The ^{13}C NMR Spectra of Organotransition Metal Complexes, I (Cyclododecatriene)- and (Bicycloheptene)nickel Complexes

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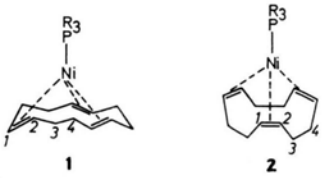
^{13}C NMR, Nickel-olefin Complexes

The ^{13}C NMR spectra of a number of nickel complexes of 1,5,9-cyclododecatriene and bicyclo-[2,2,1]-heptene have been studied and it has been shown that detailed structural information can be obtained relatively easily.

Although the use of ^{13}C NMR spectroscopy in organotransition metal chemistry is now becoming commonplace[1–3], its application to organonickel complexes has been relatively neglected. Investigations involving nickel-olefin complexes are limited to a study of a series of bisphosphite-nickel-(olefin) complexes[4] and bis(cyclooctadiene)nickel and related compounds[5,6]. We report here some preliminary results for the nickel complexes of cyclododecatriene (CDT) and bicycloheptene. The results are summarized in Tables I and II.

Complexation of CDT to nickel is accompanied by a large shift of the olefinic-carbon signal to higher field while the methylenic carbon atoms experience a smaller shift to lower field. It has been suggested that the greater stability of (all *cis*-CDT)Ni compared to (all *trans*-CDT)Ni is the result of the geometrically more favourable planar arrangement of the three double bonds around the nickel atom in the former case, in contrast to the propeller-like arrangement observed in (all *trans*-CDT)Ni[7–10]. In agreement with this suggestion, it is observed that the shift to higher field of the signal due to the olefinic-carbon atoms upon complexation of the CDT molecules is 16.6 ppm greater for the isomer containing all *cis*-CDT.

The fourth position on the nickel atom in (CDT)Ni can be occupied by a donor-ligand and a number of (CDT)Ni-*tert*-phosphine and -phosphite complexes have been isolated[10]. The arrangement of the ligands around the central metal atom in these complexes is assumed to be pseudotetrahedral (**1** and **2**)[11].



1 **2**

In agreement with this four signals are found in the ^{13}C NMR spectra of the (all *trans*-CDT)Ni–PR_3 complexes (Table I). The trimethylphosphine adduct (**1**) ($R=CH_3$) has been studied in greatest detail: at +80 °C two relatively broad signals are observed for the olefinic- and aliphatic-carbon atoms ($\delta_{1,2}$ = 90.0 ppm, $\Delta\nu_{1/2}$ = 25 Hz; $\delta_{3,4}$ = 39.1 ppm, $\Delta\nu_{1/2}$ = 4 Hz) indicating that dissociation is occurring; at apparatus temperature (+32 °C) four signals are observed (Table I) having half height widths of 20–14 Hz; on cooling to −60 °C these signals become narrower and coupling between the ring carbon atoms and the phosphorus atom is observed ($|J(^{31}P-^{13}C_1)|$ = 7.6, $|J(^{31}P-^{13}C_2)|$ = 1.9, $|J(^{31}P-^{13}C_{3\,or\,4})|$ = 3.1, 0 Hz). The assignment has been made by assuming that the P–Ni–C_1 angle is greater than the P–Ni–C_2 angle and hence C_1 is "more *trans*" than C_2 and will show a larger coupling[12]. The observation of only two signals for the CDT molecule in

(all *cis*-CDT)Ni–$P(OC_6H_4\text{-}o\text{-}C_6H_5)_3$

Table I. ^{13}C NMR spectra of (CDT)Ni and (CDT)Ni–PR_3 complexes[a].

Compound	δ_1[b]	Δ_1	δ_2	Δ_2	δ_3	Δ_3	δ_4	Δ_4
all *trans*-CDT	131.6	–	–	–	32.7	–	–	–
(all *trans*-CDT)Ni	106.6	−25.0	–	–	41.2	+8.5	–	–
(all *trans*-CDT)Ni–$P(CH_3)_3$[c]	88.0	−43.6	89.9	−41.7	38.3	+5.6	39.5	+6.8
(all *trans*-CDT)Ni–$P(OC_6H_4\text{-}o\text{-}C_6H_5)_3$	94.7	−36.9	97.9	−33.7	36.4	+3.7	37.7	+5.0
all *cis*-CDT	130.5	–	–	–	28.3	–	–	–
(all *cis*-CDT)Ni[d]	89.0	−41.5	–	–	28.8	+0.5	–	–
(all *cis*-CDT)Ni–$P(OC_6H_4\text{-}o\text{-}C_6H_5)_3$[e]	99.5	−31.0	–	–	29.9	+1.6	–	–

[a] Measurements (Varian XL-100-15 FT spectrometer) in d-toluene at +32 °C in 12 mm tubes.
[b] Chemical shifts (δ; ±0.1 ppm) rel. to TMS. $\Delta n = \delta n$(complex) − δ(CDT).
[c] δ_{CH_3} = 18.4 ppm; $|^1J(^{31}P-^{13}C)|$ = 13.0 Hz.
[d] Measured at 0 °C.
[e] Measured at −20 °C.

