A Templated Synthesis of a Dinickel(II) Double-helicate and its Demetallation to Free 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2′′′′′-Sexipyridine

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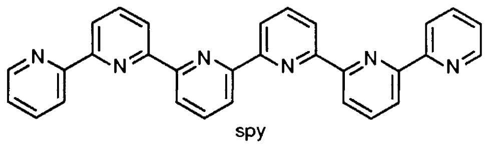
The double-helical complex $[Ni_2(spy)_2][PF_6]_4$ of the hexadentate ligand 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2′′′′′-sexipyridine (spy) is readily prepared in good yield in a nickel(0) templated coupling of 6-bromo-2,2′ : 6′,2″-terpyridine. The free ligand is obtained in quantitative yield by demetallation of this complex with cyanide.

The specific coordination requirements of transition metal ions may be utilised in the self-assembly of molecular threads to form double-[1–3] and triple-helical[4] coordination compounds. We have shown that oligopyridines are readily assembled into double-helical arrays upon coordination to transition metal ions.[5,6] Recently, we have shown that 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2′′′′′-sexipyridine (spy) spontaneously assembles double-helical arrays containing two six-coordinate metal ions upon reaction with transition metal ions (Scheme 1).[6] Our studies of the coordination properties of spy have been somewhat limited by the unreproduceable and low yields of the free ligand obtained from double-Kröhnke syntheses.[7] In this communication we report a facile and convenient template assembly of $[Ni_2(spy)_2]^{4+}$ from simple precursors and the subsequent quantitative decomplexation to yield free spy.

We have investigated many potential routes for the preparation of spy and its substituted derivatives. One approach involved the symmetric coupling of 6-bromo-2,2′ : 6′,2″-terpyridine (Brterpy). The desired bromo compound, Brterpy, is readily prepared as a white crystalline solid in 60% yield by a Kröhnke reaction[7] of *N*-[2-(2′-pyridyl)-2-oxoethyl]pyridinium iodide with *N*,*N*,*N*-dimethyl[3-(6′-bromo-2′-pyridyl)-3-oxopropyl]ammonium chloride in the presence of ammonium acetate.†



spy

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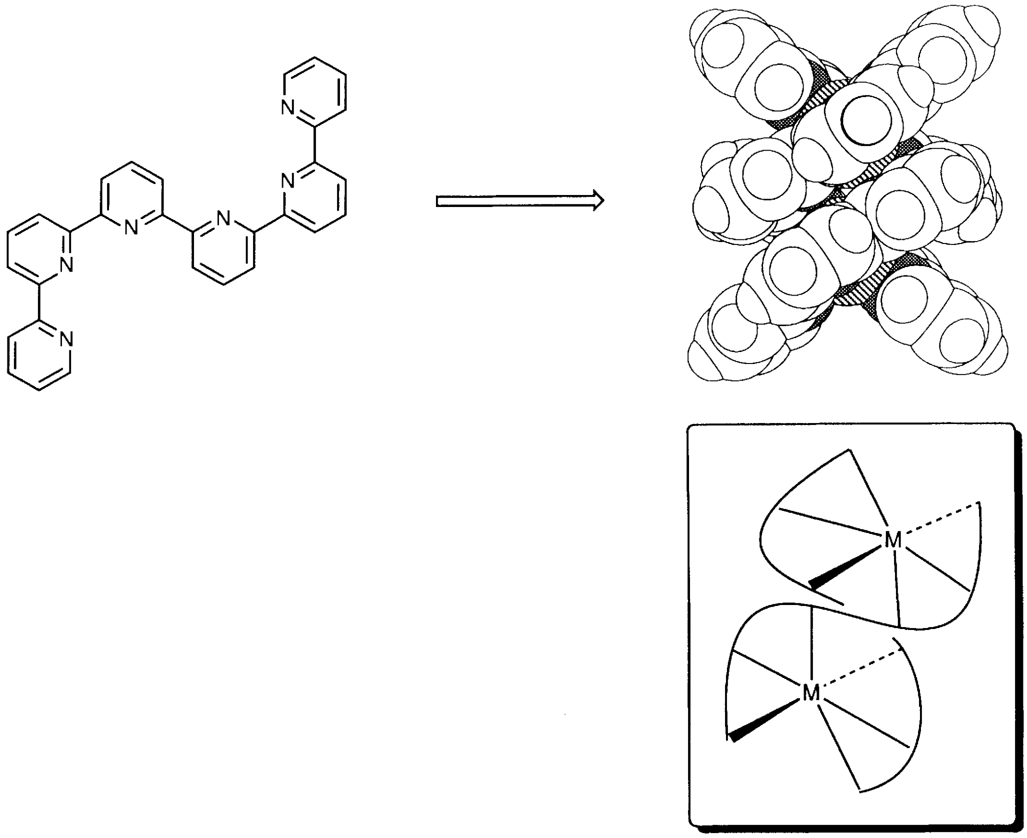
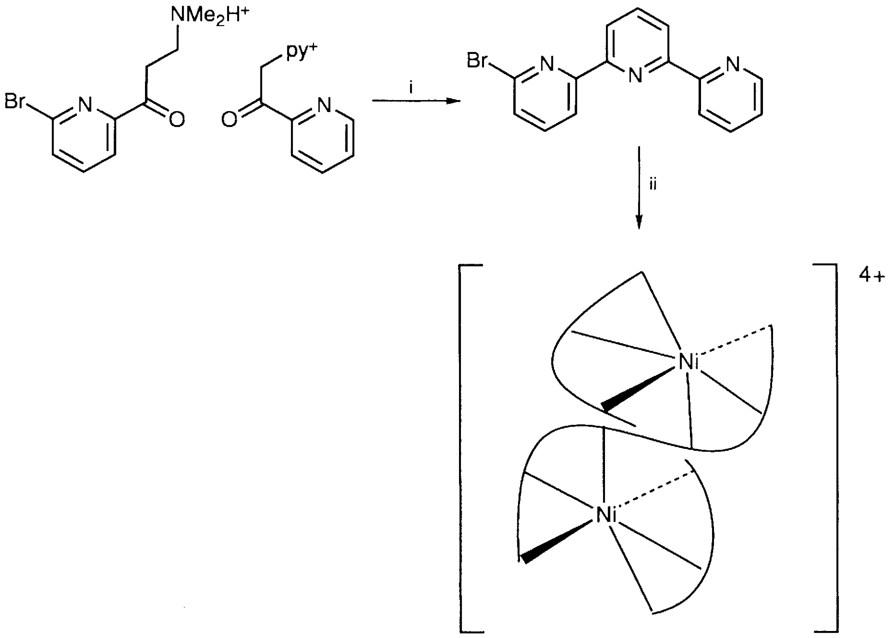
† All compounds gave satisfactory spectroscopic and analytical results.



