New pincer-type diphosphinito (POCOP) complexes of Ni^{II} and Ni^{III} †

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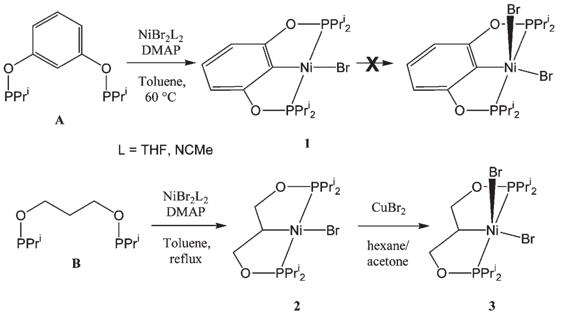
Received (in Berkeley, CA, USA) 21st September 2006, Accepted 14th November 2006
First published as an Advance Article on the web 12th December 2006
DOI: 10.1039/b613812h

This communication reports the synthesis and characterization of the new, pincer-type, square-planar, 16-electron compounds {2,6-($OPPr^i_2$)$_2$$C_6H_3$}$Ni^{II}$Br, 1, and {($Pr^i_2POCH_2$)$_2$CH}$Ni^{II}$Br, 2, and the square-pyramidal, 17-electron complex {($Pr^i_2POCH_2$)$_2$CH}$Ni^{III}Br_2$, 3.

Transition metal complexes featuring PCP or POCOP type pincer ligands can promote unusual stoichiometric transformations[1] and exceptionally efficient catalytic processes.[2,3] Curiously, most PCP and POCOP complexes reported to date are based on 4d and 5d metals, while the chemistry of analogous complexes based on 3d metals remains underdeveloped. Our interest in the chemistry of organonickel complexes[4] and the exciting results reported by van Koten's group[5] on NCN–Ni compounds inspired us to investigate the reactivities of the PCP–Ni and POCOP–Ni complexes. In earlier reports, we have described the chemistry of the $PC_{sp^2}P$–Ni^{II} species {1,3-($Ph_2PCH_2CH_2$)$_2$indenyl}NiCl[6] and the $PC_{sp^3}P$–Ni^{II} complexes {($Bu^t_2PCH_2CH_2$)$_2$CH}NiX (X = Cl, Br, I, Me, H) and [($Bu^t_2PCH_2CH_2$)$_2$CH)NiL]$^+$ (L = $NCCH_3$, $NCCH{=}CH_2$).[7] PCP–Ni^{II} complexes have also been reported by other groups.[8]

As an extension to our earlier studies, we have set out to explore the synthesis and reactivities of Ni complexes based on the diphosphinito type $POC_{sp^2}OP$ and $POC_{sp^3}OP$ ligands (**A** and **B** in Scheme 1) in order to probe the influence of ligand electronics on the structures and reactivities of these closely related families of pincer complexes. Herein we report our preliminary results on the synthesis and full characterization of the compounds {2,6-($OPPr^i_2$)$_2$$C_6H_3$}$Ni^{II}$Br (**1**) and {($Pr^i_2POCH_2$)$_2$CH}$Ni^{II}$Br (**2**), the oxidation of the latter to the pentacoordinated 17-electron species {($Pr^i_2POCH_2$)$_2$CH}$Ni^{III}Br_2$ (**3**), and the promotion by **3** of the Kharasch type addition of CCl_4 to olefins. Related POCOP–Ni^{II} [9] and PNCNP–Ni^{II} [10] complexes have also been reported recently.

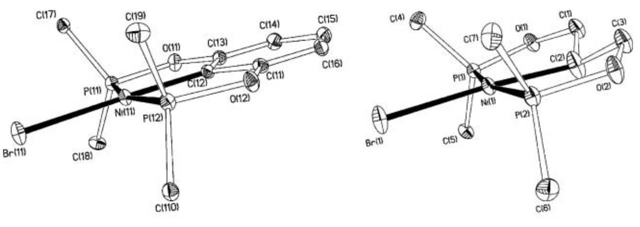
Stirring a toluene solution of $NiBr_2(THF)_2$ and ligand **A** at room temperature for 1 h gave complex **1** as a yellow solid in 80% yield. The yield of this reaction can be increased to 95% by adding 4-dimethylaminopyridine (DMAP) to the reaction mixture and heating it to *ca.* 60 °C for 1 h (Scheme 1). The analogous reaction of $NiBr_2(THF)_2$ with ligand **B** in the presence of DMAP gave complex **2** in 60–65% yield after a 5 h reflux; alternatively, **2** can be obtained in 90–93% yields if $NiBr_2(NCCH_3)_2$ is used as the Ni precursor.



