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SYNTHESIS OF ALLYL-TRANSITION METAL COMPLEXES BY PHASE TRANSFER CATALYZED REACTIONS OF METAL CARBONYL HALIDES

III *. CONSIDERATIONS OF THE MECHANISMS **

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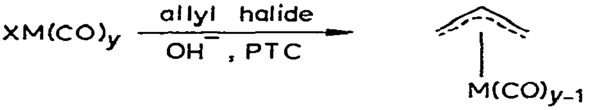
Summary

Mechanisms are proposed for the hydroxide ion-initiated reactions of metal carbonyl halides which lead to allyl-transition metal complexes under phase transfer conditions. Evidence is presented for intermediate anionic metallocarboxylic acids in reactions leading to η^3-allyl products of molybdenum, iron, ruthenium and manganese, whereas η^1 complexes are shown to result from halide displacement reactions in which simple metal carbonyl anions are generated. In some cases phosphorus-containing ligands inhibit the hydroxide-promoted reactions of metal carbonyl halides with allyl bromide; a rationale involving decreased acidity of the carbonyl ligands is presented. Syntheses of η^3-$C_3H_5Mn(CO)_3P(OCH_3)_3$ and η^3-$C_3H_5Mn(CO)_2[P(OCH_3)_3]_2$ by phase transfer catalysis are also described.

Introduction

We have recently described efforts to develop a general synthetic route to η^3-allyl-transition metal complexes through unique reactions in which phase-transferred OH^- acts on a metal carbonyl halide in the presence of an allylic halide [2,3]. The generalized transformation is illustrated below:



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* For part II see ref. 3.

** Taken, in part, from the Ph.D. thesis of Wen-Liang Hsu [1].

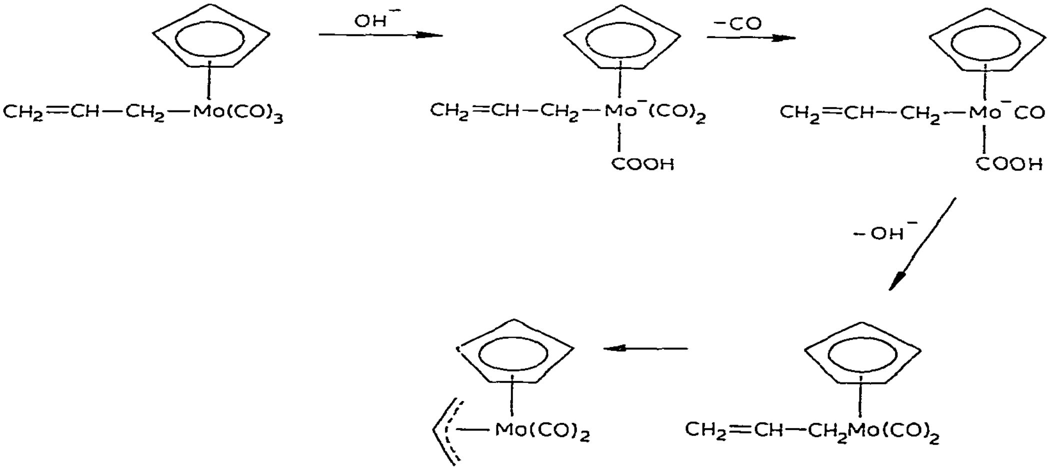
Reactions in which the cyclopentadienyl carbonyl halides of molybdenum and iron are used can be controlled to provide either η^1 or η^3 product [2]. With the related ruthenium halides, however, η^3 product predominates under all conditions [3].

Since our initial communication, we have studied these reactions in greater detail in an effort to determine the factors which control product selectivity as well as the probable reaction mechanisms. We now wish to report the results of these studies.

Results and discussion

Based on Shaw's observations about ligand substitution reactions which occur under phase transfer catalysis (PTC) conditions [4], it seemed possible that OH^- catalyzed η^1—η^3-allyl conversion could be taking place with the cyclopentadienyl metal carbonyl halides as illustrated below for the molybdenum system:

SCHEME 1



As noted earlier [2], we have examined this possibility with both the η^1-allylmolybdenum complex shown above and with η^1-allylmanganese pentacarbonyl. In neither case does conversion to the η^3 complex occur under PTC conditions; however, the two η^1 complexes behave differently. The molybdenum complex is stable to the PTC media but the manganese complex suffers cleavage as discussed below (vide infra).

Reaction conditions which are used to generate the η^3 products differ markedly from those in which the η^1 product is predominant. In the former, the metal carbonyl halide is added slowly to the remaining reactants; in such cases, the available hydroxide concentration is as much as 10^3 times greater than in the reactions which provide η^1 product (see Tables 1 and 2 for the variation in product distribution with changes in the quantities of reactants for the molybdenum and iron halides). As Table 1 shows, increasing the amount of phase transfer catalyst also enhances the formation of η^3 product.

