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REACTIONS OF NICKELOCENE WITH BENZYLMAGNESIUM COMPOUNDS. PHENYLTRIS(π-CYCLOPENTADIENYLNICKEL)-METHANE

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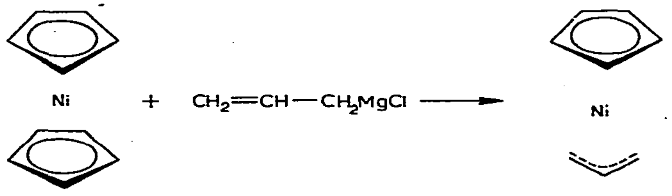
SUMMARY

Nickelocene reacts with benzylmagnesium compounds to form phenyltris-(π-cyclopentadienylnickel)methane derivatives whose structures have been verified by IR, PMR, and mass spectra. Alkylation of the cyclopentadienyl ring occurs in the presence of excess Grignard reagent.

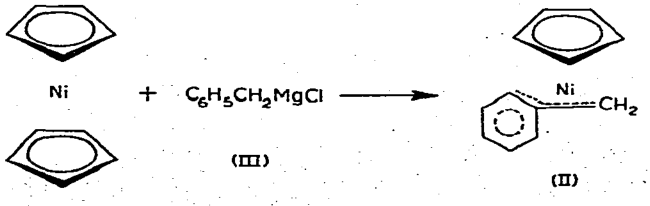
The ready entry of nickelocene into ligand exchange reactions has often been demonstrated (see *e.g.*, ref. 1 and references cited therein). Thus, we have found that nickelocene reacts with various organomagnesium or -lithium compounds under mild conditions, but the products were hard to identify because they were highly sensitive to oxygen, moisture, and elevated temperatures.

In 1961, McClellan *et al.*[2] reported the synthesis of π-allyl-π-cyclopentadienylnickel (I) which is the most stable compound of the type:



(I)

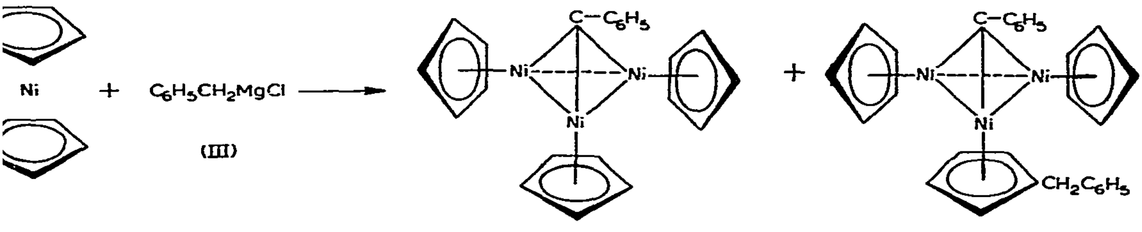
Reports have also appeared of the formation of π-benzyl compounds of high stability[3] and for this reason we have attempted the reaction of nickelocene with benzylmagnesium compounds which was anticipated to produce a new π-benzyl compound (II).



(III)

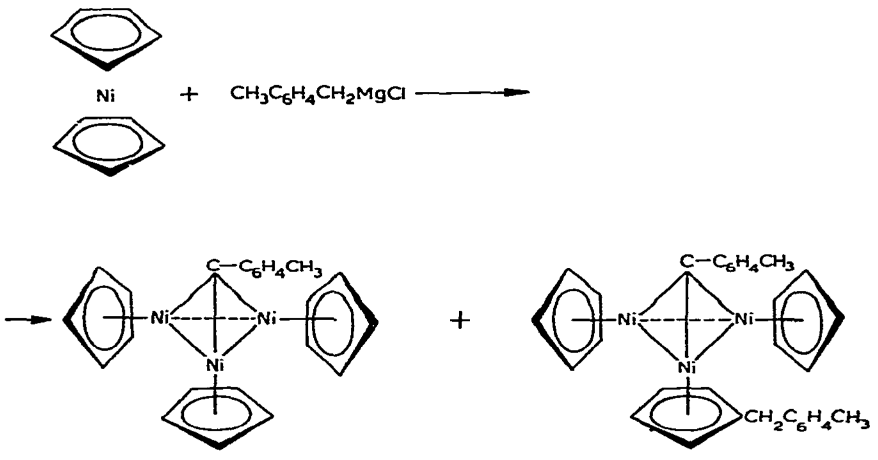
(II)

Nickelocene reacts with benzylmagnesium chloride (III), in a 1/1 reactant ratio, over the temperature range −10 to 0° to produce a red, highly unstable liquid whose properties suggest a structure similar to that of (I). A correct assignment of the structure is now in progress in these laboratories. At room temperature, however, the reaction proceeds somewhat differently. After the mixing of the reactants, the mixture very rapidly acquires a black coloration, and chromatographic separation yields two black crystalline diamagnetic products, (IV) and (V).