Scheme 1

The diamagnetic complexes **1** and **2** were identified readily on the basis of their NMR spectra. For instance, their $^{31}P\{^1H\}$ NMR spectra displayed singlet resonances at δ 188 ppm (**1**) and 186 ppm (**2**) for two equivalent P nuclei, in accord with the *trans* disposition of the Pr^i_2P moieties in these compounds. The ^1H NMR spectrum of **1** showed only one signal for the four equivalent methyne protons and two signals corresponding to the non-equivalent methyl groups in each Pr^i moiety; these features are consistent with the presence of a mirror plane encompassing the square plane and the planar aromatic system of the ligand backbone. In complex **2**, on the other hand, the non-planar aliphatic linker system breaks the symmetry relating the groups above and below the coordination plane, thus giving rise to two signals for the non-equivalent methyne protons and four signals for the non-equivalent methyl groups in each Pr^i_2 moiety. The $^{13}C\{^1H\}$ NMR spectra of **1** and **2** were also consistent with these symmetry considerations. Moreover, these spectra showed the characteristic virtual triplets for *C*–P–O–*C* and for the metallated carbon nuclei.

The solid-state structures of **1** and **2** have been elucidated by single-crystal X-ray diffraction studies (Fig. 1).‡ The overall



1 **2**

Fig. 1 ORTEP diagrams for complexes **1** and **2**. Thermal ellipsoids are shown at the 30% probability level. Methyl groups and hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Ni–C2 1.885(3) (**1**), 1.964(3) (**2**); Ni–P1 2.1534(8) (**1**), 2.1574(8) (**2**); Ni–P2 2.1422(8) (**1**), 2.1527(8) (**2**); Ni–Br1 2.3231(5) (**1**), 2.3458(5) (**2**); C2–Ni–Br1 178.10(8) (**1**), 176.29(14) (**2**); P1–Ni–P2 164.92(4) (**1**), 166.50(3) (**2**).

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† Electronic supplementary information (ESI) available: Complete experimental details on the synthesis and characterization of complexes **1**, **2** and **3**, the electrochemical studies, and the Kharasch additions. See DOI: 10.1039/b613812h

geometry around the Ni centre in both complexes is square planar, the largest distortions arising from the P–Ni–P angles of *ca.* 166°. The Ni–P distances are fairly symmetrical in **1** and **2** (2.14–2.16 Å) and slightly shorter than the corresponding distances in the related complexes $\{(^tBu_2PCH_2CH_2)_2CH\}NiBr$[7] and $(2,6\text{-}(NHPBu^t)_2\text{-}C_6H_3)NiCl$[7] (*ca.* 2.20–2.21 Å). The Ni–C bonds also follow the same trend, being somewhat shorter in **1** (*ca.* 1.89 Å) *vs.* its $PNC_{sp^2}NP$ analogue (*ca.* 1.91 Å),[10] and in **2** (*ca.* 1.96 Å) *vs.* its $PC_{sp^3}P$ analogue (*ca.* 1.97 Å).[7] The generally shorter Ni–L distances in **1** and **2** relative to the analogous PCP– and PNCNP–Ni complexes may be attributed to the increased π-acidity of the OPR_2 moieties in **1** and **2**.