In trying to gain some insight into the reaction paths which might be operating in the PTC reactions, we have conducted some studies without allyl

TABLE 1

PTC REACTIONS OF η^5-$C_5H_5Mo(CO)_3Cl$ WITH ALLYL BROMIDE

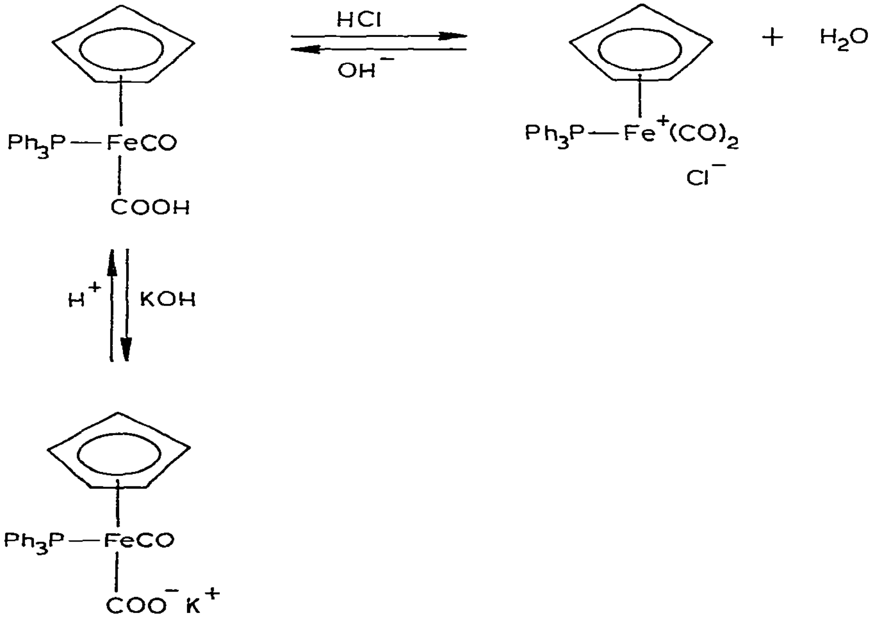
No.	η^5-$C_5H_5Mo(CO)_3Cl$ (eq)	BTEAC (eq)	Allyl bromide (eq)	Solvent	Method [a]	Product distribution [b]		Temp. (°C)	Rea tion time (h)
						η^1	η^3		
1	1	0.5	3	C_6H_6	A	85	15	24	5
2	1	3	15	C_6H_6	B	10	90	24	5
3	1	3	10	C_6H_6	B	20	80	24	5
4	1	1	10	C_6H_6	B	31	69	45	8
5	1	3	10	C_6H_6	B	5	95	45	8
6	1	5	10	C_6H_6	B	0	100 [c]	45	8
7	1	0.5	3	CH_2Cl_2	A	100 [d]	0	24	5
8	1	5	10	CH_2Cl_2	B	67	33	24	1.25

[a] Method A: rapid addition to η^5-$C_5H_5Mo(CO)_3Cl$ and allyl bromide (in C_6H_6 or CH_2Cl_2) of the aqueo PTC media. Method B: slow addition of η^5-$C_5H_5Mo(CO)_3Cl$ in C_6H_6 (or CH_2Cl_2) into a mechanically stirred solution containing allyl bromide, aqueous PTC media and C_6H_6 (or CH_2Cl_2). [b] Determined by PMR or IR. [c] Yield: 95%. [d] Yield: 75%.

bromide in hopes of being able to observe reaction intermediates. Rapid addition of η^5-$C_5H_5Mo(CO)_3Cl$ (I) into the PTC media (conditions used to generat η^1 complexes) results in formation of η^5-$C_5H_5Mo(CO)_3^-$ (II) in high yield (see Experimental) [5]. Alternatively, slow addition of this halide (in CH_2Cl_2) to the PTC mixture yields a somewhat unstable adduct whose spectral properties and reaction characteristics appear to be consistent with its formulation as an anionic metallocarboxylic acid. The adduct shows two strong carbonyl stretching bands at 1901 and 1792 cm^{-1} and a medium intensity band at 1668 cm^{-1} (all of these are distinct from the bands of the starting material and anion II).

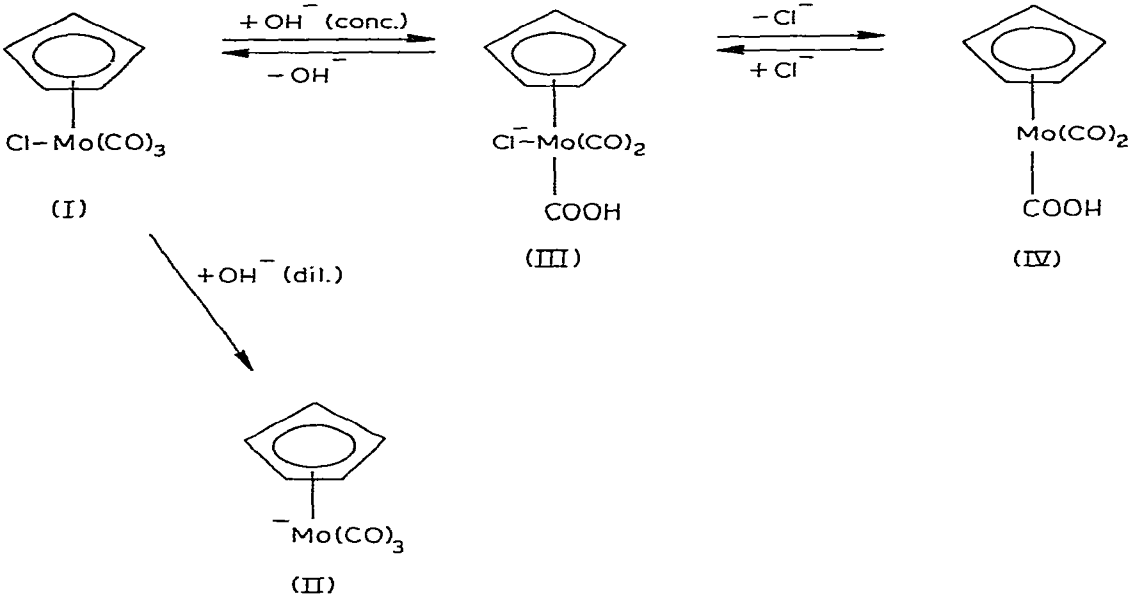
Metallocarboxylic acids formed by direct addition of OH^- to metal carbony complexes have been reported recently by Pettit [6] and by Casey [7]. The amphoteric nature of one such complex has been noted by Pettit:

