi-reversible wave at $E_{1/2}$ = −1.02 and −1.06 V *vs.* Fc/Fc$^+$ for Cp-substituted **1** and **2**, respectively, and a reversible wave at −1.18 V *vs.* Fc/Fc$^+$ 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 $[Cp_2Fe]PF_6$ affords the THF adduct $[(C_5H_5)Ni(IDipp)(THF)]PF_6$ (**1-THF**) (ESI‡).§

Complexes **1–3** show identical magnetic moments of 2.3(1), 2.3(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_e pointing to metalloradical character. DFT calculated g_{11} and g_{22} values are somewhat smaller than the experimental ones, but show a similar rhombicity (Fig. 1).

[a] *University of Regensburg, Institute of Inorganic Chemistry, 93040 Regensburg, Germany. E-mail: robert.wolf@ur.de*
[b] *University of Amsterdam, Van't Hoff Institute for Molecular Sciences, Science Park 904, 1098 XH Amsterdam, The Netherlands*
[c] *University of Reading, Department of Chemistry, Whiteknights, Reading, RG6 6AD, UK*

† Dedicated to the memory of Prof. Michael F. Lappert.

‡ Electronic supplementary information (ESI) available. Full experimental details, electrochemical, EPR and crystallographic data. CCDC 995931–995941 and 999501. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc02601b

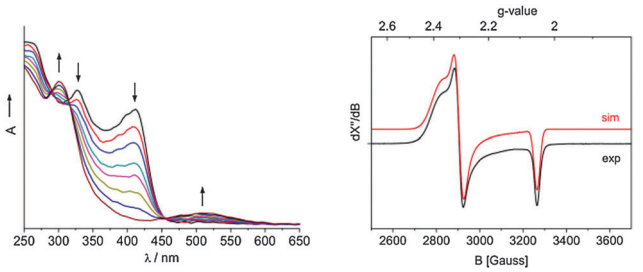


Fig. 1 Left: UV/Vis monitoring of the oxidation of **1** performed at −0.83 V *vs.* Fc/Fc^+ within an OTTLE cell equipped with a Pt minigrid working electrode, THF/TBAH under Ar, 293 K. Right: experimental and simulated X-band EPR spectrum of **1** in frozen THF. Freq. 9.3646 GHz, 0.063 mW, 20 K, mod. 4 Gauss; *g*-tensor parameters obtained from simulations and DFT calculations (b3-lyp, def2-TZVP) are: g_{11} = 2.377 (2.220), g_{22} = 2.306 (2.187), g_{33} = 2.050 (2.078) (DFT-calculated values in parentheses).

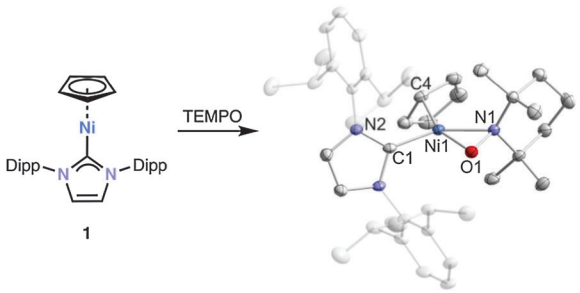
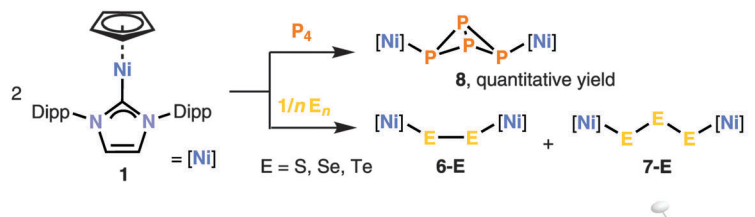


Fig. 2 Reaction of **1** with TEMPO and solid-state molecular structure of $[(C_5H_5)Ni(TEMPO)(IDipp)]$ (**5**). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°]: Ni1–O1 1.8408(14), Ni1–N1 1.9581(16), N1–O1 1.3989(20), Ni1–C1 1.8824(19), Ni1–C4 2.034(2), C1–Ni1–O1 104.50(7), O1–Ni1–N1 43.07(6), C1–Ni1–C4 97.104(4), N1–Ni1–C4 115.325(2).

