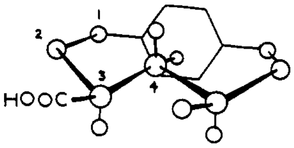
7.2 (d, 4, aromatic), 3.2–0.1 (m, 12, side-chain protons), −1.4 (m, 1, unique aliphatic proton). The highly deshielded proton at δ −1.4 is noteworthy. This is clearly one which is pushed deep into the π cloud by the constraints imposed by the ring. These data prove that VII is a carboxy[7]paracyclophane.

The compound VII has been tentatively formulated as the 3-carboxy derivative,[7] rather than the 4 isomer (which it might be, depending on which position of V was attacked in the formylation). The available pertinent information at present is that the proton at δ −1.4 is seen as a pair of doublets, with coupling constants of 11 and 15 Hz.

Models of the 4-carboxy compound show that the proton pushed into the ring should be anti to two equivalent vicinal protons, and show a triplet, perhaps further split by smaller coupling constants with the gauche vicinal protons. In the *exo*-3-carboxy compound the upfield proton is anti to one vicinal proton, but is also geminally coupled. The dihedral angles with the gauche protons are presumably large enough that no coupling is observed. The nmr spectrum of the upfield proton is thus consistent with the 3-carboxy, not the 4-. Further, when VII is reduced to the alcohol (with sodium bis(2-methoxyethoxy)aluminum hydride, the upfield proton is unchanged in coupling constant and in chemical shift. The lines from the $-CH_2OH$ protons are immersed in the complex multiplet at δ 2.95 assigned to two benzyl protons. It can be noted that the two $-CH_2OH$ protons of the 4-hydroxymethyl are equivalent (enantiotopic), and hence would appear as a doublet, which would be easily observed when superimposed on the benzyl multiplet. This is *not* found. The $-CH_2OH$ protons are much more split up and mixed into the multiplet, and cannot be separated out by visual inspection. In the 3-hydroxymethyl derivative, these $-CH_2OH$ protons are diastereotopic, and hence will give at least (to the first order) a doublet of doublets of doublets (barring accidental degeneracy). Such a situation is compatible with the observed spectrum. Accordingly, the carboxyl group in VII is tentatively assigned to the 3 position. Further discussion will be deferred to the full paper.



(9) National Science Foundation Trainee, 1971–1972.

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Alkyl Group Isomerization in the Cross-Coupling Reaction of Secondary Alkyl Grignard Reagents with Organic Halides in the Presence of Nickel–Phosphine Complexes as Catalysts

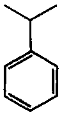
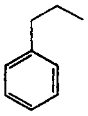
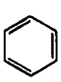
Sir:

We recently reported[1] that nickel–bisphosphine complexes exhibit extremely high catalytic activity for selective cross coupling of Grignard reagents with aromatic and olefinic halides and showed that *n*-alkyl Grignard reagents lead to *n*-alkyl derivatives without any isomerization of the alkyl group.

We now wish to report that a secondary alkyl Grignard reagent also undergoes the cross coupling very easily with chlorobenzene, but the coupling reaction is accompanied by alkyl group isomerization from secondary to primary, the extent of which is strongly dependent upon the electronic nature of the phosphine ligand in the catalyst.

The results of the reaction between isopropylmagnesium chloride and chlorobenzene using nickel(II) complexes containing various phosphines are summarized in Table I.

Table I. Products from the Reaction of i-C_3H_7MgCl with PhCl in the Presence of NiL_2Cl_2[a]

		Products distribution,[b] %		
L_2 in catalyst	Total yield,[b] %			
$Ph_2PCH_2CH_2PPh_2$	74	96	4	0
$Me_2PCH_2CH_2PMe_2$	84	9	84	7
$Ph_2PCH_2CH_2CH_2PPh_2$	89	96	4	0
dmpf[c]	48	8	74	18
dmpc[d]	7	12	88	0
dppc[e]	18	78	1	21
$Ph_2PCH{=}CHPPh_2$	8	92	8	0
$2PEt_3$	9	1	11	88
$2PBu_3$	8	2	16	82
$2PPh_3$	44	16	30	54

[a] To a mixture of chlorobenzene (5 mmol) and a nickel complex (0.05 mmol) in 5 ml of ether was added an isopropyl Grignard solution (6.9 mmol) at 0°. The mixture was refluxed for 20 hr, hydrolyzed, and then analyzed by glpc. [b] Determined by glpc using an internal standard. [c] 1,1′-Bis(dimethylphosphino)ferrocene. [d] Bis(dimethylphosphino)-*o*-carborane. [e] Bis(diphenylphosphino)-*o*-carborane.