SCHEME 2



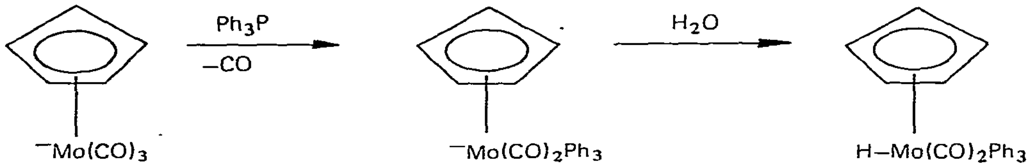
Also, anionic metallocarboxylic acids have been proposed as intermediates in other PTC reactions involving hydroxide ion [4,8]. The complex generated in our PTC reaction with the molybdenum halide is formulated as η^5-$C_5H_5Mo(CO)_2(Cl)COOH^-$ (III). As such, this anion could reasonably be expected to have either a labile Cl^- or OH^- as shown below:

SCHEME 3



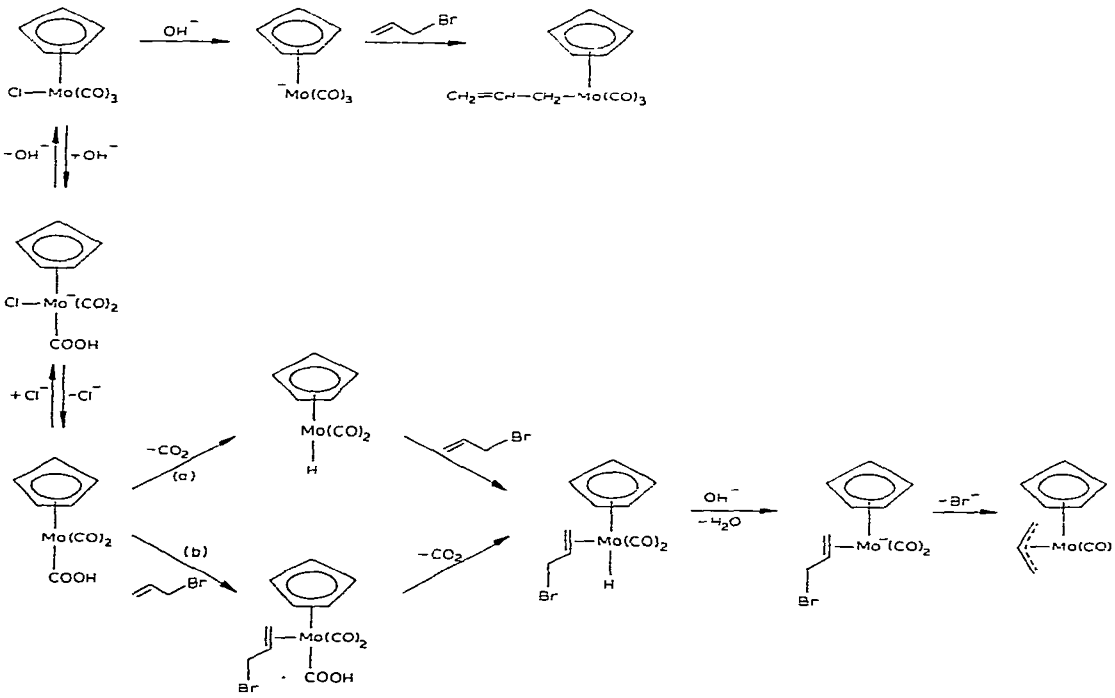
We have not been completely successful in isolating anion III; separation of the organic layer from the PTC reaction and removal of solvent yields a dark red oily material with the carbonyl bands described above, but after standing for a few hours at −15°C this material is converted to anion II. Similarly, separation of an aliquot of the organic layer followed by extraction with water also yields anion II (identified as its triphenyltin derivative) together with a small amount of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$. These results are consistent with reversible addition of hydroxide followed by reaction of the starting material with more dilute base to provide anion II. Acidification of a solution containing the presumed anion III afforded the starting halide, as expected.

We then sought to obtain evidence for the formation of intermediate IV which we believe to be essential in the PTC reactions which generate η^3 allyl products. Since this species is formulated as a coordinatively unsaturated metallocarboxylic acid, we attempted to trap it by adding triphenylphosphine to a solution of III. After a few minutes, examination of the IR spectrum of the mixture showed that III had completely disappeared and IR spectral bands for η^5-$C_5H_5Mo(CO)_2(PPh_3)H$ (isolated, see Experimental) and a small amount of II had replaced them. Although the hydride is the decarboxylation product of the expected metallocarboxylic acid, we thought there might be an alternate route to it. The following sequence was deemed possible, however, anion II is stable toward triphenylphosphine under the reaction conditions we used. Therefore, we feel that isolation of the hydride does provide support for the intermediacy



of IV. With these results in mind it is now possible to formulate reaction paths for the formation of η^1 and η^3 products as shown in Scheme 4; paths a and b to the η^3 product differ only by the point in time where CO_2 loss occurs. There is some disagreement about whether metallocarboxylic acids [6] or the corresponding carboxylate anions ($MCOO^-$) [9] undergo decarboxylation more readily. Alternatively, it has been suggested that decarboxylation of a metallocarboxylic acid may be promoted by a coordination vacancy on the metal atom [10]. Our results do not allow a distinction to be made in the present case although the latter explanation, through intermediate IV, is preferred.

