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METHYL–TRANSITION METAL SYSTEMS AND DIPHENYLACETYLENE

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SUMMARY

Methylmagnesium chloride reacts with the chlorides of Ti^{III}, Ti^{IV}, Zr^{IV}, V^{III}, Nb^{V}, Cr^{II}, Cr^{III}, Mo^{V}, Mn^{II}, Fe^{III}, Ru^{III}, Co^{II}, Rh^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Cu^{I}, Cu^{II}, Au^{III} and Zn^{II} at −70° in tetrahydrofuran to give methyl–transition metal reagents. These reagents react with diphenylacetylene giving methylation and hydrogenation products, as well as oligomerization.

INTRODUCTION

The reaction of the methylchromium reagent prepared from methylmagnesium chloride and chromium trichloride tris(tetrahydrofuranate) with diphenylacetylene has been studied quite thoroughly[1–4]. During this study it was observed[2] that halides of cobalt and nickel gave broadly similar reactions to the chromium salt, *i.e.* they promote methyl and hydrogen transfer to the acetylene. This observation has now been extended to a representative selection of transition metal halides.

RESULTS AND DISCUSSION

In a series of small scale reactions methylmagnesium chloride was mixed with a little less than the stoichiometric quantity of the metal halide in tetrahydrofuran (THF) at −70°, according to the equation:

$$n\ \text{MeMgCl} + \text{MCl}_n \longrightarrow \text{MMe}_n + n\ \text{MgCl}_2 \qquad (1)$$

Diphenylacetylene in THF was added at −70° such that the methyl–metal reagent was in a 5–10 fold excess (for exact ratios see Table 5). The mixture was warmed slowly to ambient temperature and hydrolyzed after 24 h. Chromatography on silica gel separated the monomeric products on elution with hexane. These were analyzed by gas–liquid chromatography (GLC). Those metals which gave the largest yield of monomeric products were studied in more detail, this usually requiring a larger scale experiment.

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TABLE 1

GLC ANALYSIS OF HEXANE ELUTED FRACTION[a]

Halide	Diphenylacetylene		*cis*-Stilbene	Dibenzyl	*trans*-Stilbene	*trans*-α-Methylstilbene	Benzyl, Styrene[b]	*d,l*-2,3-Diphenylbutane[c]	*cis*-α-Methylstilbene	1,2-Diphenylpropane	*cis*-Dimethylstilbene	*meso*-2,3-Diphenylbutane	Unknown[d]	Total (excluding PhC≡CPh)
	Used	Recovered												
None	307	294												0
	255	237												0
$CaCl_2$	344	294												0
$ScCl_3$	258	227												0
$TiCl_3$	214	3	14	1	7	12	9	4[e]	7	2		4	5[f]	65
$TiCl_4$	353	109	11	1	4	18	7		7			10		58
$ZrCl_4$	168	104	2		5		2		2			2		13
VCl_3	178	2	4		8		1		3			1		17
$NbCl_5$	181	2	6		2				3					11
$CrCl_2$	301	2	9		10				5			2		26
$CrCl_3$	178[g]	49	7		8		5		5			3		28
	178[h]	4	3	2	10	4	5		3	2		4		33
$MoCl_5$	348	156	2		7		3		3			3		18
$MnCl_2$	244	133			2						14	6[i]		22
$FeCl_3$	443	11	33	5	18	1	8		6	6		2		77
$RuCl_3$	83	1			1					<1				1
$CoCl_2$	224	5	2		4	<1	6			17		5		34
$RhCl_3$	174	1	3		6	<1					14	1		29
$NiCl_2$	286	2	16	18	8	17		11	9	13		1	14	107
$PdCl_2$	273	102	23		4	3			3		7	4[i]		44
$PtCl_2$	184	1	2		4				14	2	9	1		32
CuCl	328	233[j]			3				10		10			23
	246	203[k]									4			4
$CuCl_2$	248	118			5						31		2	38
$CuBr_2$	244	135			1						11		5	17
$AuCl_3$	176	73												0
$ZnCl_2$	232	208			1		2							3

[a] All figures are in mg. [b] Positively identified in the mixtures. [c] Possibly present in the mixtures. [d] Probably *trans*-dimethylstilbene. [e] Containing some impurity. [f] Different from the nickel unknown. [g] Using aged $CrCl_3(THF)_3$. [h] Using freshly prepared $CrCl_3(THF)_3$. [i] Containing at least a trace of *meso*-2,3-diphenylbutane. [j] Only a 2-fold excess of methyl–metal reagent. [k] Usual stoichiometry.

