Synthesis and Reactivity of Cyclonickelated Compounds. Crystal and Molecular Structure of $[Ni(CCF_3{=}CCF_3CH_2C_6H_4NMe_2)(PEt_3)(\mu\text{-}Cl)]_2$

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o-N,N-Dimethylaminobenzyl-lithium reacted with $NiCl_2(PR_3)_2$ to give cyclonickelated compounds; hexafluorobut-2-yne was inserted into their Ni–C bonds giving rise to a seven-membered organometallic ring when the phosphine was PMe_3, whereas in the case of PEt_3 a dimeric compound was obtained.

The key importance of cyclometallated compounds of nitrogen-containing ligands as reactive intermediates for the synthesis of organic heterocycles has been recognized recently.[1] These compounds may also be used as starting materials to obtain organometallic molecules with unusual properties.[2] However, investigations seem to be restricted almost entirely to palladium complexes, and only a few cyclometallated compounds involving nickel have been reported.[1a] We describe here our preliminary results on the synthesis of new cyclonickelated compounds whose Ni–C bonds react readily with alkynes.

Treating a solution of $NiCl_2(PR_3)_2$ [(**1**); **a**, R = Me; **b**, R = Et] in Et_2O under argon with a suspension of *o-N,N*-dimethylaminobenzyl-lithium (dmabLi; 2 equiv.) in Et_2O at −50 °C afforded, after crystallisation from n-hexane at −20 °C, yellow crystals of (**2a**) and (**2b**) respectively.† These compounds were rather unstable and were characterized only by their n.m.r. spectra. The CH_2 protons appeared as a doublet with coupling to only one phosphorus atom; the formation of $Ni(dmab)_2(PR_3)_2$ can therefore be ruled out. Despite the fact that the NMe_2 protons appeared as a singlet, we believe that chelation of the ligand must have occurred since one equivalent of free PR_3 was evolved during the reaction. The absence of $^3J_{PH}$ on the NMe_2 signals can be explained by a rather weak $N{\rightarrow}Ni$ bond which would be easily displaced, on the n.m.r. time-scale, by some free PR_3 which might have been present in trace amounts with (**2a**) and (**2b**).

The formation of the monocyclonickelated species is in marked contrast to observations in a related reaction using lithiated *N,N*-dimethylbenzylamine as the ligand for which a bicyclic monomeric compound has been obtained.[3]

Hexafluorobut-2-yne (hfb) reacted almost instantaneously at room temperature with (**2a**) in hexane solution to give orange-red crystals of (**3a**) in high yields. The geometry of (**3a**) has been fully established by analytical and spectroscopic data.† It is a 1 : 1 mixture of two isomers in which the PMe_3 is bonded either *trans* or *cis* with respect to the NMe_2 moiety. Two Ni–Cl stretching frequencies can be tentatively assigned in the far i.r. spectra at 302 and 237 cm^{-1}. As a result of the existence of a non-planar seven-membered metallocyclic ring

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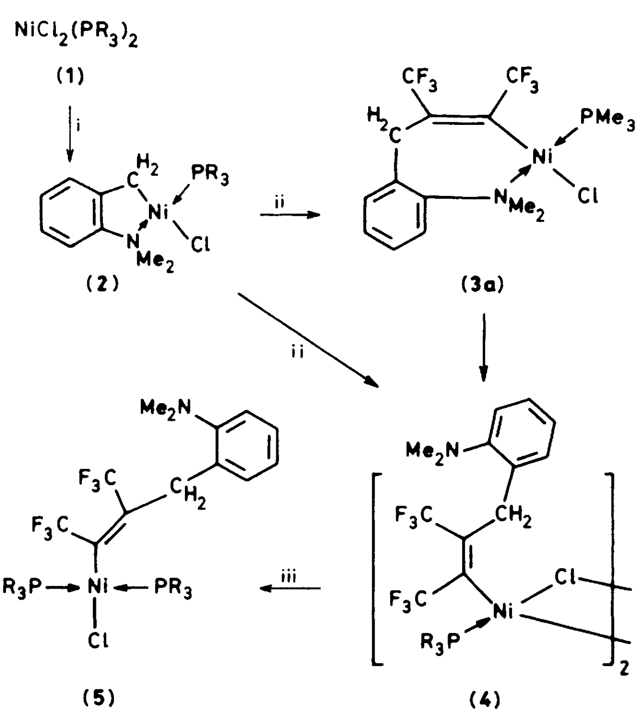
† Selected n.m.r. data; δ (C_6D_6), (**2b**) ^{1}H: 2.99 (s, 6 H, NMe_2), 1.80 (d, 2 H, $^3J_{PH}$ 8, CH_2Ni), 1.5 (m, 6 H, PCH_2), and 1.16 (m, 9 H, P–C–Me); (**3a**) ^{1}H: 5.8 and 5.2 (dd, 2 H, CH_2, $^2J_{HH}$ 17), 5.4 and 5.0, (dd, 2 H, CH_2, $^2J_{HH}$ 15), 2.84 (s, 6 H, NMe_2), 2.6 (s, 6 H, NMe_2) 0.84 (d, 9 H, PMe_3, $^2J_{PH}$ 11.0), and 0.67 (d, 9 H, PMe_3, $^2J_{PH}$ 11.4 Hz); $^{31}P-\{^1H\}$: −8.8 (m) and −9.2 p.p.m. (m); (**5a**) ^{1}H: 4.76 (s, 2 H, CH_2), 2.63 (s, 6 H, NMe_2), and 0.99 (t, 18 H, PMe_3, $|^2J_{PH} + {}^4J_{PH}|$ 8 Hz); $^{31}P-\{^1H\}$: −16.0 p.p.m. (q, $^4J_{FP}$ 5.8 Hz).