SCHEME 4



Particularly interesting is the failure of quaternary ammonium hydroxides to effect ready transformations of the molybdenum halide under homogeneous conditions. Addition of η^5-$C_5H_5Mo(CO)_3Cl$ to a mixture containing $PhCH_2NMe_3OH$ in CH_2Cl_2 resulted in no reaction until aqueous NaOH was added; anion II was then slowly formed. Addition of the halide to a mixture containing $(CH_3)_4NOH \cdot 5\ H_2O$ and allyl bromide in CH_2Cl_2 provided only about 60% conversion of the halide (to a mixture containing η^1 and η^3 products) after 26 hours. A second reaction utilizing $(CH_3)_4NOH \cdot 5\ H_2O$ and aqueous NaOH showed no conversion of the halide to allyl products after four hours reaction.

TABLE 2

PTC REACTIONS OF η^5-$C_5H_5Fe(CO)_2X$ WITH ALLYL BROMIDE [a]

No.	Metal carbonyl halide	η^5-$C_5H_5Fe(CO)_2X$ (eq)	BTEAC (eq)	Allyl bromide (eq)	Method [b]	Product distribution [c]			Temp. (°C)	Reaction time (h)
						η^1	η^3	dimer		
1	η^5-$C_5H_5Fe(CO)_2I$	1	0,5	3	A	60	40	0	24	54
2	η^5-$C_5H_5Fe(CO)_2Cl$	1	0,5	3	A	42	30	28	24	3
3	η^5-$C_5H_5Fe(CO)_2Cl$	1	3	20	B	12	85	3	24	10
4	η^5-$C_5H_5Fe(CO)_2Cl$	1	3	10	B	13	79	8	45	10
5	η^5-$C_5H_5Fe(CO)_2Cl$	1	5	10	B	12	80 [d]	8	24	4
6	η^5-$C_5H_5Fe(CO)_2Br$	1	0,5	3	A	68	16	16	24	4
7	η^5-$C_5H_5Fe(CO)_2Br$	1	3	10	B	10	85	5	24	10
8	η^5-$C_5H_5Fe(CO)_2Br$	1	3	10	B	10	83	7	24	4
9	η^5-$C_5H_5Fe(CO)_2Br$	1	5	10	B	0	100 [e]	0	24	4
10	η^5-$C_5H_5Fe(CO)_2Br$	1	0,5	3	A	55 [f]	0	45 [f]	24	2
11	η^5-$C_5H_5Fe(CO)_2Br$	1	5	10	B [g]	21 [h]	72 [h]	7 [h]	24	2

[a] Reactions 1—9 were conducted in C_6H_6; 10 and 11 were conducted in CH_2Cl_2. [b] See Table 1, footnote *a*. [c] Determined by PMR or IR. [d] Yield: 60% (after column chromatography). [e] Yield: 60%. [f] Yield: 36% η^1-product, 30% dimer. [g] η^5-$C_5H_5Fe(CO)_2Br$ was added into the PTC media during 75 min and product distribution was determined after a total of 2 h reaction time. [h] Relative product distribution.

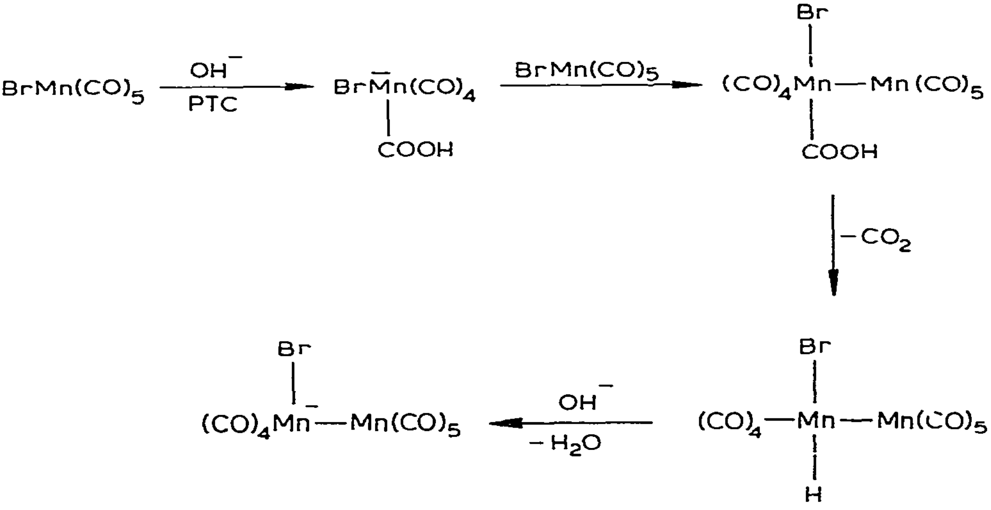
These observations tend to support the recent proposals by Makosza [11] that PTC reactions involving OH^- take place primarily at the interface between the aqueous and organic phases. This behavior has been thought to be due both to the low solubility of quaternary ammonium hydroxides in organic solvents and to the fact that the quaternary ammonium hydroxide exists mainly as the ion pair in solvents of low polarity.