(*a*). *Monomeric products*

Table 1 shows the monomeric products formed by hydrogen and methyl group transfer to diphenylacetylene. Because addition of even two methyl groups to PhC≡CPh increases the molecular weight by only 17%, the weights shown in Table 1 are closely related to the yields. Since a large excess of methyl–metal reagent was used, the amount of diphenylacetylene consumed is an indication of the reactivity of the reagent. On this basis the methyl–metal systems fall into three distinct classes.

(*i*). Ti^{III}, V^{III}, Nb^{V}, Cr^{II}, Cr^{III}, Fe^{III}, Ru^{III}, Co^{II}, Rh^{III}, Ni^{II}, and Pt^{II} chlorides give systems which produce over 90% reaction of the diphenylacetylene. Of these, those giving the highest yield of methylated and reduced monomers are Ni^{II} 37%, Ti^{III} 30%, Cr^{III} 19%, and Fe^{III} 18%. Ruthenium trichloride gives only 2%, the rest of the diphenylacetylene going to high molecular weight products.

(*ii*). Ti^{IV}, Zr^{IV}, Mo^{V}, Mn^{II}, Pd^{II}, Cu^{I}, Cu^{II} and Au^{III} all give considerable but by no means complete consumption of the diphenylacetylene. It was also found that as $CrCl_3(THF)_3$ aged so the reagent prepared from it became less effective in reaction with diphenylacetylene, although the ratios of individual monomeric products remained constant. Some of these metals give a high proportion of monomeric products on the basis of diphenylacetylene actually consumed: Cu^{II} 29%, Cu^{I} and Ti^{IV} 24%, Pd^{II} 22%.

(*iii*). Ca^{II}, Sc^{III} and Zn^{II} chlorides give less than 10% reaction. From the two blank runs it can be seen that the loss of diphenylacetylene from working-up procedures is 4–7%. Since only for Zn^{II} were any traces of monomeric products detected, it seems likely that no reaction at all occurs with Sc^{III} and Ca^{II}.

It is possible that the proportion of volatile products from reactions in the first class could be increased by reducing the reaction time; and the extent of reaction in the second class by increasing the reaction time (*i.e.* the pre-warm up time).

The results in Table 1 show that only certain metals in the second half of the transition metal series give rise to *cis*-dimethylstilbene. They are Mn^{II}, Rh^{III}, Pd^{II}, Pt^{II}, Cu^{I} and Cu^{II}. Of these $CuCl_2$ gives the best yield (82% of the monomeric product) and since published preparations of *cis*-dimethylstilbene are all tedious, this may provide a better method of making it.

The current view[5] of the reaction between a methyl Grignard and a Cu^{II} salt can be summarized as in eqn. (2):

$$Cu^{II} \xrightarrow{MeMgCl} Cu^{I} \xrightarrow{MeMgCl} MeCu \xrightarrow{MeMgCl} Me_2Cu^- \tag{2}$$

Furthermore it has been found that the addition of Me_2CuLi to $n\text{-}C_7H_{15}C{\equiv}CCO_2Me$ in THF gives[6,7] 99.8% *cis* addition at −78°, but 39% *cis* and 61% *trans* at 0°. The present investigation shows that the Cu^{II} reagents give a much higher yield of *cis*-dimethylstilbene than the Cu^{I} reagent, when the usual ratio of methyl–metal reagent to diphenylacetylene is used. When this ratio is halved, the Cu^{I} reagent gives a higher total yield, but the products consist of equal amounts of the *cis*-mono- and dimethylstilbenes. Thus it appears that reduction of the Cu^{II} is closely linked with methylation of the acetylene, leading to the dimethylstilbene, indicating that metals which are easily reduced should give good methylating agents. It is also significant that the methyl group undergoes little if any disintegration.