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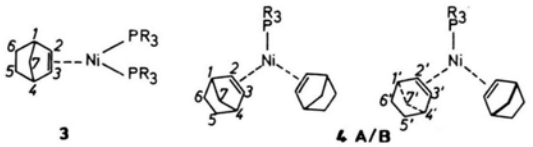
indicates that the planar arrangement of the three double bonds has been retained in the phosphite adduct.

The investigations were extended to the nickel complex of bicyclo-[2,2,1]-heptene in anticipation of observing dynamic effects. The nickel atom in these complexes has been shown to occupy an exo position[8,13]. The ^{13}C NMR spectra of (bicycloheptene)Ni–$[P(C_6H_5)_3]_2$ (**3**) shows the expected 4 signals for the organic ligand. Somewhat surprising is that coupling is observed between the phosphorus atoms and $C_{5,6}$ but not $C_{1,4}$ or C_7. The ^{13}C NMR spectrum of (bicycloheptene)$_2$NiPMe$_3$ is of particular interest. At room temperature only 5 signals (4 from the olefin and 1 from the phosphine) are observed and the olefin-carbon signals is broad ($\Delta\nu_{1/2} \sim 150$ Hz). On lowering the temperature to —34 °C, a well resolved spectrum is obtained. The presence of 4 doublets for the olefinic carbon atoms and two doublets for the phosphorus bonded methyl groups (as well as additional signals in the aliphatic region) indicate that two isomeric forms (**4a** and **4b**), which differ only in the mutual arrangement of the bicycloheptene molecules, are present in solution. The intensity of the doublets indicate that the two isomers are present in the ratio 1:3. An absolute assignment was not, however, attempted.



3 **4 A/B**

The bicycloheptene ligands in tris(bicycloheptene)nickel are also free to rotate at room temperature and only 4 signals are observed in the ^{13}C NMR spectrum. At —60 °C 9 signals are observed consistent with the adoption by the complex of the same configuration (**5**) demonstrated by X-ray crystallography to be present in the solid[13].

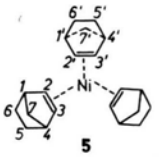


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Table II. ^{13}C NMR spectra of (bicycloheptene) nickel complexes[a].

Compound	T [°C]	δ_1	δ_4	δ_2	δ_3	δ_5	δ_6	δ_7
Bicycloheptene	+ 32	42.1	–	135.4	–	24.9	–	48.8
(Bicycloheptene)[NiP$(C_6H_5)_3]_2$[b] (**3**)	+ 32	44.6	–	66.3	–	28.8	–	44.1
(Bicycloheptene)$_2$NiP$(CH_3)_3$ (**4**)	+ 32	44.2	–	67.8	–	29.1	–	41.6
	— 34	44.7 or	43.7	70.9	64.8	29.4 or	28.5	41.6
		43.9[c] or	43.2	69.1	65.7	≃ 29.1	≃ 29.1	41.6
(Bicycloheptene)$_3$Ni (**5**)	+ 32	43.7	–	76.0	–	28.2	–	40.4
	— 60	43.8[d]	–	76.5	–	28.5	–	40.3
		43.8		76.2		28.2		40.3
		42.6		73.1		27.6		

[a] Measurement conditions, see Table I.
[b] $|J(^{31}P\text{–}^{13}C_2) + J(^{31}P\text{–}^{13}C_3)| = 14.6$, $|J(^{31}P\text{–}^{13}C_5) + J(^{31}P\text{–}^{13}C_6)| = 7.2$ Hz.
[c] $\delta_{1'}\text{—}\delta_{7'}|J(^{31}P\text{–}^{13}C_2)| = 12.8$, $|J(^{31}P\text{–}^{13}C_{2'})| = 13.8$, $|J(^{31}P\text{–}^{13}C_3)| = 6.7$, $|J(^{31}P\text{–}^{13}C_{3'})| = 6.8$, $|J(^{31}P\text{–}^{13}C_{5\text{or }6})| = 8.5$ Hz; $\delta_{CH_3} = 16.7$ ppm, $|J(^{31}P\text{–}^{13}C_{CH_3})| = 21.4$ Hz.
[d] The signals for the 11 magnetically different carbon atoms have been assigned to the four types of carbon atoms (olefinic, methylenic, tertiary and bridgehead) in bicycloheptene and not to the individual atoms.

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