Attempts to generate an intermediate similar to III from η^5-$C_5H_5Fe(CO)_2Cl$ resulted only in formation of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, the product expected from reaction of the highly nucleophilic η^5-$C_5H_5Fe(CO)_2^-$ with the starting material. However, as Table 2 illustrates, the iron halides react toward changes in the available concentrations of reactants in very much the same way that the molybdenum halide does in the PTC syntheses of allyl complexes; therefore, mechanisms similar to those outlined in Scheme 4 are believed to operate.

The preparation of η^3-allyl-ruthenium complexes by PTC was reported earlier [3]. The η^5-cyclopentadienylruthenium dicarbonyl halides are much more reactive than their iron counterparts and show a greater preference for η^3-allyl product formation. Efforts have also been made to observe an intermediate metallocarboxylic acid in PTC reactions of η^5-$C_5H_5Ru(CO)_2Br$. Addition of the halide to the PTC media gave a solution with carbonyl bands at 1925, 1740 and 1710 cm^{-1} (again all of these bands are distinct from those of the starting halide and from η^5-$C_5H_5Ru(CO)_2^-$, which was prepared and characterized for comparison). Unlike the molybdenum system, no changes occurred upon water treatment of an aliquot of this solution. Neutralization of another aliquot with trifluoroacetic acid gave a mixture with a complicated IR pattern but no evidence for η^5-$C_5H_5Ru(CO)_2Br$. Treatment of a third aliquot with triphenylphosphine gave a mixture with carbonyl bands at 1950, 1740, 1730 and 1680 cm^{-1}. These bands are not in accord with expectations for η^5-$C_5H_5Ru(CO)(PPh_3)H$ [12] but one of them (1950 cm^{-1}) is at the same position reported for ν(Ru—H) in η^5-$C_5H_5Ru(PPh_3)_2H$ [13], a possible secondary product. We have not been able to obtain any crystalline product from this mixture.

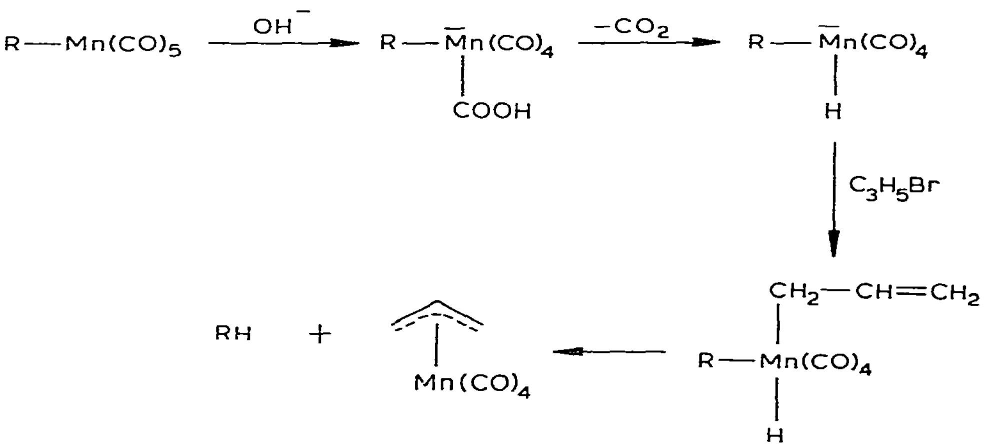
In our earlier work [2], we isolated an intermediate from the PTC reactions involving $BrMn(CO)_5$ which we proposed to be formed as follows:

SCHEME 5



The binuclear anion was completely formed within a few minutes and isolated, in high yield, as the quaternary ammonium salt; however, no direct evidence has been obtained for the proposed intermediate metallocarboxylic acids [14]. The PTC reactions of $BrMn(CO)_5$ with allylic halides usually provide only η^3-allyl product. Only in one case, in which an extremely small quantity of base was used, were we able to observe the η^1 product. We synthesized η^1-$C_3H_5Mn(CO)_5$ by an alternate route and subjected it to the PTC media (without allyl bromide) but, again, no η^1—η^3 conversion took place. Instead, the metal complex vanished from the organic layer (benzene); when allyl bromide was added to this mixture, η^3-allyl complex rapidly appeared in the organic layer. Interestingly, $CH_3Mn(CO)_5$ behaves in the same way; reaction of the methyl complex with allyl bromide under PTC conditions leads to complete destruction of $CH_3Mn(CO)_5$ and formation of η^3-$C_3H_5Mn(CO)_4$. The following scheme is proposed [15] as a rationale for the cleavage of the alkyl groups from these η^1 complexes:

