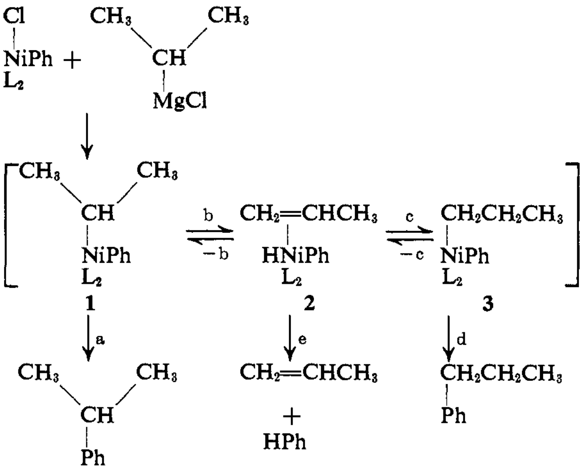
ization of other secondary alkyls to primary ones. For example, 3-pentylmagnesium chloride was coupled with chlorobenzene in the presence of this catalyst to afford a mixture of normal and secondary amylbenzenes in the ratio of 92:8, while with Ni(dpp)Cl_2 as catalyst the ratio of 1-:2-:3-pentylbenzene 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 σ–π conversion (step b). This may be understood in terms of β effect,[5] which should lower the activation energy for the σ–π 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] $[\alpha]^{18}\mathrm{D}$ +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**), $[\alpha]^{25}\mathrm{D}$ +10.54° (neat), $n^{25}\mathrm{D}$ 1.4869 (lit.[10] $n^{25}\mathrm{D}$ 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, $[\alpha]^{25}\mathrm{D}$ +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 σ–π 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); $[\alpha]^{18}\mathrm{D}$ +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 $[\alpha]^{24}\mathrm{D}$ +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).

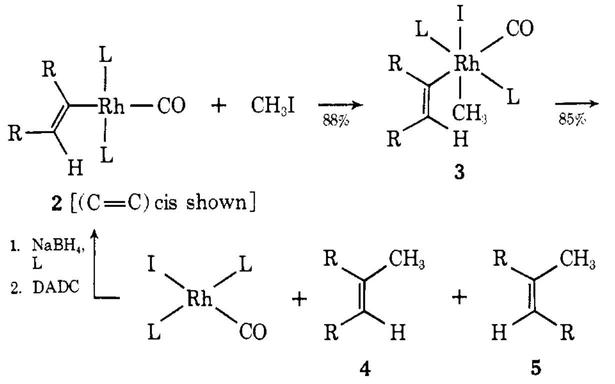
(3) E. J. Corey, C. U. Kim, R. H. K. Chen, and M. Takeda, *J. Amer. Chem. Soc.*, **94**, 4395 (1972).

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

complexes and organolithium or -magnesium species, their use depends on the availability of these precursors and upon the susceptibility of the substrate to the basic reaction conditions presupposed by them. An attractive route which could be used to effect C-C coupling under neutral, mild reaction conditions is based upon oxidative addition of organic species to coordinatively unsaturated, low-valent transition organometallic reagents to yield complexes in which two organic moieties are bonded to the high-valent transition metal by σ carbon-metal bonds.[5,6] Reductive elimination from the high-valent complex, according to this scheme, yields a C-C coupled product.

We describe herein our observations concerning a new coupling reaction in which C-C bonds are produced with high stereochemical control in high yield, conveniently, and under mild reaction conditions. We discuss this new reaction as it pertains to the stereospecific synthesis of trisubstituted olefins from disubstituted acetylenes. In this work, alkyl halides were oxidatively added to vinylrhodium(I) complexes to yield isolable alkylvinylrhodium(III) species. Heating of such a Rh(III) complex gives the trisubstituted olefin, and by selecting the correct conditions used in this step, the (C=C) stereochemistry[7] of the olefinic product can be controlled. In the sequences described, the rhodium reagent initially used can be easily and effectively recycled. An example of this reaction is shown in Scheme I.