Complexes **1** and **2** are stable to atmospheric oxygen and moisture in the solid state and thermally stable up to 200 °C in DMF solutions. Cyclic voltammetry measurements showed, however, that both complexes can be oxidized. Thus, **1** undergoes a quasi-reversible single-electron oxidation ($E_{1/2}$ = 1.17 V; Fig. 2), implying that a Ni^{III} species derived from **1** should, in principle, be accessible. The single-electron oxidation of **2** was even more facile but irreversible (E_{ox} = 0.88 V). Significantly, a second oxidation was also detected for this complex, implying that Ni^{IV} species might be accessible under certain conditions. We found that the large-scale oxidation of **2** proceeds in nearly quantitative yield in the presence of $CuBr_2$ to give a paramagnetic product identified as the pentacoordinated Ni^{III} complex $(POC_{sp^3}OP)NiBr_2$ (**3**) (Scheme 1). Unfortunately, however, our efforts at preparing d^7 $POC_{sp^2}OP$–Ni compounds (by one-electron oxidation of **1**) or d^6 $POC_{sp^3}OP$–Ni compounds (by two-electron oxidation of **2**) were unsuccessful.

The dark red, air-stable crystals of **3** are freely soluble in almost all solvents but only sparingly soluble in hexane. That complex **2** is thermodynamically more stable than **3** is inferred from the observation that red solutions of the latter undergo a color change to yellow over 2 days, forming the diamagnetic parent complex. The characterization of **3** was as follows. Consistent with its (formal) 17-electron count, complex **3** displayed no ^{31}P NMR signal and its ^1H NMR spectrum showed significantly broadened signals. The paramagnetism of **3** was also confirmed by the Evans NMR method: analysis of a 10^{-3} M $CDCl_3$ sample of **3** gave an approximate value of 1.73 μ_{eff}, corresponding to one unpaired electron per molecule at 23 °C.[11]

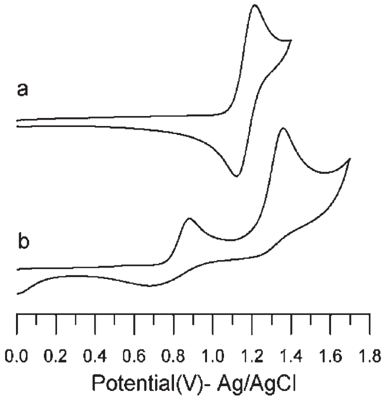


Fig. 2 Cyclic voltammetry scans of 10^{-3} M solutions of **1** (a) and **2** (b) at a Pt electrode in acetone (0.1 M Bu_4NPF_6, scan rate 0.20 V s^{-1}).

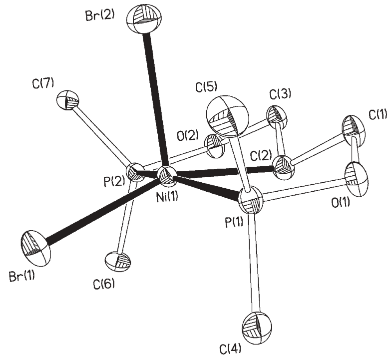
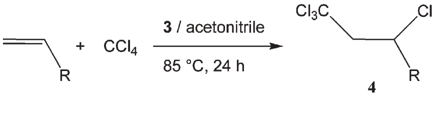


Fig. 3 ORTEP diagram for **3** $(POC_{sp^3}OP)NiBr_2$ complex. Thermal ellipsoids are shown at the 30% probability level. Methyl groups and hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Ni–C2 2.011(5), Ni–P1 2.235(1), Ni–P2 2.251(1), Ni–Br1 2.3683(9), Ni–Br2 2.436(1); C2–Ni–Br1 157.09(15), P1–Ni–P2 160.57(6).

An X-ray diffraction analysis of **3** showed that it is the square-pyramidal pincer complex shown in Fig. 3.‡ The Ni atom is displaced out of the basal plane (defined by the atoms C2, P1, P2 and Br1) in the direction of the apical atom Br(2) by 0.0972 Å. The angular structural parameter τ for the solid structure of **3** was calculated to be 0.05,§ implying only a small degree of distortion towards a trigonal bipyramidal geometry.[12] By comparison, the $NCN\text{–}Ni^{III}(I)_2$ complex reported by van Koten displayed a greater trigonal distortion (τ ~ 0.25).[5a] The bond distances for Ni–C2 (2.011(5) Å) and Ni–P (average 2.243(1) Å) in **3** are *ca.* 0.088 Å longer than the corresponding distances in the four-coordinate Ni(II) complex **2**, presumably reflecting the greater coordination number of the metal center (5 *vs.* 4) and the partial population of the antibonding d_{z^2} orbital (SOMO). A similar lengthening of $Ni\text{–}L_{basal}$ bonds was also observed for van Koten's $NCN\text{–}Ni^{III}(I)_2$ complex.[5a] The much longer Ni–Br distance for the apical Br (2.44 *vs.* 2.37 Å) is consistent with a similar observation in the structure of $NiBr_3(PPhMe_2)_2$,[13] whereas the two Ni–I bond distances in van Koten's $NCN\text{–}Ni^{III}(I)_2$ complex are fairly similar (2.61 and 2.63 Å).[5a]