SCHEME 6

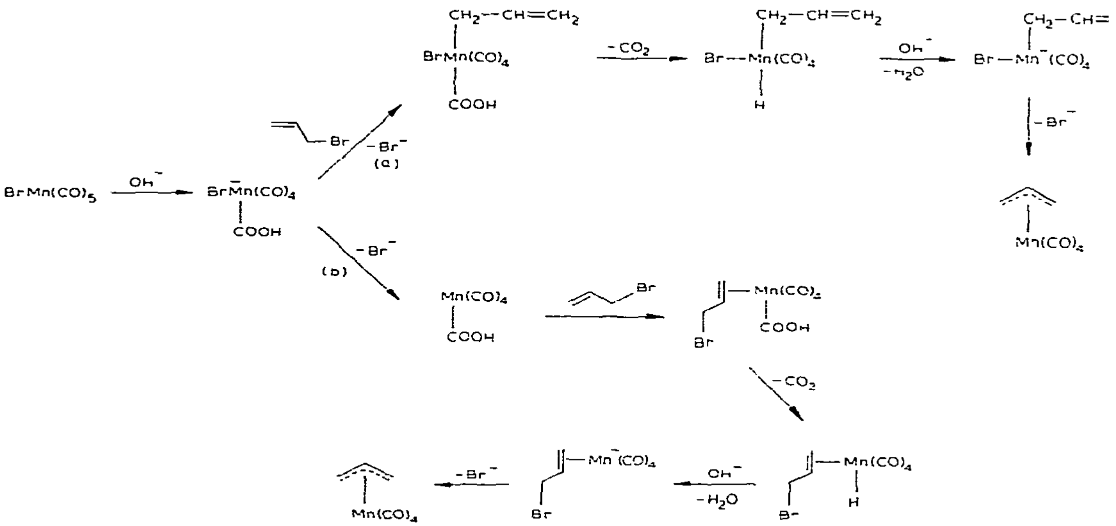


Reductive elimination of methane has been proposed [16], but not demonstrated, in other reactions of $CH_3Mn(CO)_5$; reductive elimination of methane has been demonstrated with a different metal system, however [17].

PTC reactions of $BrMn(CO)_5$ with allylic halides have been conducted with either benzene or CH_2Cl_2 as the organic phase [2]. We noted that somewhat higher yields of the η^3 products are obtained with CH_2Cl_2 but there are other differences as well. The binuclear anion discussed above is generated readily in CH_2Cl_2 and is very soluble in this solvent. The anion is not soluble in benzene and although $BrMn(CO)_5$ was completely consumed within a few minutes in a reaction conducted in this solvent without any allylic halide, no metal carbonyl product was evident in solution. The interfacial layer, however, was red-orange and exhibited a complicated pattern in the carbonyl region which showed evidence for the binuclear anion as one component. Syntheses of η^3-$C_3H_5Mn(CO)_4$ conducted in benzene proceed to completion in about an hour [2]; however, the reaction is essentially complete after only 30 minutes. Similar reactions in CH_2Cl_2 require 4—5 hours to go to completion but are about 75% complete after an hour. These differences in behavior in the two solvents led us to believe that there might be two different reaction paths available for $BrMn(CO)_5$. We tested this by using $Mn_2(CO)_9Br^-$ as the starting material in both solvents; formation of the η^3 product is much slower with either solvent than in comparable reactions where $BrMn(CO)_5$ was the starting material. Also, dropwise addition of $BrMn(CO)_5$, in CH_2Cl_2, to the remaining reactants results in more rapid generation of the η^3 product than when all reactants were rapidly mixed (conditions known to generate substantial amounts of the binuclear anion).

Since it is known that $Mn(CO)_5^-$ and *cis*-$Mn(CO)_4Br_2^-$ are formed thermally by reaction between $Mn_2(CO)_9Br^-$ and quaternary ammonium bromides [18], we have also tested the dihalo anion for its activity toward allyl bromide; it does not react with allyl bromide either thermally or under our PTC conditions. Also, although $BrMn(CO)_5$ is known to undergo ligand substitution by CO dissociation [19], no direct reaction (i.e., oxidative addition) takes place between allyl bromide and this compound. No direct reaction takes place between allyl bromide and the binuclear anion either.

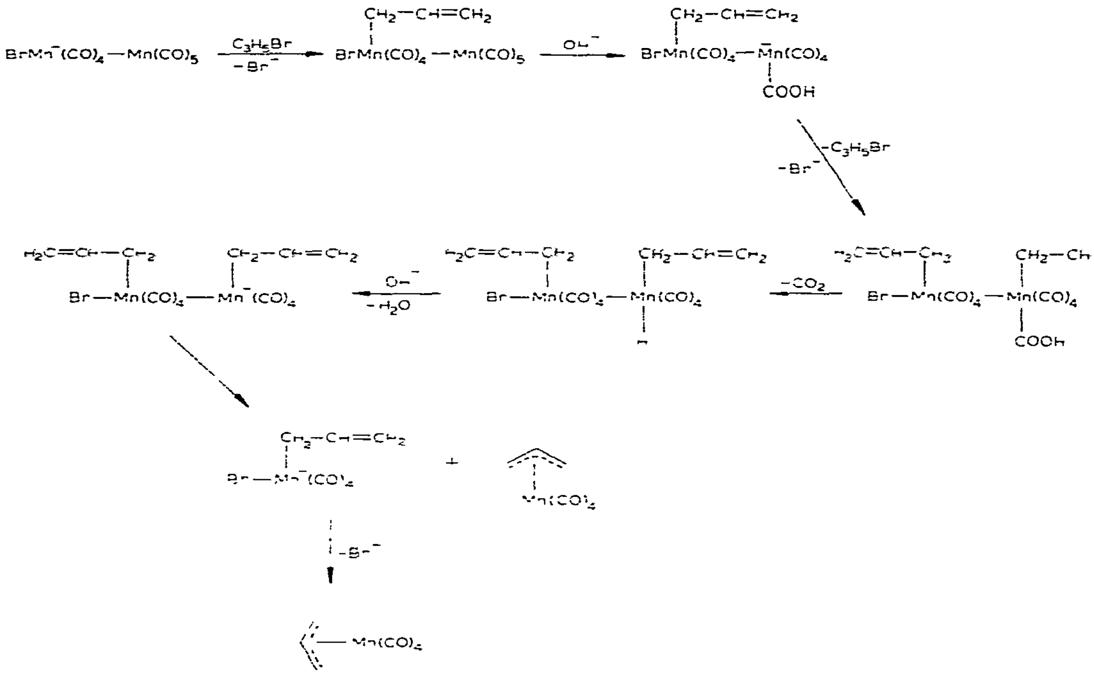
SCHEME 7



Scheme 7 illustrates two possible pathways, via mononuclear intermediates, for the formation of η^3-$C_3H_5Mn(CO)_4$; Scheme 8 shows the proposed reaction path to η^3 product from the binuclear anion. Since it appears that a highly nucleophilic species is responsible for the formation of the binuclear anion, we prefer path a in Scheme 7 (which involves nucleophilic displacement of bromide from allyl bromide) to path b. Also, reactions involving mononuclear intermediates (Scheme 7) are believed to predominate in benzene.