Scheme I



R = -CO$_2$CH$_3$
L = triphenylphosphine

Although it is possible to prepare vinyl transition metal complexes from vinyllithium species,[8] it would be preferable, for the reasons mentioned above, to be able to synthesize vinyl derivatives of low-valent transition metals (C=C) stereospecifically without using lithium reagents. A convenient synthesis of vinyl transition metal complexes involves the addition of transition metal hydrides to acetylenes. In this way, (C=C) *cis*-vinyliridium(I)[9] and *cis*- or *trans*-vinylmanganese(I)[10] species have been produced. It was reported,[11] based on hydrolysis studies, that hydridotris(triphenylphosphine)carbonylrhodium(I) (HRh(CO)L$_3$, **1**) adds (C=C) stereospecifically to dimethyl acetylenedicarboxylate (DADC) to yield a *trans*-vinylrhodium(I) compound. We have examined this reaction and have shown that addition of **1** to the acetylene occurs with (C=C) cis stereochemistry,[12] just as does the iridium(I) analog,[9] to produce **2**.

In a typical C-C coupling study (see Scheme I), 180 mg (0.225 mmol) of yellow crystalline **2** was stirred with an excess of neat methyl iodide (2 ml) for 30 min at 25°. During this time, the crystals of **2** slowly dissolved. The solvent was then removed by evacuation and dimethyl [iodocarbonylbis(triphenylphosphine)methylrhodium(III)]maleate (**3**) was obtained. The reaction product was washed several times with ether to yield cream-colored crystals (187 mg; 88%; ir (KBr) $\nu_{C=O}$ 2023, $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1560 cm^{-1}. *Anal.* Calcd for $C_{44}H_{40}IO_5P_2Rh$: I, 13.5, P, 6.6. Found: I, 13.5; P, 6.7). The stereochemistry about Rh(III) in **3** is tentatively assigned as trans based on the many reported examples of trans oxidative addition of methyl iodide to d^8 metals.[13]

To effect C-C coupling with (C=C) stereochemistry cis, 76 mg (0.081 mmol) of **3** was placed in a flask attached to a long condensation tube. The entire assembly was evacuated to 80 μ. The flask was then placed in a Kugelrohr oven preheated to 115°. Colorless vapor immediately condensed in the cold tube. The condensate was unambiguously identified by vpc and spectral comparison with authentic materials to contain >98% dimethyl citraconate (**4**) and <2% dimethyl mesaconate (**5**). No other volatile products could be detected. The total yield of recovered esters was 11 mg (85%).

A sample of **3** was placed in a similar evacuated assembly which was then inserted into a cold oven. The oven was allowed to warm slowly to 115°. Product began to appear in the condensation tube when the oven temperature reached 70°. In this way, a sample identified as containing >75% **5** and <25% **4** was slowly obtained. No dimethyl fumarate, the expected product of C-Rh homolytic cleavage, was produced. We have shown that **4** is not converted to **5** *under the reaction conditions* either alone or in the presence of HRh(CO)L$_3$ or IRh(CO)L$_2$. We have also shown, by rapid pyrolysis at 115° of methyl iodide adducts, that the *cis*-Rh(I) species, *cis*-**2**, is not converted to its trans isomer, *trans*-**2**, thermally below its decomposition temperature. It appears, thus, that (C=C) cis to trans isomerization must occur only for the Rh(III) complex studied. In both cases of the coupling reaction, the transition metal was recovered as IRh(CO)L$_2$ which was identified spec-

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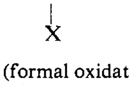
(5) The low-valent organotransition metal complex C-M^{n-2} (formal metal oxidation state, n - 2) undergoes oxidative addition of C-X to



$$\underset{\displaystyle X}{C\text{—}M^{n}\text{—}C}$$

yield the high-valent complex (formal oxidation state, n).