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 $[(C_5H_5)Ni(SPh)(IDipp)]$ (**4**)[9] and the new TEMPO adduct **5** in quantitative yield (Fig. 2). The molecular structure of **5** shows a side-on η^2-coordinated TEMPO ligand and an η^1-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 S_8 (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-S_3^{2-} 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 $[\{(C_5H_5)Fe(CO)_2\}_2(\mu\text{-}S_3)]$.[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 P_4 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)



^1H NMR yield (isolated yield)		
E_n	6-E	7-E
S_8	70% (45%)	30% (15%)
Se_∞	82% (31%)	6% (/)
Te_∞	quant.(31%)	/

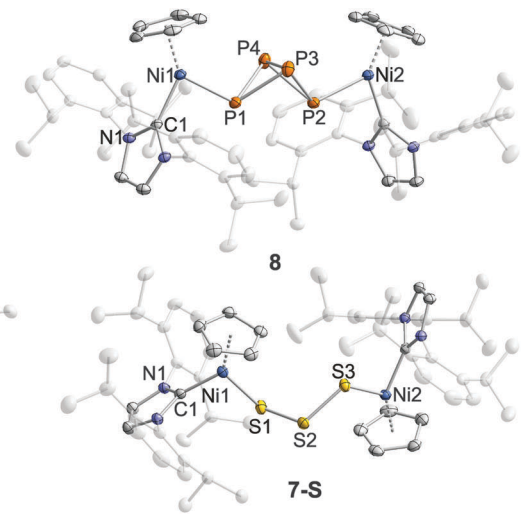


Fig. 3 Left: reactions of **1** with P_4, S_8, Se_∞ and Te_∞. Right: solid-state molecular structures of the products **6-S**, **7-S** and **8**. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°]: **6-S**: Ni1–S1/Ni2–S2 2.1800(1)/2.1797(1), S1–S2 2.0476(1), Ni1–S1–S2–Ni2 78.601(5), **7-S**: Ni1–S1/Ni2–S3 2.1936(6)/2.1748(5), S1–S2/S2–S3 2.0561(7)/2.0522(7), S1–S2–S3 111.58(3), **8**: Ni1–P1/Ni2–P2 2.2107(6)/2.2103(6), P1–P3/P4 2.2334(7)/2.2111(7), P3–P4 2.1649(7), P1–P2 2.8897(8).

shows an *exo*/*exo* configuration for the two [(C_5H_5)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 δ = −307.4 and −45.8 ppm with $^1J_{P-P}$ = −190.5 Hz. These values are similar to those of [$\{Cp^RFe(CO)_2\}_2$-(μ-η^1:η^1-P_4)] (Cp^R = C_5H_3-1,3-*t*Bu_2, C_5H_2-1,2,4-*t*Bu_3, C_5H-iPr_4, C_5Me_5) and [$\{Cp^*Cr(CO)_3\}_2$(μ-η^1:η^1-P_4)], which also display a tetraphospha-[1.1.0]bicyclobutane framework.[13]

In conclusion, we have prepared rare mononuclear cyclopentadienyl nickel(I) complexes **1–3** with significant metalloradical character.[6,7] This feature was successfully utilized for the high-yield synthesis of the novel tetraphosphido complex [$\{(C_5H_5)$Ni(IDipp)$\}_2$(μ-η^1:η^1P_4)] (**8**), which features an uncommon μ-η^1:η^1-bridging P_4^{2-} ligand.[14] 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 $C_{carbene}$–Ni–$(C_5H_5)_{centroid}$ angle in the structure of **1** was attributed to the asymmetric spin density distribution.
¶ The hydride complex [(C_5H_5)NiH(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 ESI‡ for details.

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14 For related work on P_4 activation by Ni^0 complexes, see: B. Zarzycki, T. Zell, D. Schmidt and U. Radius, *Eur. J. Inorg. Chem.*, 2013, 2051, and literature cited therein.