Since we submitted our earlier communication [2], support for the proposed addition of OH^- to a carbonyl ligand of $BrMn(CO)_5$ to provide an anionic metallocarboxylic acid has become available from the observations of Lukehart [20] and Gladysz [21] and their coworkers about nucleophilic additions to manganese and rhenium pentacarbonyl halides. Lukehart [20] has indicated that addition of the nucleophile takes place at a carbonyl ligand *cis* to the

SCHEME 8



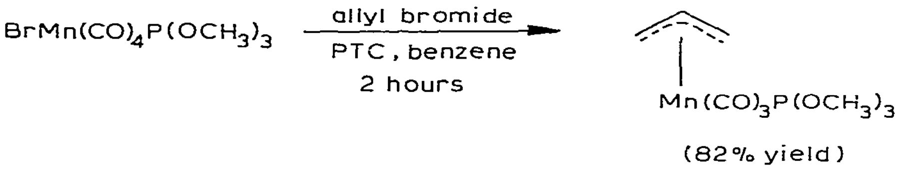
halide; when methyllithium is used, the initially formed acyl complex loses halide ion and yields the methyl-substituted derivative [21]. A similar process also presumably takes place in Reger's [22] recent synthesis of η^5-$C_5H_5Fe(CO)(PPh_3)R$ complexes from the corresponding iodides via alkyllithium reactions.

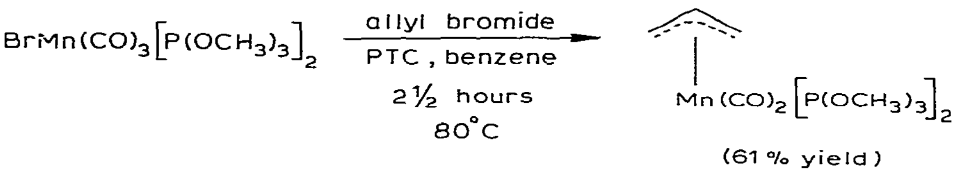
In contrast to $BrMn(CO)_5$, the corresponding rhenium bromide provided only a trace of allyl product (exclusively η^3) after a very long time when reaction was accomplished by method A or B. Reaction of $BrRe(CO)_5$ with the PTC media does take place; the product has not yet been characterized.

We have also examined the behavior of two groups of metal carbonyl halides bearing phosphorus ligands toward the PTC media and allyl bromide. The first group consisted of η^5-cyclopentadienyl complexes of molybdenum, iron and ruthenium with one triphenylphosphine ligand (all chlorides), the iron bromide was also examined. Reactions were done in benzene since the first compound studied, η^5-$C_5H_5Mo(CO)_2(PPh_3)Cl$, was unreactive in CH_2Cl_2. The molybdenum complex was the only one to show any conversion to an allyl product; in that system, the phosphine ligand is lost and a small amount of mixed allyl products is formed. The η^5-$C_5H_5Fe(CO)_2Cl$ suffered decomposition in the PTC media, but the ruthenium compound was recovered unscathed. The presence of one triphenylphosphine completely inhibits the normal reactions [2,3] of these metal carbonyl halides toward PTC conditions.

The members of the second group were of the type $BrMn(CO)_4L$ and $BrMn(CO)_3L_2$ ($L = Ph_3P$ or $(CH_3O)_3P$). The first one studied was $BrMn(CO)_4PPh_3$ which gives η^3-$C_3H_5Mn(CO)_3PPh_3$ in high yield as reported earlier [2]. The bisphosphine bromide, however, yielded none of the expected η^3-allyl product but did provide a small amount of the complex with one less triphenylphosphine ligand. With these first two systems, CH_2Cl_2 was used as the organic solvent. When similar reactions were done with the corresponding trimethyl phosphite-substituted analogs, the PTC reactions with allyl bromide gave mixtures containing the expected η^3-allyl product and a small amount of the complex with one less phosphite ligand. We also noted the greatly diminished reactivity of $BrMn(CO)_3[P(OCH_3)_3]_2$ in these reactions as compared to the monosubstituted complex.

Reactions of the phosphite-substituted complexes were also carried out in benzene and the expected compound was readily obtained in each case:





These results also appear to support the view that reactions of the manganese halides take a route involving mononuclear intermediates in reactions conducted in benzene. The enhanced rate of reaction with $BrMn(CO)_4PPh_3$ in CH_2Cl_2 (as compared to $BrMn(CO)_5$ [2]) may be due to the bulky phosphine ligand which prevents the formation of any binuclear intermediate. The nature of the reactions which yield allyl complexes having one less phosphorus ligand than the starting halide are not yet understood.