(6) For the synthesis of such a reagent, see J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, **94**, 6226 (1972).

(7) This denotes cis or trans stereochemistry about the olefinic bond of organic compounds or of σ-vinyl organometallic complexes.

(8) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

(9) W. H. Baddley and M. S. Fraser, *ibid.*, **91**, 3661 (1969).

(10) B. L. Booth and R. G. Hargreaves, *J. Organometal. Chem.*, **33**, 365 (1971).

(11) B. L. Booth and A. D. Lloyd, *ibid.*, **35**, 195 (1972).

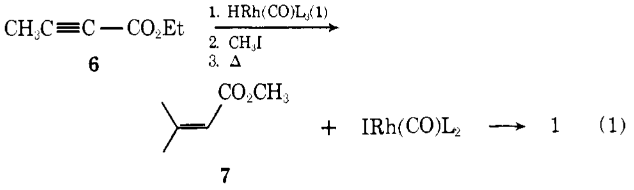
(12) Treatment of **2**, prepared as described and spectrally identical with the complex reported (ref 11), with dry, gaseous HCl in benzene for less than 1 min followed by washing with aqueous NaHCO$_3$ and vpc analysis of the organic fraction showed that dimethyl *maleate* was the initial product of C-M protonolysis. If the reaction time prior to washing with aqueous NaHCO$_3$ is lengthened, the yield of maleate decreases rapidly and dimethyl fumarate is produced.

(13) For example, see J. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); J. Halpern, *ibid.*, **3**, 386 (1970); R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970), and references cited therein.

trally and by elemental analysis and which was recycled, in 86% yield, overall, to $HRh(CO)L_3$ (**1**).

We believe that the C–C coupling step is a concerted one. The formation of trisubstituted olefin with greater than 98% cis stereochemistry from the *cis*-methylvinylrhodium(III) complex **3** indicates that the coupling step does not proceed through free radcals.[14]

The scope of the Rh(I) based coupling reaction is not limited to the choice of metal hydride, acetylene, and alkyl group discussed in detail herein. In preliminary studies, we have shown that L_4RhH reacts readily with DADC to yield **2** after carbonylation. We have also observed that ethyl iodide reacts smoothly with **2** to yield, upon gentle heating at 80°, ethyl-substituted cis- and trans-trisubstituted olefins.[15] Finally, initial studies show that $HRh(CO)L_3$ reacts with ethyl tetrolate (**6**) to give an isolable Rh(I) complex which, upon treatment with methyl iodide, yields ethyl β,β-dimethylacrylate (**7**) (see eq 1), at room temperature.



We are now examining the effect of varying metal ligands upon the metal hydride addition reaction. We are also studying the (C=C) isomerization reaction for Rh(III) complexes in order to produce trans-trisubstituted olefins from acetylenes with greater stereoselectivity than is now possible. The detailed results of these studies will be reported in the near future.

Acknowledgment. The authors gratefully acknowledge support for this work given by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF-2454-GI), and by the Research Corporation. They also acknowledge the generosity of Hoffmann-La Roche, Inc., in providing them with elemental analysis services.

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[14] For similar reasoning ruling out free-radical coupling of vinyl groups arising from the thermal decomposition of vinylcopper(I) species, see ref 8.

[15] Thus far, product yields of up to 72%, based on DADC, have been observed.