(IV) (V)

(p-Methylbenzyl)magnesium chloride reacts similarly with nickelocene:



(VII) (VIII)

The yield of (V) or (VIII) may be increased if the reactions are carried out at elevated temperature.

The structure of the cluster compounds (IV), (V), (VII), and (VIII) have been verified by PMR, IR, and mass spectral analysis.

Typical PMR spectra measured on a JNM-4H-100 apparatus at 100 MHz in CS_2 are shown in Fig. 1. The spectrum of (IV) (Fig. 1a) contains a singlet at δ 4.87 ppm (the cyclopentadienyl protons), and multiplets at 6.80 ppm (*meta* and *para* protons of the phenyl) and 7.35 ppm (the *ortho* protons), the integral intensity ratio being 15/3/2. The spectrum of (I) (Fig. 1b) consists of a singlet at δ 3.3 ppm (CH_2), a poorly resolved multiplet at 5.0 ppm (protons of the substituted cyclopentadienyl), a singlet at 5.15 ppm (the unsubstituted cyclopentadienyl), and multiplets at 7.70 ppm (*ortho*

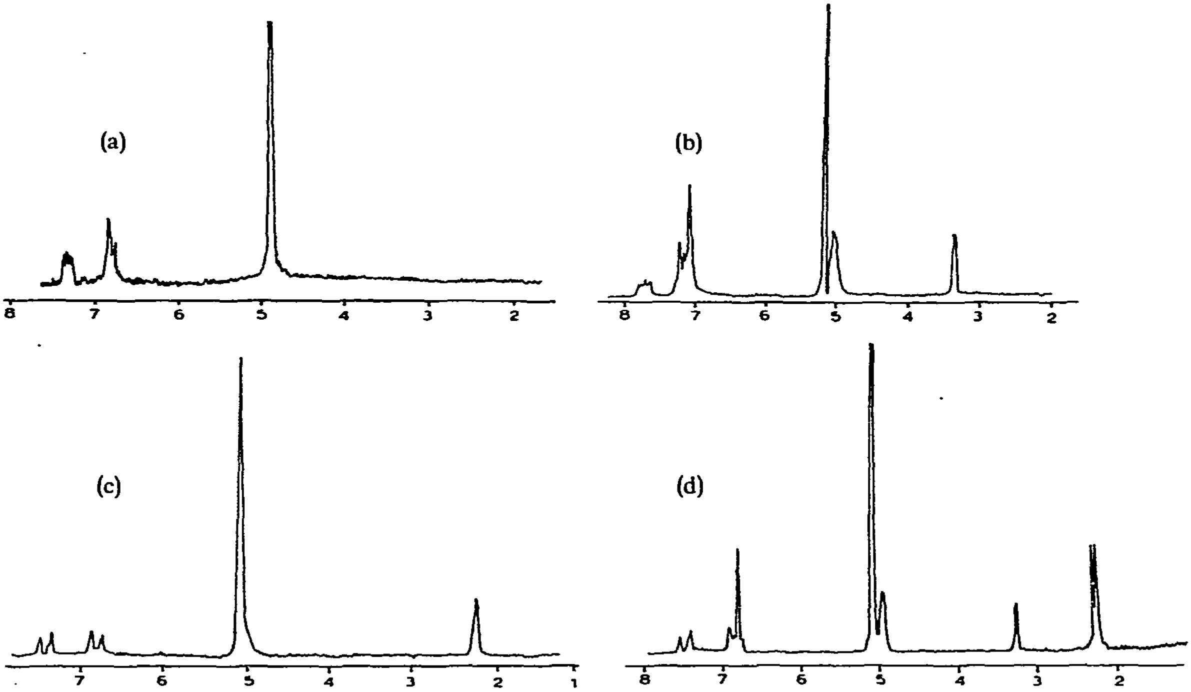


Fig. 1. (a) PMR spectrum (100 MHz) of compound (IV); (b) PMR spectrum (100 MHz) of compound (V); (c) PMR spectrum (100 MHz) of compound (VII); (d) PMR spectrum (100 MHz) of compound (VIII).

protons of C_6H_5) and at 7.1 ppm (the *meta* and *para* protons). The latter signal is superimposed by a singlet (7.07 ppm) of the C_6H_5 group belonging to the benzyl bonded to the cyclopentadienyl ring. The integral intensity ratio is close to the theoretical value of 1/2/5/5.

