Template Synthesis of a New P_2N_2 Macrocyclic Ligand *via* Direct Alkylation of Co-ordinated Amido Nitrogen Atoms; *X*-Ray Structure Analysis of the Free Ligand and its Neutral Ni^{II} Complex

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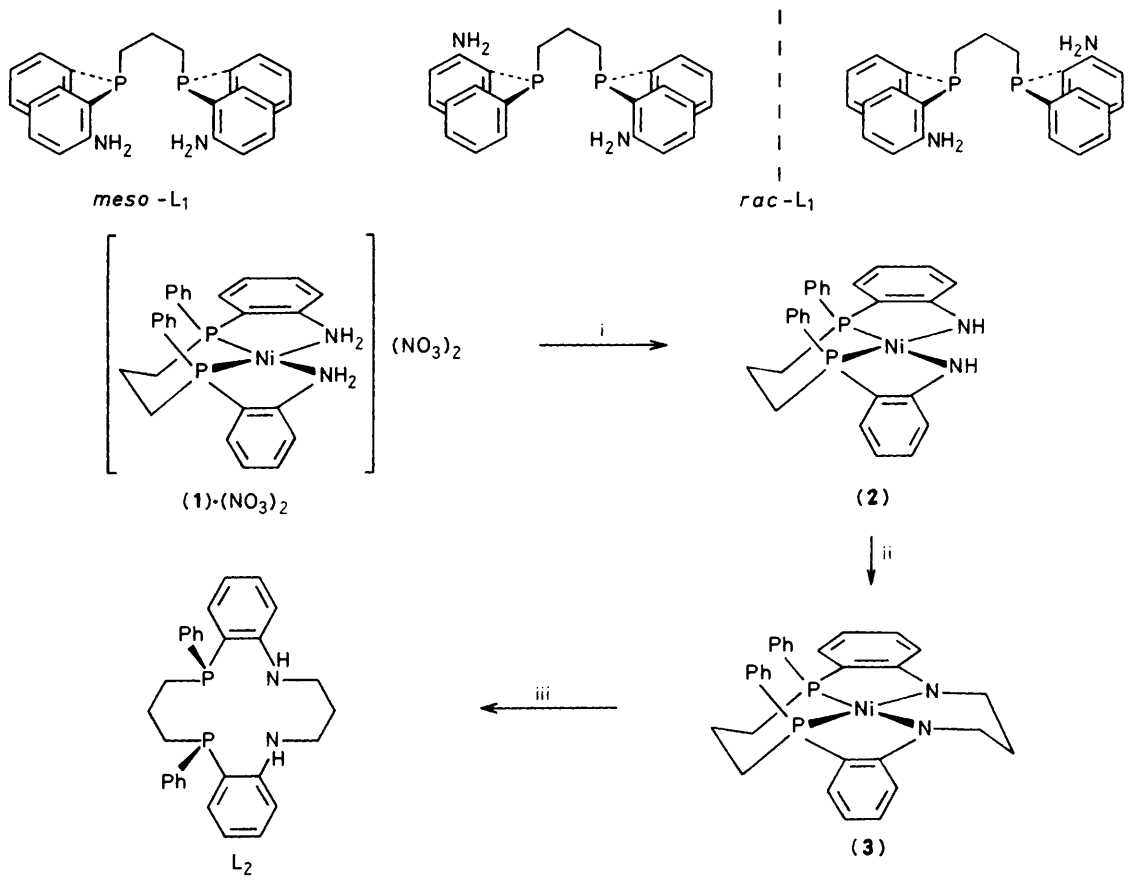
The dication $[Ni(meso\text{-}L_1)]^{2+}$, (**1**), [the N^{II} complex of the *meso* diastereoisomer of the ligand 1,3-bis{(*o*-aminophenyl)phenylphosphino}propane, *meso*-L_1] on deprotonation gives the neutral complex, $[Ni(meso\text{-}L_1-2H)]$, (**2**), with a *cis*-disposition of the two amido groups which undergo facile alkylation with propane-1,3-ditoluene-*p*-sulphonate to give $[Ni(L_2-2H)]$, (**3**), a complex of the new P_2N_2 macrocycle *meso*-L_2; *X*-ray structure analyses of the nitrate salt of (**1**), L_2, and (**3**) confirm the *meso*-configuration of the ligands.

Preparation of macrocyclic ligands *via* direct alkylation of co-ordinated amines using 'template' conditions is rare,[1] because unless the amine can be deprotonated,[2] the nitrogen atoms have no nucleophilic activity. The successful cyclisation to give the new P_2N_2 macrocyclic ligand, L_2, depends on the presence of the *o*-aminophenylphosphino moiety in the linear precursor *meso*-L_1.[3] Such phenylamino groups can be readily deprotonated[4] to give complexes in which the co-ordinated amido (R_2N^-) nitrogen atoms show pronounced nucleophilic activity.[5,6]



Scheme 1. i, NEt_3, MeOH; ii, $TsO[CH_2]_3OTs$, K_2CO_3, refluxing toluene, TsO = toluene-*p*-sulphonate; iii, 10% NaCN, benzene.