Pt^{II}, like Cu^{I}, also gives rise to both *cis*-methylstilbene and *cis*-dimethylstilbene, together accounting for 72% of the monomeric products. Pd^{II} gives a high yield of *cis*-stilbene (52% of the monomeric product) and no dibenzyl whereas Ni gives these two compounds in almost equal amounts. The Ni^{II} reaction is also of interest because of the amount of *d,l*-2,3-diphenylbutane formed, eleven times as much as the *meso*-2,3-diphenylbutane. The unidentified compound is quite prominent in this reaction, and is almost certainly *trans*-dimethylstilbene. The most important product from the $cobalt^{II}$ reaction is 1,2-diphenylpropane (50% of the monomeric products).

The Au^{III} and Ru^{III} reactions appear to give almost no monomeric product, although a large proportion of the diphenylacetylene is consumed (99% for Ru^{III}).

With Fe^{III} the ratio of *cis* and *trans*-stilbenes to *cis* and *trans*-methylstilbenes is 7/1, in contrast with the same ratio in Ni^{II} which is approximately 1/1. The unknown compound in the Cr^{III} reaction is probably the same as that in the nickel reaction, since it has the same mass spectrum, and is considered to be *trans*-dimethylstilbene, whereas that in the Ti^{III} reaction is different as it has a different GLC retention time on certain stationary phases.

With Ti^{III} the ratio of stilbenes to methylstilbenes is again approximately unity. Ti^{IV} gave much less reaction, but of the diphenylacetylene which did react, the proportion reduced or methylated (24%) was almost as great as that for Ti^{III} (30%) and the ratios of the individual products are similar.

(*b*). *Oligomeric products*

After removal of the monomeric products by hexane elution from silica gel, further elution with benzene, ether and ethanol led to the recovery of higher molecular weight material. As previously mentioned, the monomeric products identified show addition of not more than two CH_3 units per $PhC{\equiv}CPh$ unit, and if such addition were complete the total weight of material should not increase by more than 17%. For this reason it was expected that the total weight of material recovered would be fairly close to the weight of diphenylacetylene used. In most cases this is so (Table 2). With Nb^{V} however (and to a much lesser extent with Cr^{II} and Ru^{III}) the weight of material eluted is greatly in excess of the weight of diphenylacetylene taken. The IR spectra of the ether and ethanol eluted fractions in these cases suggests that they are THF derived polymers. With Pt^{II} and Au^{III} on the other hand, an appreciable proportion of the material remained on the silica gel and is presumably in the form of a very high molecular weight polymer derived from diphenylacetylene.

The ether and ethanol eluates proved too involatile for satisfactory study by GLC, but the benzene eluates were more tractable, and it was possible to identify some of the compounds present (Table 3). It should be noted that because of the small quantities of material involved, and the large number of products generally formed, identification was attempted for only the most prominent peaks. Therefore only compounds identified unequivocally are listed. It can at any rate be said that in the first half of the series the formation of 1,2,3-triphenylnaphthalene, 1,2,3,4-tetraphenyl-1,3-cyclopentadiene and hexaphenylbenzene predominates, whereas in the second half of the series two unknown compounds are by far the most prominent products. For Mn^{II} and the copper halides these two compounds are the only significant ones. Their mass spectra (molecular ions at 372 and 386) suggest they may be a tetraphenylpentadiene and a tetraphenylhexadiene respectively, and since they are

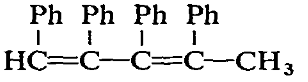
TABLE 2

SILICA-GEL COLUMN CHROMATOGRAPHY OF REACTION MIXTURES[a]

Halide	Diphenylacetylene used	Hexane eluate	Benzene eluate	Ether eluate	Ethanol eluate	Total recovered
None	307	294	1	3	5	303
	255	237	4	5	7	253
$CaCl_2$	344	294	8	7	7	316
$ScCl_3$	258	227	6	4	4	241
$TiCl_3$	214	68	126	28	7	229
$TiCl_4$	353	167	92	65	19	343
$ZrCl_4$	168	117	22	6	7	152
VCl_3	178	19	72	35	22	148
$NbCl_5$	181	13	32	296	561	903
$CrCl_2$	301	28	244	368	23	663
$CrCl_3$	178[b]	77	68	26	10	181
	178[c]	37	118	62	9	216
$MoCl_5$	348	174	70	152	39	435
$MnCl_2$	244	155	50	149	24	378
$FeCl_3$	443	88	247	37	12	384
$RuCl_3$	83	2	17	125	52	196
$CoCl_2$	224	39	125	120	19	303
$RhCl_3$	174	30	71	126	22	249
$NiCl_2$	286	109	103	33	17	262
$PdCl_2$	273	146	23	14	10	193
$PtCl_2$	184	33	30	6	5	74
CuCl	328[d]	256	8	5	6	275
	246[e]	203	18	5	3	229
$CuCl_2$	248	156	46	10	11	223
$CuBr_2$	244	152	26	10	10	198
$AuCl_3$	176	73	6	13	1	93
$ZnCl_2$	232	211	14	6	13	244