In order to compare the reactivities of **3** to van Koten's NCN–Ni^{III} species,[5e,f] we have evaluated the effectiveness of complex **3** for promoting the addition of CCl_4 to alkenes (Kharasch addition, eqn (1)).



(1)

The reaction of 0.1 mol% of **3** with CCl_4 and styrene, 4-methylstyrene, or methyl methacrylate in refluxing acetonitrile gave 95–97% isolated yields of the addition product **4**; significantly, no telomerisation or polymeric products were detected.[5f] Lower yields were obtained for the addition to acrolein (85%), methyl acrylate (80%) and acrylonitrile (65%).

As observed in the Kharasch additions promoted by the NCN–Ni^{III} species, the additions promoted by **3** had to be carried out in the absence of O_2 to prevent the quenching of the intermediate organic radicals. Moreover, complex **3** could be generated *in situ* from the Ni^{II} species **2** in air; the addition reaction was then carried out under anaerobic conditions. In contrast to the case of the

NCN–Ni^{III} systems, the Kharasch additions promoted by complex **3** do not proceed at room temperature, presumably because of the greater steric bulk of the phosphinite moieties in **3**.

In conclusion, complexes **1** and **2** can be prepared *via* simple C–H bond activation reactions, and the facile oxidation of **2** to **3** gives access to the first Ni^{III} derivative of POCOP type pincer complexes. The easy access to **3** and its effectiveness in promoting the Kharasch addition bode well for further developments in the chemistry of POCOP–Ni complexes.

The authors gratefully acknowledge NSERC of Canada for financial assistance of these studies.

Notes and references

‡ *Crystal data* for complexes **1–3**. **1**: $C_{18}H_{31}BrNiO_2P_2$, M = 479.99, triclinic, space group $P\bar{1}$, a = 12.9840(3), b = 13.0363(3), c = 13.4366(3) Å, α = 78.494(2), β = 77.305(1), γ = 88.467°, V = 2173.79(9) Å^3, T = 100 K, Z = 4, μ(Cu-Kα) = 4.889 mm^{-1}, 26 424 reflections measured, 8305 unique (R_{int} = 0.034), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0358, $wR2$ = 0.084; R indices (all data): $R1$ = 0.0482, $wR2$ = 0.0875. CCDC 620341. **2**: $C_{15}H_{33}BrNiO_2P_2$, M = 445.97, orthorhombic, space group $P2_12_12_1$, a = 8.7081(1), b = 13.9372(2), c = 17.1214(2) Å, V = 2077.97(5) Å^3, T = 100 K, Z = 4, μ(Cu-Kα) = 5.062 mm^{-1}, 25 133 reflections measured, 4116 unique (R_{int} = 0.044), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0298, $wR2$ = 0.0698, R indices (all data): $R1$ = 0.0322, $wR2$ = 0.0709. CCDC 620342. **3**: $C_{15}H_{33}Br_2NiO_2P_2$ M = 525.88, monoclinic, space group $C2/c$, a = 34.4889(8), b = 7.0423(2), c = 22.1302(5) Å, β = 127.664(1)°, V = 4254.90(2) Å^3, T = 200 K, Z = 8, μ(Cu-Kα) = 7.163 mm^{-1}, 29 028 reflections measured, 3930 unique (R_{int} = 0.026), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0520, $wR2$ = 0.1735, R indices (all data): $R1$ = 0.0546, $wR2$ = 0.1758. CCDC 620343. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613812h

§ For comparison, the corresponding values of τ for a purely square-pyramidal and trigonal-bipyramidal structures would be 0 and 1, respectively.

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