$$i\text{-}C_3H_7MgCl + PhCl \xrightarrow{\text{catalyst}} i\text{-}C_3H_7Ph + n\text{-}C_3H_7Ph + HPh$$

The catalysts which give rise to the preferential formation of isopropylbenzene contain, as the ligand, $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$ (dpp), $Ph_2PCH{=}CHPPh_2$, and bis(diphenylphosphino)-*o*-carborane.[2] The complexes which induce the alkyl group isomerization to afford *n*-propylbenzene preferentially comprise $Me_2PCH_2CH_2PMe_2$ (dmpe), 1,1′-bis(dimethylphosphino)ferrocene,[3] bis(dimethylphosphino)-*o*-carborane,[2b] PEt_3, and PBu_3.

This classification does not relate to the catalytic activity of the complexes but suggests that, in general, the more electron donating the phosphine ligand on nickel, the greater is the extent of the alkyl isomerization from secondary to primary. Particularly, it should be noted that with the dmpe ligand (which is good electron donating) the formation of *n*-propylbenzene is predominant, while with the dpp ligand (which appears to be sufficiently electron accepting) isopropylbenzene is formed preferentially.

The complex Ni (dmpe)Cl_2 catalyzes also the isomer-

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(1) K. Tamao, K. Sumitani, and M. Kumada, *J. Amer. Chem. Soc.*, **94**, 4374 (1972).

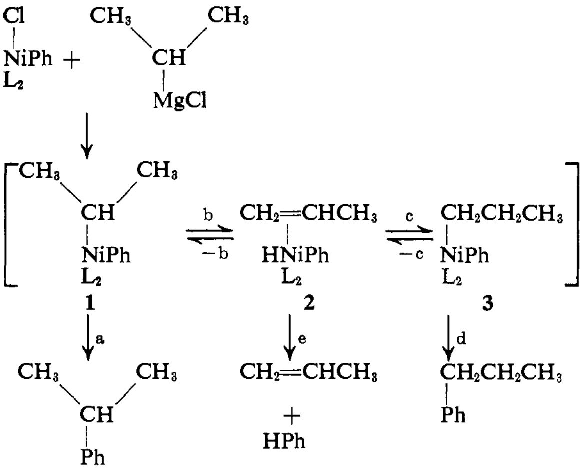
(2) (a) R. P. Alexander and H. Schroeder, *Inorg. Chem.*, 2, 1107 (1963); (b) M. Kumada, K. Sumitani, Y. Kiso, and K. Tamao, *J. Organometal. Chem.*, in press.

(3) Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, *ibid.*, in press.

ization of other secondary alkyls to primary ones. For example, 3-pentylmagnesium chloride was coupled with chlorobenzene in the presence of this catalyst to afford a mixture of normal and secondary amylbenzenes in the ratio of 92:8, while with Ni(dpp)Cl_2 as catalyst the ratio of 1-:2-:3-pentylbenzene was 2:31:67.

It seems likely that the isomerization occurs by a mechanism involving σ-alkylnickel intermediates[1] and a hydrido–olefin nickel intermediate[4] **2** (Scheme I).

Scheme I



The validity of Scheme I is supported by the fact that benzene which would arise from the decomposition of the hydrido–olefin intermediate **2** (step e) is formed, with a few exceptions, only in the cases where not isopropyl- but *n*-propylbenzene is formed preferentially.

The electronic effects of the ligands attached to nickel channel the reaction *via* one of the pathways in preference to the other. An increase in the electron density on nickel owing to the good electron-donating ligands may facilitate the $\sigma-\pi$ conversion (step b). This may be understood in terms of β effect,[5] which should lower the activation energy for the $\sigma-\pi$ conversion and become strong in view of the high electron density on nickel.[6]

The hydrido–olefin complex **2** once formed may tend to take course c rather than the reverse course −b, because of the higher stability of a primary alkyl complex **3** in comparison with the secondary one **1**.[7]

As described in the previous paper,[1] *n*-propylbenzene was a sole coupling product from the reaction of *n*-propylmagnesium bromide with chlorobenzene using Ni(dpp)Cl_2, Ni(dmpe)Cl_2, and Ni$(PPh_3)_2Cl_2$ as catalysts. In the last two cases, a small amount of benzene was also formed. Consequently, although good electron-donating ligands can cause the alkyl isomerization from secondary to primary, they cannot do it from primary to secondary. However, the formation of benzene as a by-product suggests the possibility of the primary alkyl complex **3** to rearrange to the hydrido–olefin complex **2**. The following data provide important information which serves as evidence for this.