Scheme 1



Scheme 2 *Reagents and conditions*: i, $[NH_4][OAc]$; ii, $[Ni(H_2O)_6]Cl_2$, PPh_3, dmf, Zn

Attempts to dimerise Brterpy to spy by Ullmann reactions with elemental copper under a number of conditions were unsuccessful. We have shown that oligopyridines may be prepared as their nickel(II) complexes by reactions of 2-bromopyridines with nickel(0) species,[8] and considered that this might prove to be a suitable method for the preparation of spy complexes. The reaction of Brterpy with a red suspension of 2 equiv. of $[\mathrm{Ni(PPh_3)}_n]$ ($n = 3,4$) prepared *in situ* by the reaction of $[\mathrm{Ni(H_2O)_6}]\mathrm{Cl_2}$ with Zn in dimethylformamide (dmf) in the presence of an excess of $\mathrm{PPh_3}$ results in the formation of a brown-green slurry (Scheme 2). After removal of dmf and quenching this suspension in water, followed by filtration to remove an excess of $\mathrm{PPh_3}$ results in the formation of a pale green-yellow solution. Treatment with $[\mathrm{NH_4}][\mathrm{PF_6}]$ results in the precipitation of a yellow-green solid. This solid is identical in all respects to the double-helical complex $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_4$ which may be obtained from the direct reaction of spy with nickel(II) salts.[4] The FAB mass spectrum of the yellow solid exhibits peaks at m/z 1481 $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_3$, 1336 $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_2$, 1191 $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]$, 669 $\{[\mathrm{Ni(spy)}][\mathrm{PF_6}] + 2\mathrm{H}\}$, 522 $[\mathrm{Ni(spy)}]$; all sets of peaks exhibit the calculated isotopomer distributions, and it is significant that the m/z 669 set exhibit half-mass peaks corresponding to the doubly charged ion $\{[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_2\}^{2+}$. The coupling of Brterpy results in the formation of $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_4$ in 50% overall yield from Brterpy. The ease of isolation of the hexafluorophosphate salt makes this the synthetic method of choice for the complex.

The treatment of $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_4$ with KCN in aqueous acetonitrile results in the formation of a clear yellow solution containing $[\mathrm{Ni(CN)_4}]^{2-}$ and the precipitation of spy as white solid. The free ligand spy is obtained in quantitative yield from the cyanide demetallation of $[\mathrm{Ni_2(spy)_2}][\mathrm{PF_6}]_4$ and is identical in all respects to spy prepared as previously described.[4] The free ligand exhibits a strong parent ion in its mass spectrum at m/z 464 and fragmentation peaks at m/z 386 (spy − py) and 233 (spy − 3py).

The synthetic method we have described allows facile access to *all* of the even-ring oligopyridines by template coupling of appropriate haloderivatives containing half the number of pyridine rings. We are currently investigating sexi-, octa-, deca- and dodeca-pyridines prepared by this method and also septi- novi- and undeca-pyridines prepared by routes analogous to those we have reported previously.[3]

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