a; R = Me
b; R = Et

Scheme 1. *Reagents:* i, dmabLi, Et_2O, −50 °C; ii, hfb, n-hexane; iii, in solution or in the solid state; the additional PR_3 is due to some decomposition of (**4**).

the two protons of the CH_2 groups are anisochronous and they give rise to two AB type signals.[4] As for (**2a**) neither the coupling ($^3J_{PH}$) nor the diastereotopic nature of the NMe_2 groups can be detected suggesting again a very weak interaction between the nitrogen lone pair and the nickel atom. After *ca.* 2 h (**3a**) isomerised in solution into (**4a**) which could not be isolated since it decomposed quickly to give (**5a**)† (see Scheme 1).

On the other hand (**2b**) gave a rather different reaction with hfb, affording red crystals of (**4b**). Its ^1H n.m.r. spectrum is very similar to that of (**4a**): *i.e.* only one signal can be detected for the NMe_2 moiety and one singlet for the CH_2 protons. Surprisingly (**4b**) was much more stable (several hours in solution) than (**4a**) and could be isolated. Its decomposition in a toluene solution to give (**5b**) could only be detected after two days.

In order to establish the geometry of (**4a**) and (**4b**) an *X*-ray diffraction study was undertaken on (**4b**) for which suitable crystals were available.‡ The molecule (Figure 1) is dinuclear,

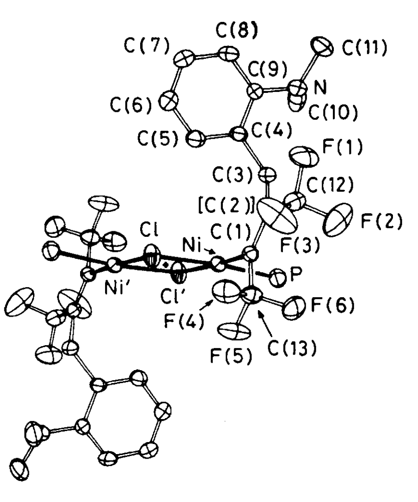


Figure 1. Molecular structure of $[Ni(CCF_3{=}CCF_3CH_2C_6H_4NMe_2)(PEt_3)(\mu\text{-}Cl)]_2$ (**4b**) (the Et groups of the PEt_3 are omitted for clarity). Bond lengths: Ni–Cl 2.237(1), Ni–Cl′ 2.251(1), Ni–P 2.169(1), Ni–C(1) 1.902(3), C(1)–C(2) 1.320(5), C(2)–C(3) 1.531(5), C(9)–N 1.383(6) Å. Angles: Cl–Ni–Cl′ 86.03(4), Ni–Cl–Ni′ 93.97(4), Cl–Ni–P 92.81(5), Cl–Ni–C(1) 175.7(1), Ni–C(1)–C(2) 125.6(3), Ni–C(1)–C(13) 112.4(2)°.

two nickel atoms being bridged by two chlorine atoms. It has a crystallographic centre of symmetry. The acetylene hfb has indeed inserted into the Ni–C bond of (**2b**). The dmab ligand is orientated in such a way that no interaction can be invoked between the N lone pair and the Ni atom. This dimeric structure is, to our knowledge, the first of this type which has been characterized by an *X*-ray diffraction study for an organonickel compound.[5] Its formation can be rationalized by an intermolecular process, a chlorine atom of one hypothetical molecule (**3b**) displacing the N→Ni bond of a seven-membered ring of another molecule giving the dinuclear species.

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‡ *Crystal data:* $C_{19}H_{27}ClF_6NiNP$, $M = 508$, spherical crystal of mean diameter 0.26 mm, monoclinic, $a = 10.574(3)$, $b = 15.000(4)$, $c = 14.934(4)$ Å, $\beta = 98.54(2)°$, $U = 2342$ Å^3, $D_m = 1.42$ g cm^{-3}, $Z = 4$, $D_c = 1.44$ g cm^{-3}, space group $P2_1/c$, $\lambda(Cu\text{-}K\bar{\alpha}) = 1.5405$ Å, $\mu(Cu\text{-}K\alpha) = 33.3$ cm^{-1}, $F(000) = 1048$. The structure was solved by direct methods and refined by full least-squares methods. 2206 Independent reflections for which $I/\sigma(I) > 3.0$ were collected on a Philips PW 1100/16 diffractometer in the range $4 < \theta < 57°$ They were refined to a conventional R value of 0.059. 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.

References

1 (a) M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73; C. H. Chao, D. W. Hart, R. Bau, and R. F. Heck, *J. Organomet. Chem.*, 1979, **179**, 301; (b) I. R. Girling and D. A. Widdowson, *Tetrahedron Lett.*, 1982, 4281.

2 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115; G. R. Newkome, M. Onishi, W. E. Puckett, and W. A. Deutsch, *ibid.*, 1980, **102**, 4551; D. M. Grove, G. Van Koten, H. J. C. Ubbels, and A. L. Spek, *ibid.*, 1982, **104**, 4285.

3 G. Longoni, P. Chini, F. Canziani, and P. Fantucci, *J. Organomet. Chem.*, 1972, **39**, 413.

4 C. Arlen, M. Pfeffer, O. Bars, and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, in the press.

5 See for example P. W. Jolly and G. Wilke, 'The Inorganic Chemistry of Nickel', Academic Press, New York and London, 1974, vol. 1.