A Grignard reagent prepared from optically active (+)-(*S*)-2-methylbutyl chloride,[8] $[\alpha]^{18}\text{D}$ +1.68° (neat) (98% optical purity),[9] was allowed to react with chlorobenzene in the presence of Ni(dpp)Cl_2 as catalyst to give optically active (+)-(*S*)-2-methylbutylbenzene (**4**), $[\alpha]^{25}\text{D}$ +10.54° (neat), $n^{25}\text{D}$ 1.4869 (lit.[10] $n^{25}\text{D}$ 1.4862), with a little loss of optical purity.[10] On the other hand, with Ni(dmpe)Cl_2 as catalyst the optical purity of the product **4** was relatively low, $[\alpha]^{25}\text{D}$ +9.56° (neat). Although the extent of racemization is rather small, the figure is meaningful and we have again observed a facilitating effect by the electron-donating ligand on the $\sigma-\pi$ conversion.

The present results probably furnish the first example of the transition metal complex-catalyzed alkyl group isomerization,[11] in which the product distribution varies significantly with the nature of the ligand on the metal.

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(4) Hydrido–nickel complexes are effective catalysts for olefin isomerization [C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 2994 (1972), and references cited therein] and also diene-skeletal rearrangement [R. G. Miller, H. J. Golden, D. J. Baker, and R. D. Stauffer, *ibid.*, **93**, 6308 (1971), and references cited therein], in which the intermediate formation of σ-alkyl-nickel species has been proposed. A hydrido-olefin-alkylplatinum intermediate has recently been confirmed in thermal decomposition of *cis*-di-*n*-butyldiphosphineplatinum [G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *ibid.*, **94**, 5258 (1972)].

(5) M. L. H. Green, "Organometallic Compounds," Vol. II, 3rd ed, Methuen, London, 1968, pp 215–216.

(6) Similar d orbital participation has recently been discussed for the facile carbon–cobalt bond cleavage in substituted alkyl cobaloximes containing a cobalt(I) atom of high electron density [G. N. Schrauzer, J. H. Weber, and T. M. Beckham, *J. Amer. Chem. Soc.*, **92**, 7078 (1970)].

(7) For pertinent discussion about the stability of transition metal–carbon bonds, see *e.g.*, W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972), and references cited therein.

(8) We thank Dr. K. Yamamoto of this laboratory for a gift of this compound.

(9) L. Spialter and D. H. O'Brien, *J. Org. Chem.*, **31**, 3048 (1966); $[\alpha]^{18}\text{D}$ +1.71° (neat).

(10) Letsinger reported a rather ambiguous maximum rotation of this compound lying in the range of 10.7–11.6° [R. L. Letsinger, *J. Amer. Chem. Soc.*, **70**, 406 (1948)], but the maximum rotation may be at best 11.8° based on the Letsinger's paper and the specific rotation $[\alpha]^{24}\text{D}$ +4.22° for 1-bromo-2-methylbutane [W. M. Foley, F. J. Welch, E. M. LaCombe, and H. S. Mosher, *ibid.*, **81**, 2779 (1959)].

(11) Alkyl Grignard reagents have been found to undergo isomerization induced by titanium tetrachloride [G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, **27**, 1493 (1962)] and by a nickel catalyst in the presence of olefin [L. Faráday, L. Bencze, and L. Markó, *J. Organometal. Chem.*, **17**, 107 (1969); L. Farády and L. Markó, *ibid.*, **28**, 159 (1971)]. Alkyl group isomerization in alkyliridium complexes has recently been reported [M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, **94**, 666 (1972)].

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Carbon–Carbon Bond Formation *via* Oxidative Addition to Vinylrhodium(I) Complexes. A New Stereospecific Synthesis of Trisubstituted Olefins from Disubstituted Acetylenes

Sir:

The use of organic derivatives of transition metals as convenient reagents for the generation of carbon–carbon bonds has had profound effect upon modern synthetic organic chemistry. Even though the versatility of these reagents is already great, new procedures must be developed which will allow for C–C bond formation to occur under milder reaction conditions than those now possible for use with known organometallic reagents. Many of the new synthetic procedures based on organocopper(I) reagents bear this out.[1–4] Since organocopper(I) reagents are prepared from copper(I)

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(1) For a review, see J. F. Normant, *Synthesis*, **2**, 63 (1972).

(2) J. Schwartz, *Tetrahedron Lett.*, 2803 (1972).

(3) E. J. Corey, C. U. Kim, R. H. K. Chen, and M. Takeda, *J. Amer. Chem. Soc.*, **94**, 4395 (1972).

(4) E. J. Corey and D. J. Beames, *ibid.*, **94**, 7210 (1972).