The spectra of (VII) and (VIII) (Figs. 1c and 1d) may be interpreted in a similar manner, the occurrence of two CH_3 singlets in the spectrum of (VIII) being noteworthy.

The IR spectra of all compounds run as KBr mulls or as solutions in CCl_4 on a Perkin–Elmer 221 spectrometer contain intense bands at 1000 and 1100 cm^{-1}

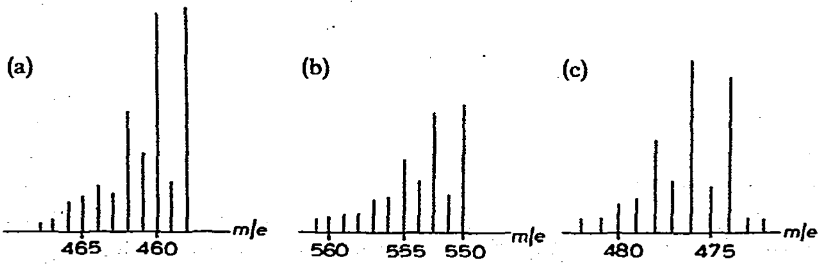


Fig. 2. (a) Molecular fragment distribution in the mass spectrum of compound (IV); (b) Molecular fragment distribution in the mass spectrum of compound (V); (c) Molecular fragment distribution in the mass spectrum of compound (VII).

which may be attributed to the unsubstituted cyclopentadienyls, and bands at 1370–1400 or 600–800 cm^{-1} (C–C stretching and C–H bending vibrations). The spectrum of (IV) does not reveal any C–H vibrations of the CH_2 type at 2800 to 2900 cm^{-1}. The spectrum of (VII) exhibits only CH_3 frequencies in this range at 2920 and 2862 cm^{-1}.

Fig. 2 illustrates the molecular fragment distribution in the mass spectra obtained with compounds (IV), (V), and (VII). The spectra were measured on an MKh-1303 machine, the samples being inserted directly into the ionizing chamber. The spectrum of (IV) displays peaks at *m/e* values equal to 458, 459, 460, 461, 462, 463, 464, 465 (Fig. 2a). The highest natural abundances of the nickel isotopes ^{58}Ni and ^{60}Ni are 68.0 and 26.2% respectively, and hence if three atoms of the element are present in the molecule the peaks at *m/e* values of 458, 460, 462, 464 should exhibit an intensity ratio of 13/20/7/1, which accords well the experimental results. The ratio obtained with the $(m+1)$ peaks (459, 461, 463, and 465), which are associated with the ^{13}C and ^{2}D isotopes, is in complete agreement with the ratio of the main peak values. All mass spectra contain intense peaks at *m/e* 66 (C_5H_6) and 39 (ion $C_3H_3^+$). Peaks at lower mass values correspond to the typical fragmentation pattern of π-cyclopentadienyl compounds. It should be noted that the spectrum of (IV) displays a peak of very low intensity at an *m/e* value of 91 (tropylium ion) and thus demonstrates the absence of the $C_6H_5CH_2$ group from the molecule.

The spectrum of (V) is shifted by 90 units towards higher mass values in comparison with that of (IV) (see Fig. 2b). This fact, and the existence of an intense peak at an *m/e* value of 91 indicate the presence of a $CH_2C_6H_5$ group. This group is detached rather easily, with the result that the peak obtained from (IV) coincides with those obtained from (V) with regard to both position and intensity.

Compound (VII), which contains a methyl group bonded to the aromatic ring, produces a spectrum shifted by 14 units towards higher mass values in comparison with that of (IV).

The above data therefore completely verify the structures of the compounds, and an X-ray investigation at present in progress should help to provide details of their geometry.