X-Ray structure analysis† of $[Ni(meso\text{-}L_1)]^{2+}$, (**1**) [the nitrate salt of the Ni^{II} complex of the linear P_2N_2 ligand],[3] Figure 1, shows the favourable chair configuration of the central six-membered chelate ring involving the phosphorus donors, and a *cis*-disposition of the amino groups. Deprotonation of this complex occurs under mildly basic conditions to give the neutral amido complex $[Ni(meso\text{-}L_1{-}2H)]$, (**2**), which has the essential features for undergoing facile cyclisation reactions with short chain, difunctionalised, alkylating agents, *viz.* a *cis*-disposition of two deprotonated amino (amido) groups. Its reaction with propane-1,3-ditoluene-*p*-sulphonate in the presence of potassium carbonate, Scheme 1, yields $[Ni(L_2{-}2H)]$, (**3**), a complex of the doubly deprotonated P_2N_2 macrocycle, L_2. The free ligand can be liberated with aqueous cyanide. The *rac* form of the linear P_2N_2 ligand, *rac*-L_1, unlike its diastereoisomer, *meso*-L_1, does not function as a tetradentate ligand in square-planar, d^8-metal complexes[3,7] and has thus proved unsuitable for a similar cyclisation reaction.

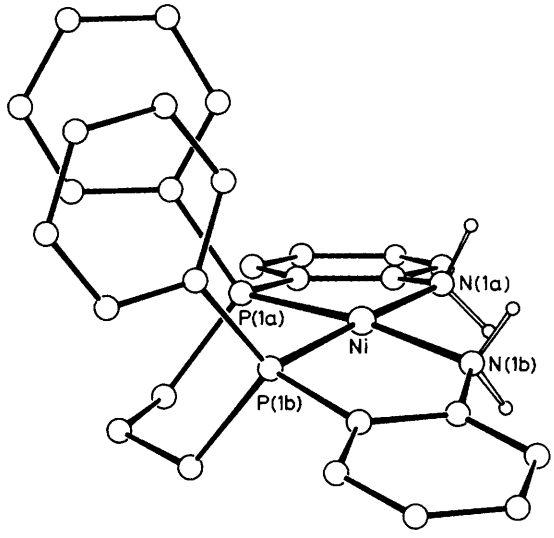


Figure 1. The structure of $[Ni(meso\text{-}L_1)]^{2+}$, (**1**). There are two independent molecules per asymmetric unit. The mean nickel to ligand bond distances are P, 2.126(10); and N, 1.95(4) Å.

† *Crystal data*: (**1**) · $(NO_3)_2$, $[C_{27}H_{28}N_2NiP_2](NO_3)_2$, from 90% EtOH, M = 625.2, monoclinic, space group $P2_1/c$, a = 17.086(3), b = 10.385(2), c = 32.151(4) Å, β = 102.80(3)°, U = 5563.1 Å^3, Z = 8, D_c = 1.492 g cm^{-3}, $F(000)$ = 2592, μ(Mo-K_α) = 9.00 cm^{-1}, $I/\sigma(I)$ >3.0, present R-factor 0.089 for 2782 unique reflections.

(**3**), $[C_{30}H_{30}N_2NiP_2]\cdot C_6H_6$, from benzene, M = 617.3, orthorhombic, space group $P2_12_12_1$, a = 22.770(4), b = 14.190(3), c = 9.587(3) Å, U = 3097.6 Å^3, Z = 4, D_c = 1.323 g cm^{-3}, $F(000)$ = 1296, μ(Mo-K_α) = 7.03 cm^{-1}, $I/\sigma(I)$ >3.0, present R-factor 0.114 for 840 unique reflections. The sample decomposed in the *X*-ray beam with loss of solvent of crystallisation.

L_2, $C_{30}H_{32}N_2P_2$, from benzene–EtOH, M = 482.5, monoclinic, space group $P2_1/c$, a = 8.982(2), b = 19.671(4), c = 14.886(3) Å, β = 95.04(3)°, U = 2619.9 Å^3, Z = 4, D_c = 1.223 g cm^{-3}, $F(000)$ = 940, μ(Mo-K_α) = 1.46 cm^{-1}, $I/\sigma(I)$ >3.0, present R-factor = 0.077 for 1499 unique reflections. Data were collected on a Philips PW1100 diffractometer in the θ range 3—25° and using Mo-K_α radiation. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

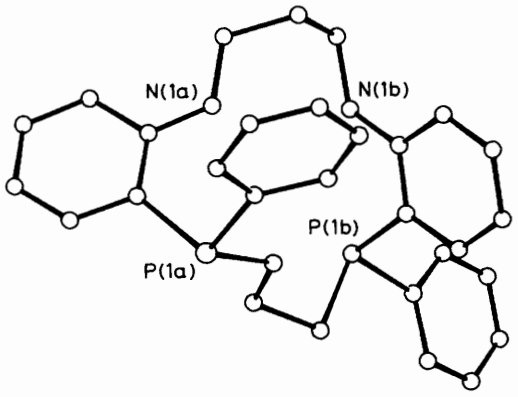


Figure 2. The structure of the free macrocyclic ligand L_2.