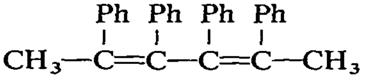
[a] All figures are in mg. [b] Using aged $CrCl_3(THF)_3$. [c] Using freshly prepared $CrCl_3(THF)_3$. [d] Only a 2-fold excess of methyl–metal reagent. [e] Usual stoichiometry.

most important for those reagents which favor methylation, structures such as



$$\overset{Ph}{HC}=\overset{Ph}{C}-\overset{Ph}{C}=\overset{Ph}{C}-CH_3$$

and



$$CH_3-\overset{Ph}{C}=\overset{Ph}{C}-\overset{Ph}{C}=\overset{Ph}{C}-CH_3$$

seem not unlikely.

The detection of 1-benzylidene-2,3-diphenylindene in only two cases is nevertheless significant since, unlike all the other compounds, it is not colorless, but yellow. Most of the benzene eluates obtained were yellow, and this color may therefore indicate the wide-spread occurrence of traces of 1-benzylidene-2,3-diphenylindene.

(*c*). *Reactions in nitrogenous solvents*

The reaction of the methylchromium reagent with diphenylacetylene has been investigated in benzene and diethyl ether[3] and it was found that it did not differ appreciably from that in THF. Because the methylchromium reagent was prepared from $CrCl_3(THF)_3$ there was the possibility that the reagent still contained coordi-

TABLE 3

COMPOUNDS IDENTIFIED IN BENZENE ELUATE

Halide	1,2,3-Triphenylnaphthalene	1,2,3,4-Tetraphenyl-1,3-cyclopentadiene	Hexaphenylbenzene	Unknown[a]	Unknown[b]	1,2,3,4-Tetraphenyl-1,3-butadiene	1-Benzylidene-2,3-diphenylindene
None							
$CaCl_2$							
$ScCl_3$							
$TiCl_3$	x	x	x				
$TiCl_4$	x	x	x				
$ZrCl_4$	x		x	x	x		
VCl_3	x	x					x
$NbCl_5$	x	x				x	
$CrCl_2$	x	x	x				
$CrCl_3$	x		x				
$MoCl_5$	x	x					
$MnCl_2$		x		x	x		
$FeCl_3$			x	x	x	x	
$RuCl_3$	x	x	x				
$CoCl_2$		x					
$RhCl_3$	x						
$NiCl_2$				x	x		
$PdCl_2$			x	x	x		
$PtCl_2$				x	x		x
CuCl							
$CuCl_2$				x	x		
$CuBr_2$				x	x		
$AuCl_3$							
$ZnCl_2$				x	x		

[a] Possibly tetraphenylpentadiene. [b] Possibly tetraphenylhexadiene.

nated THF. Thus it was possible to conclude only that the nature of the bulk solvent did not affect the course of the reaction.

In view of the possible participation by coordinated solvent in hydrogen abstraction reactions we were interested to try the reaction in the complete absence of THF. Interaction of methyl Grignard in dimethylaniline/triethylamine solvent with $[(NH_3)_6Cr]Cl_3$ in the presence of diphenylacetylene resulted in the recovery of the acetylene unchanged. The use of tris(pyridine)chromium trichloride was also unsuccessful.

It seemed likely that more success would attend the use of a 5-coordinate chromium complex and bis(trimethylamine)chromium trichloride[8] was chosen. With methylmagnesium chloride and diphenylacetylene reaction did occur giving similar yields of the same products as the reagent prepared from aged $CrCl_3(THF)_3$ (Table 4). Using a methyl Grignard prepared by quenching (with triethylamine) a methyl Grignard prepared in THF gave similar results. Simply mixing chromium trichloride, trimethylamine and methylmagnesium chloride at −70° with diphenylacetylene gave no reaction.

From this it is evident that the exact nature of the solvent, even that which is coordinated to the metal center, is not of vital importance, providing it does not coordinate so effectively as to exclude the formation of a methyl–metal complex.