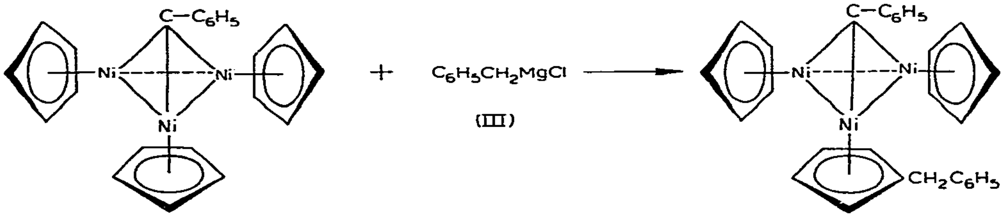
All the compounds are diamagnetic and therefore contain Ni–Ni bonds. The arrangement of the $(C_5H_5)_3Ni$ group in these molecules may be visualized as being similar to that in $(C_5H_5)_3Ni_3(CO)_3$ as synthesised by Fisher and Palm[4]. These compounds are also similar to the cobalt carbonyl clusters $XC[Co(CO)_3]_3$ where X is H, Cl, $COOCH_3$[5,6].

Compounds (IV), (V), (VII), and (VIII) are stable solids when stored in an argon atmosphere and are fairly soluble in all usual organic solvents.

Solvents containing halogens (CCl_4, $CHCl_3$, etc.), however, cause the rapid decomposition of the compounds while the solutes obtained after crystallization from heptane, cyclohexane, or other hydrocarbons contain traces of the solvents which are difficult to remove and which may be attributed to the formation of clathrates.

All the cluster compounds decompose when treated with HCl, HBr, $HgBr_2$, or CCl_4. When compound (IV) was refluxed in methanol in the presence of dimethylglyoxime, nickel dimethylglyoximate was obtained in quantitative yield.

As mentioned above, the ratio of compound (IV) to compound (V) obtained in the reactions depends on the conditions under which the nickelocene interacts with (III). The most reasonable explanation of the formation of (V) is that the process involves the unusual alkylation:



(IV) (III) (V)

Indeed, when (IV) is heated with an excess of (III) complex (V) is produced in 23% yield. At the same time, however, a number of unidentified compounds were also produced, each containing more than one substituted cyclopentadienyl ligand (as established by PMR data). The same compounds are also formed from the reaction of nickelocene with (III). They are much less stable than (IV) and (V), and may be isolated, but not identified, by chromatography.

EXPERIMENTAL

All operations were carried out in a pure dry argon atmosphere.

1. *Nickelocene and benzylmagnesium chloride*

$C_6H_5CH_2MgCl$ (15 ml of the titrated 0.8 *N* solution in ether, 0.012 mole) was added slowly to a solution of nickelocene (0.46 g, 0.0025 mole) in 30 ml of absolute ether at room temperature. The mixture became dark brown immediately. It was stirred for 30 min then hydrolysed with cold water. The organic layer was separated, dried over magnesium sulphate and the solvent removed *in vacuo*. The residue was chromatographed on a neutral (II or III activity) alumina column. Two brown bands were eluted with hexane. The first gave 0.125 g (37%) of (IV), black crystals from hexane, m.p. 158–160° (dec.). (Found: C, 57.69; H, 4.42; Ni, 37.49. $C_{22}H_{20}Ni_3$ calcd.: C, 57.37; H, 4.38; Ni, 38.24%).

In a similar manner, the second band gave (V), 0.035 g (5%) m.p. 169–171° (dec.) after crystallization from hexane. (Found: C, 63.54; H, 4.99; Ni, 31.97. $C_{29}H_{26}Ni_3$ calcd.: C, 63.26; H, 4.76; Ni, 31.98%.)

2. *Nickelocene and (p-methylbenzyl)magnesium chloride*

The above procedure when applied to (IV) (0.012 mole) and nickelocene (0.0025 mole) gave (VII), 0.14 g (36%), as black crystals from heptane, m.p. 181–183° (dec.). (Found: C, 58.11; H, 4.86; Ni, 36.46. $C_{23}H_{22}Ni_3$ calcd.: C, 57.97; H, 5.08; Ni, 36.96%.) In addition 0.027 g (7%) of (VII) was also isolated.

3. *Reactions of $C_6H_5CNi_3(C_5H_5)_3$ with benzylmagnesium chloride*

A solution of (V) (0.19 g, 0.0004 mole) in benzene (25 ml) was added dropwise to the solution of (III) prepared from Mg (0.1 g, 0.004 g-atom) and $C_6H_5CH_2Cl$ (0.5 g, 0.044 mole) in ether (10 ml), at room temperature. The mixture was heated for 4 h at 60 to 70°, and then worked up as described above. From the reaction, 0.043 g of initial (IV) were obtained together with 0.043 g of (V), which represents a yield of 23% in terms of reacted (IV). Melting points, IR and NMR spectra of the compounds coincide with those of the compounds mentioned above. Head fractions from the chromatographic column contained five bands of low intensity, their retention time being lower than that of (V).

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