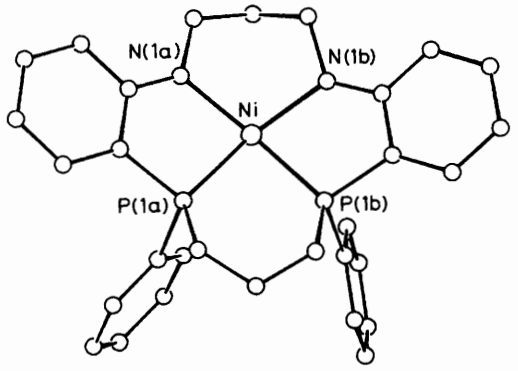
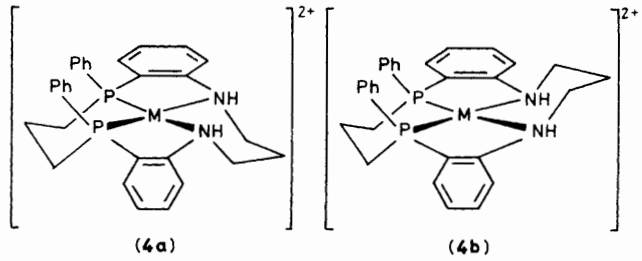


Figure 3. The structure of the neutral macrocyclic nickel complex [Ni(*meso*-L_2−2H)], (**3**). The mean nickel to ligand bond distances are P, 2.113(8); and N, 1.97(3) Å.

The cyclic nature and *meso*-configuration of the new macrocyclic ligand are confirmed by *X*-ray structure determinations† of both the free ligand, L_2, and the neutral deprotonated nickel(II) complex (**3**), Figures 2 and 3 respectively.

The macrocycle L_2 is also able to accommodate the larger palladium(II) and platinum(II) ions. Thus reaction of L_2 with $M(PhCN)_2Cl_2$, M = Pd^{II} or Pt^{II}, under basic conditions, led to the neutral analogues of (**3**), [M(L_2−2H)]. Treatment of these compounds with acid gave the corresponding amino



complexes, $[ML_2]^{2+}$, (**4**). The ^{31}P-{^1H} n.m.r. spectra‡ of these dicationic macrocyclic species each exhibited two closely spaced (<0.5 p.p.m.) sets of signals of nearly equal intensity which indicates the presence of two isomers (**4a**) and (**4b**) of similar energy. These are thought to arise from the two conformations that the ligand can adopt around a square-planar metal ion, while maintaining the low energy chair configurations of both six-membered chelate rings. Interconversion of such isomers under acid conditions would be slow since deprotonation of both nitrogen atoms would be necessary.

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References

1 'Coordination of Macrocyclic Compounds', ed. G. A. Melson, Plenum, New York, 1979.
2 M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides', Ellis Horwood, Chichester, 1980.
3 C. W. G. Ansell, M. K. Cooper, K. P. Dancey, P. A. Duckworth, K. Henrick, M. McPartlin, G. Organ, and P. A. Tasker, preceding communication.
4 M. K. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.
5 M. K. Cooper, J. M. Downes, K. Henrick, H. J. Goodwin, and M. McPartlin, *Inorg. Chim. Acta*, 1983, **76**, L159.
6 J. M. Downes, Ph.D. Dissertation, University of Sydney, 1978.
7 P. A. Duckworth, Ph.D. Dissertation, University of Sydney, 1984.

‡ ^{31}P-{^1H} (36.43 MHz) N.m.r. data (chemical shifts relative to 85% H_3PO_4): L_2 (in CH_2Cl_2), δ −30.9 p.p.m.; (**3**) (in benzene) δ 26.3; [Pd(L_2−2H)] insoluble; [Pd(L_2)](TFA)$_2$ (in CH_2Cl_2, TFA = trifluoroacetate), δ 31.7, 31.4 p.p.m.; [Pt(L_2−2H)] (in dimethylformamide), δ 12.2 p.p.m. [*J*(Pt–P) 2781 Hz]; [Pt(L_2)](TFA)$_2$ (in 1:4 MeOH–CH_2Cl_2), δ 13.3 [*J*(Pt–P) 2922 Hz], 12.9 p.p.m. [*J*(Pt–P) 2920 Hz].