TABLE 4

PRODUCT DISTRIBUTION (%) FROM THE INTERACTION OF DIPHENYLACETYLENE WITH METHYLCHROMIUM REAGENTS A (FROM AGED $CrCl_3(THF)_3$ AND MeMgCl IN THF) AND B (FROM $(Me_3N)_2CrCl_3$ AND MeMgCl IN Et_3N AND Me_2NPh)

Product	A	B
Hexane eluate		
PhC≡CPh recovered	28	37
cis-Stilbene	3	3
trans-Stilbene + *trans*-methylstilbene	4	3
Dibenzyl	1	
Benzyl styrene	3	1
cis-Methylstilbene	3	6
Unidentified product[a]	2	
Benzene eluate[b]	38	34
Ether eluate	15	7
Ethanol eluate	6	2
Total recovered	103	93

[a] Probably *trans*-dimethylstilbene. [b] Mainly hexaphenylbenzene.

Mechanism

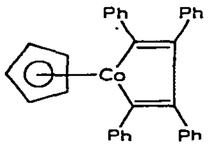
It has been suggested[2,4] that in the reaction between the methylchromium reagent and diphenylacetylene, a reactive complex is formed in which methyl groups are σ-bonded to the chromium, and diphenylacetylene is also bound to the metal, presumably by interaction of the acetylene π-bonds with the metal *d*-orbitals. Since the solvent was also assumed to participate in the reaction, the reactive complex must also have coordinated THF. It was further suggested[4] that the initiating step in the reaction was disruption of the chromium–methyl bond, possibly brought about by the displacement of stabilizing THF by PhC≡CPh with subsequent attack of the liberated or partially liberated methyl group on the diphenylacetylene. Hydrogenation resulted mainly from hydrogen transfer from methyl bound chromium groups or coordinated solvent to activated acetylene.

The work described here on the reactions of other metal-based methyl reagents supports this general picture. The lack of reactivity of the calcium, scandium and magnesium reagents, and the very low reactivity of the zinc reagent supports the view that coordination of the acetylene to the metal is necessary, since these metals would not be expected to coordinate the acetylene. Elements (Cu, Mn) which give fairly stable methyl derivatives give less extensive reaction, but a greater portion of methylation, and less hydrogenation.

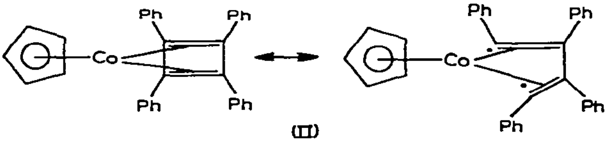
The experiments using the methylchromium complex derived from $CrCl_3(THF)_3$ in benzene and diethyl ether indicated that the bulk solvent played no significant part in the reaction, except to provide a convenient medium[3]. It is not even established that a good solvent is required, since most of the reaction mixtures are heterogeneous. That solubility, or the amount of coordinated solvent affect the reaction is demonstrated by the differences between freshly prepared, and aged

$CrCl_3(THF)_3$. It seems likely that it is not a solubility effect, but rather a coordination effect. This would be reasonable if the solvent were involved in the reaction. Furthermore, when $(Me_3N)_2CrCl_3$ is used to provide the methylchromium complex, the extent of reaction is very similar to that obtained with aged $CrCl_3(THF)_3$. Me_3N would not be expected to provide hydrogen atoms as readily as THF does, and if the aged THF contains fewer molecules of coordinated THF than the freshly prepared sample, it too might give a slower reaction.

It is well known that in reactions leading to complexes having two acetylene molecules coordinated to a metal, the usual result is the fusion of the acetylenes to give a condensed ligand π- or σ-bonded to the metal. For this reason, one must assume that when monomeric products (*i.e.* stilbenes, etc.) are formed in high yield, it is because the metal does not find it easy to coordinate more than one acetylene unit at a time. This may be because it cannot easily back-donate the excess charge resulting from π-donation by the acetylene, or because the first acetylene is bonded in such a way as to occupy two coordination sites and steric interactions become important. Conversely, when condensed products are important, this must be a result of the ease of coordination of more than one acetylene.