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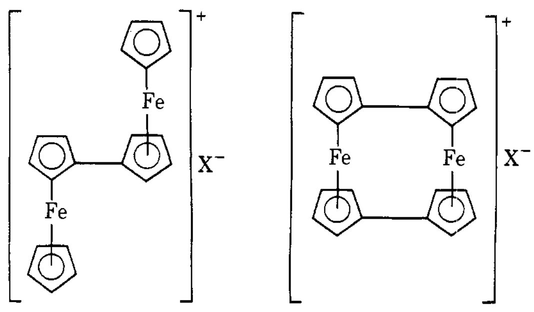
1,1′-Biferrocenylene[Fe(II)Fe(III)] Salts[1]

Sir:

The interesting properties recently observed for the mixed valence compound biferrocene[Fe(II)Fe(III)] picrate (**1**)[2] prompted us to prepare mixed valence salts of 1,1′-biferrocenylene: 1,1′-biferrocenylene[Fe(II)Fe(III)] picrate (**2**) and 1,1′-biferrocenylene[Fe(II)Fe(III)] $(TCNQ)_2^-$ (TCNQ = tetracyano-*p*-quinodimethane) (**3**). The rigid geometry of the 1,1′-biferrocenylene could allow greater through-bond and through-space interaction of the two component parts.[3] As a result of this increased interaction the properties of **2** and **3** should be different from those of **1**.



1, X = picrate

2, X = picrate
3, X = $(TCNQ)_2^-$

The biferrocenylene was prepared by a modification of the method of Hedberg and Rosenberg.[4] Inasmuch as the yield in the coupling reaction of 1,1′-diiodoferrocene in the presence of copper bronze depends upon the purity[5] of the low-melting 1,1′-diiodoferrocene and this compound is extremely difficult to purify, the 1,1′-diiodoferrocene was replaced with the more easily purified 1,1′-dibromoferrocene.[6] When the coupling reaction was performed with 1,1′-dibromoferrocene in biphenyl at 190° an 18% yield of the red crystalline 1,1′-biferrocenylene was obtained. The properties of this compound are identical with those previously reported.[4,7] Oxidation of 1,1′-biferrocenylene with benzoquinone in the presence of picric acid (benzene solvent)[8] gave **2** while **3** was obtained by the TCNQ oxidation of 1,1′-biferrocenylene in acetonitrile.

Anal. Calcd for **2**, $C_{26}H_{18}N_3O_7Fe_2$: C, 52.38; H, 3.04; N, 7.05. Found: C, 52.20; H, 3.05; N, 6.71. Calcd for **3**, $C_{44}H_{24}N_8Fe_2$: C, 68.07; H, 3.11; N, 14.42. Found: C, 67.96; H, 3.22; N, 14.21.

The infrared spectrum of **2** measured in a KBr pellet was what would be expected based on the infrared spectra of 1,1′-biferrocenylene and biferrocene[Fe(II)-Fe(III)] picrate[8] (for example, three transitions were observed in the far-infrared ring-tilt, stretch region: 350, 458, and 492 cm^{-1}). The infrared spectrum of **3** measured in a KBr pellet indicated similar but very weak transitions on a background of almost total absorption or reflection from 4000 to 400 cm^{-1}. Compound **2** had two overlapping absorptions of approximately equal intensity in the cyclopentadienyl C–H out-of-plane bending region[9] (835 and 842 cm^{-1}). Ferricenium ions exhibit absorption in the 840–870-cm^{-1} region while ferrocenes have the corresponding absorption at 810–835 cm^{-1}. This suggests that the two ferrocenyl rings are not identical.[10]

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[1] The Organic Solid State. X. For part IX see J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Amer. Chem. Soc.*, in press.

[2] (a) D. O. Cowan and F. Kaufman, *ibid.*, **92**, 219 (1970); (b) F. Kaufman and D. O. Cowan, *ibid.*, **92**, 6198 (1970).

[3] D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Accounts Chem. Res.*, 6, 1 (1973).

[4] F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **91**, 1258 (1969).

[5] F. L. Hedberg, personal communication and unpublished data of C. LeVanda.

[6] R. F. Kovar, M. D. Rausch, and H. Rosenberg, *Organometal. Chem. Syn.*, 1, 173 (1971).

[7] M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 91, 1259 (1969).

[8] D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, **75**, 2025 (1971).

[9] C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prado, *Macromolecules*, 3, 746 (1970).