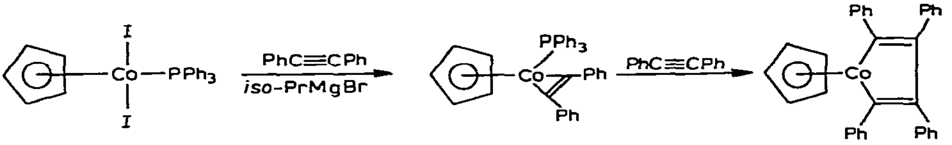


(I)



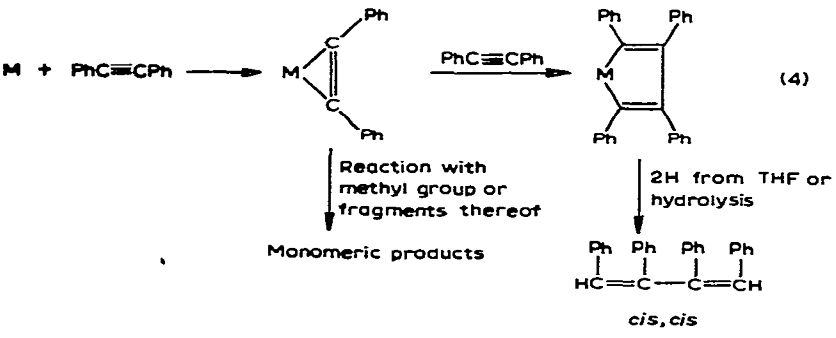
(II)

The two possibilities of π- or σ-interaction between the condensed acetylenes are illustrated by (I) and (II)[9]. A model reaction leading to the five-membered metallocene ring has been described[10]:



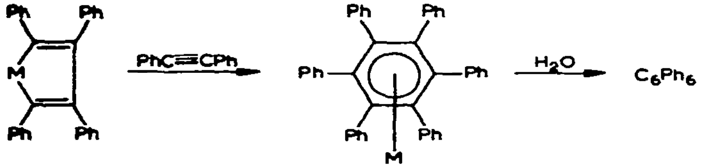
(3)

Thus in the present reactions the monoacetylene derivatives must be regarded as arising from intermediates with one acetylene complexed to the metal, and the con-



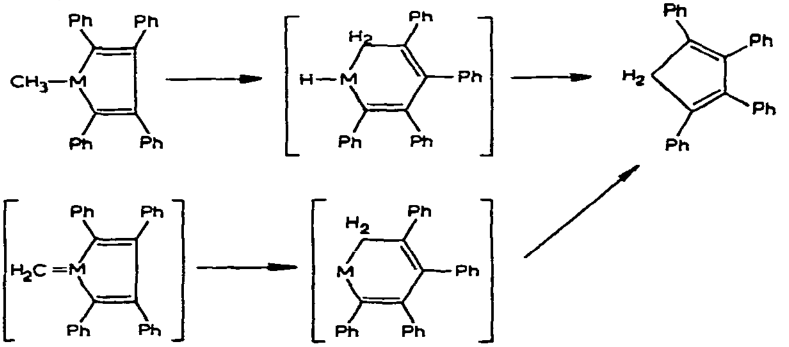
(4)

densed acetylene derivatives from two or more. The 5-membered ring is preferred over the cyclobutadiene as an intermediate because recent evidence showed[11] that catalysts for acetylene trimerization such as $Ph_3Cr(THF)_3$ and $(mesityl)_2Co$ do not give cyclobutadiene-type intermediates, but may go through a 5-membered metallocyclic stage. The catalyst $(PhCN)_2PdCl_2$ probably does go through a cyclobutadiene intermediate, but this is not similar to the methylmetal reagents described here, as it does not as far as is known, produce hydrogenation and alkylation[12]. If a third molecule of PhC≡CPh is captured, it seems certain that formation of a 6-membered π-complexed ring would be favored over the σ-bonded 7-membered ring. This sort of mechanism has been proposed for the catalysis by Rh and Ir complexes of the trimerization of acetylenes[13].



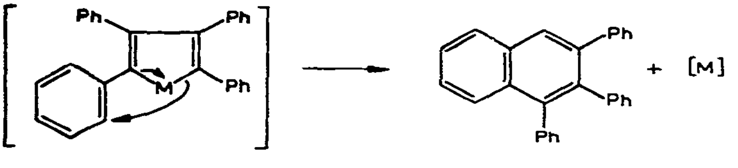
(5)

Where methyl or CH_2 are in close association with the metal, insertion of these species may occur:



(6)

The formation of 1,2,3-triphenylnaphthalene is straightforward:



(7)

EXPERIMENTAL (With Mr. W. HESS)

Experiments for comparing the reactivity of methyl–metal systems were all carried out in the same way. 2–3 mmole of the metal salt, or tetrahydrofuranate, were stirred with THF at −70° under nitrogen. A 1.2 to 1.5-fold excess of methylmagnesium chloride (prepared from methyl chloride and magnesium in THF) was added according to eqn. (8):

$$\mathrm{MX}_n + n\ \mathrm{MeMgX} \longrightarrow \mathrm{Me}_n\mathrm{M} + n\ \mathrm{MgX}_2 \tag{8}$$

The addition was made over approximately $\frac{1}{4}$ h. A solution of diphenylacetylene in THF was added, such that the methyl–metal reagent was in 5 to 10-fold excess on the basis of methyl groups per diphenylacetylene molecule (see Table 5 for exact stoichiometry). The mixture was allowed to warm slowly to room temperature (3–4 h), and stirred for a further 20 h. The reaction mixture was then hydrolyzed with dilute hydrochloric acid and extracted with diethyl ether. The ethereal layer was washed with water and dried over $CaCl_2$.

TABLE 5

QUANTITIES OF REAGENTS USED

M[a]	(mmoles)	Me[b]MgCl (mmoles)	$\frac{\text{Me}}{\text{M–Cl}}$	PhC≡CPh (mmoles)	$\frac{\text{Me–M}}{\text{PhC≡CPh}}$
Ca^{II}	4.4	13.3	1.5	1.9	4.6
Sc^{III}	3.3	13.4	1.4	1.5	6.6
Ti^{III}	2.8	10.9	1.3	1.2	7.0
Ti^{IV}	4.6	22.8	1.2	2.0	9.2
Zr^{IV}	2.2	10.9	1.2	1.0	8.8
V^{III}	2.3	9.2	1.3	1.0	6.9
Nb^{V}	2.4	14.7	1.2	1.0	12.0
Cr^{II}	3.9	11.7	1.5	1.7	4.6
Cr^{III}	2.3[c]	9.2	1.3	1.0	6.9
	2.3[d]	9.2	1.3	1.0	6.9
Mo^{V}	4.5	27.0	1.2	2.0	11.3
Mn^{II}	3.2	9.5	1.5	1.4	4.6
Fe^{III}	5.8	23.4	1.3	2.5	7.0
Ru^{III}	1.1	4.3	1.3	0.5	6.6
Co^{II}	2.9	8.7	1.5	1.3	4.5
Rh^{III}	2.3	9.0	1.3	1.0	6.9
Ni^{II}	3.7	11.1	1.5	1.6	4.6
Pd^{II}	3.5	10.6	1.5	1.5	4.7
Pt^{II}	2.4	7.1	1.5	1.0	4.8
Cu^{I}	4.2[e]	8.5	2.0	1.8	2.3
	6.3[f]	9.5	1.5	1.4	4.5
Cu^{II} (Cl)	3.2	9.6	1.5	1.4	4.6
(Br)	3.2	9.5	1.5	1.4	4.6
Au^{III}	2.3	9.1	1.3	1.0	6.9
Zn^{II}	3.0	9.0	1.5	1.3	4.6

[a] M = metal. [b] Me = methyl. [c] Using aged $CrCl_3(THF)_3$. [d] Using freshly prepared $CrCl_3(THF)_3$. [e] Only a 2-fold excess of methyl-metal reagent. [f] Usual stoichiometry.

The ether was evaporated and the residue redissolved in hexane and chromatographed on silica gel (Merck A.G., 0.05–0.20 mm). Hexane (200 ml) removed all the diphenylacetylene and the monomeric products. These were analyzed by GLC (Hewlett–Packard F&M 700 Laboratory chromatograph) on a silicone rubber stationary phase (UC-W98, 10%, on chromosorb-P packing, 60–80 mesh in $\frac{1}{8}''$ copper tubing, 6 ft. long; helium carrier gas, 30 ml/min; thermal conductivity detector, 180°). Few of the peaks were due to single compounds. Analysis on other columns (XF-1150, 10% on chromosorb, 100/120 mesh, 5 ft. long and Carbowax 20M, 10%) gave different combinations, but no general improvement. Attempted analysis by comparison of the integrated results (disc integrator) from injections on the three different columns was unsuccessful, probably because of the small quantities of some of the products compared with others. The technique finally adopted was to integrate the chromatograph on the UC-W98 column and then separate the multiple peaks, and analyze these for % constituents on the appropriate column of the other two. Where necessary, larger scale reactions were used for these separations. Where products were obtained which had not been described in the earlier work, they were isolated and identified by mass (CEC 21-104 and CEC 21-110B spectrometers) and PMR (Varian HA-60-IL) spectroscopy, as well as by GLC comparison with authentic samples.

Elution with benzene (200 ml) gave a second fraction. This was inspected by recrystallization for hexaphenylbenzene (characteristic crystal transition at 280°), and GLC (at 280° on UC-W98) for a number of other compounds expected from these reactions.

Reactions in nitrogenous solvents

As a solvent triethylamine was chosen as being liquid at −70°, and reputedly a good medium for the preparation of alkyl Grignards[14]. In fact we found it difficult to repeat the published procedures for the preparation of Grignards in triethylamine and these have since been modified[15,16]. We found, however, that methyl Grignards were readily prepared from methyl chloride and magnesium in dimethylaniline, a crystal of iodine starting the reaction which continued exothermically. The reagent was kept liquid at −70° by the addition of triethylamine, and the reactions were effected in this solvent.

The first substance tried for the production of a methylchromium reagent was $[(NH_3)_6Cr]Cl_3$, obtained from $CrCl_3$ and liquid ammonia[17]. Neither this nor $(C_5H_5N)_3CrCl_3$ gave a methylchromium reagent which would react with PhC≡CPh under the usual conditions.

$(Me_3N)_2CrCl_3$ was prepared as described in the literature[8], and gave a methylchromium reagent when treated in the usual fashion.

Authentic compounds

These were prepared as described previously[2,3]. In addition the following were prepared:

(1). *meso- and d,l-2,3-Diphenylbutane.* The recipe given for dimethylstilbene[18] was followed exactly, but gave instead of the expected product, *meso*-2,3-diphenylbutane and *d,l*-2,3-diphenylbutane.

Redistilled styrene (50 g) was dissolved in hexane (100 g) at −75° and dry HCl passed for 5 h until all the solid had dissolved. The hexane was evaporated leaving 64.7 g colorless liquid which was distilled at 10 mm. The fraction boiling at 73–75° (34.7 g) was α-chloroethylbenzene (52%), identified by NMR [τ(Ph) = 2.77, multiplet; τ(CH) = 5.08, quartet; $\tau(CH_3)$ = 8.26, doublet; areas 5/1/3].

A solution of sodamide in liquid ammonia was prepared[19]. α-Chloroethylbenzene (20 g) diluted with toluene (20 ml) was added slowly to the stirred sodamide solution at −35°. The mixture did not become the expected dark red. After 2 h the NH_3 was evaporated and 100 ml toluene added. After 15 h H_2O was added and the mixture extracted with toluene, and the extract dried over $CaCl_2$. Evaporation of the toluene left a solid residue which was distilled, 4.0 g of white crystals being collected at 136–140°/9 mm. GLC showed the presence of two major products. These were separated by fractional crystallization giving a white crystalline solid, m.p. 125°, *meso*-2,3-diphenylbutane [NMR: $\tau(Ph)=2.86$; $\tau(CH)=7.25$, multiplet; $\tau(CH_3)=9.00$, doublet; areas 10/2/6; literature m.p. 124°] and a colorless liquid probably *d,l*-2,3-diphenylbutane.

(2). *cis-Dimethylstilbene. meso*-2,3-Diphenylbutane (1.5 g) and *N*-bromosuccinimide (1.33 g) were dissolved in 40 ml CCl_4 and tert-butyl peroxide (0.5 ml) added. The mixture was refluxed for 1 h, filtered and the CCl_4 evaporated. Excess collidine was added and the mixture heated at 150° for $\frac{1}{2}$ h. The product was extracted with ether and the collidine washed out with dilute acid. GLC showed a small amount of product. This was separated from starting material by preparative GLC and the NMR showed dimethylstilbene [$\tau(CH_3)=7.87$; $\tau(Ph)=3.08$; areas 3/5], m.p. 63–65° (lit. values[20] for *cis* 66°, *trans* 107°).

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