The reactivity of the manganese bis-phosphine or -phosphite complexes is somewhat lower than that of the monosubstituted derivatives, but these halides still possess several CO ligands which can dissipate the effects of the strongly σ-donating phosphorous ligands. When the number of carbonyl ligands becomes severely limited, as with the η^5-cyclopentadienyl molybdenum, iron and ruthenium complexes, the reactivity of the halide toward the PTC media is either greatly reduced or completely inhibited. These results appear to parallel the observations of Darensbourg [9] and Pettit [6] in reactions involving hydroxide ion additions to metal carbonyl cations. Darensbourg has shown that the rate of oxygen exchange (with $H_2{}^{18}O$) decreases directly with increases in the number of electron-donating substituents. Pettit has observed that η^5-C_5H_5-$Fe(diphos)CO^+$ is unreactive toward OH^-, whereas the related complex with one Ph_3P ligand and an additional CO forms the metallocarboxylic acid readily.

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen. Benzene, hexane, pentane and allyl bromide were distilled before use. THF was distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was reagent grade and was used directly. Benzyltriethylammonium chloride (BTEAC), benzyltrimethylammonium hydroxide and tetramethylammonium hydroxide were purchased from Aldrich and used directly. The η^5-$C_5H_5Mo(CO)_3Cl$ [23] and $BrMn(CO)_5$ [24] were prepared as described previously. Samples of $[\eta^5$-$C_5H_5Ru(CO)_2]_2$, η^5-$C_5H_5Ru(CO)(PPh_3)Cl$ and η^5-$C_5H_5Fe(CO)(PPh_3)Cl$ were provided by Dr. B.V. Johnson and Alan L. Steinmetz. Tetraethylammonium bromide was prepared as described previously [25].

PMR spectra were obtained on a Bruker WH-90DS or Perkin-Elmer R-12A spectrometer; peak positions are given in ppm downfield (+) or upfield (—) from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer and calibrated against polystyrene film. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Attempted η^1—η^3 conversion of η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_3$ in the PTC media

A solution containing 0.2 g (0.7 mmol) of η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_3$ [2] in 15 ml of benzene was added slowly to a mechanically stirred mixture containing 0.81 g (3.5 mmol) of BTEAC, 20 ml of 5 *N* NaOH in 10 ml of benzene during a period of 1 hour at room temperature. Infrared spectral data indicated no evidence of η^1—η^3 conversion. The mixture was then treated with 0.3 ml (3.5 mmol) of allyl bromide and stirring was continued for a further 4 hours; there was no evidence for η^1—η^3 conversion from the infrared spectral determination.

Generation of η^5-$C_5H_5Mo(CO)_3^-$ by PTC

BTEAC, 0.11 g (0.5 mmol), was dissolved in 20 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.28 g (1 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 20 ml of CH_2Cl_2 at room temperature. The anionic product, $PhCH_2NEt_3^+$-$[\eta^5$-$C_5H_5Mo(CO)_3]^-$, could be observed (by IR) after 5 minutes of stirring; however, the formation of this compound slowed down after 1 hour. Hence, an additional 0.11 g of BTEAC was added after a total of 2 hours of stirring. The reaction mixture was then stirred for another 2 hours. The reaction was complete (as indicated by the disappearance of the carbonyl bands of η^5-$C_5H_5Mo(CO)_3Cl$ from the IR) and the organic layer was worked-up in the usual way (as described in Method A [2]); 0.432 g (92%) of crude product (reddish yellow oil) was obtained. The product had $\nu(CO)$ (CH_2Cl_2): 1895s, 1775s(br) cm^{-1} [lit. [26] for Et_4N^+ η^5-$C_5H_5Mo(CO)_3^-$: 1885s, 1775s, 1740s cm^{-1}].

Attempted isolations of η^5-$C_5H_5Mo(CO)_2(Cl)COOH^-$ (III)

(a) A solution containing 0.28 g (1 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 10 ml of CH_2Cl_2 was added slowly to a mechanically stirred mixture containing 2.28 g (10 mmol) of BTEAC, 20 ml of 5 *N* NaOH and 20 ml of CH_2Cl_2 during a period of 2.5 hours at room temperature. The color of the reaction mixture slowly changed to reddish (from yellow) when more halide was added into it and the reaction was complete (carbonyl bands of the starting halide were absent) when the addition of halide was finished. An IR spectrum of the mixture showed three distinct bands at 1901s, 1792s and 1668m cm^{-1}. The CH_2Cl_2 layer was separated, washed with two 15 ml portions of water and then dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and an IR spectral determination indicated only the presence of η^5-$C_5H_5Mo(CO)_3^-$ [ν(CO) (CH_2Cl_2): 1895s, 1775s(br) cm^{-1}].

(b) In the same manner, 0.98 g (3.5 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 35 ml of CH_2Cl_2 was added to a mixture containing 7.98 g (35 mmol) of BTEAC, 70 ml of 5 *N* NaOH and 70 ml of CH_2Cl_2 during a period of 3 hours. After finishing the addition of halide, the IR spectrum of the reaction mixture showed the same bands as observed in (a) above. The organic layer was then separated and concentrated under reduced pressure to give a reddish oil which has the same IR data as observed before (assigned structure III). However, the product converted to II when it was stored at —15°C for 3—4 hours, as indicated by the infrared spectral determination. The reddish oily residue obtained from this experiment was taken up to 15 ml of CH_2Cl_2 and the solution was washed with two 20 ml portions of water and then dried over $MgSO_4$. After filtration, solvent was removed under reduced pressure on a rotary evaporator to give 0.41 g of reddish oil which contained II and a small amount of dimer, $[\eta^5$-$C_5H_5Mo(CO)_3]_2$ (identified by IR spectral comparison with an authentic sample). This reddish oil was dissolved in 20 ml of CH_2Cl_2 and treated with 0.38 g (1 mmol) of Ph_3SnCl at room temperature for 10 minutes. Solvent was removed from the reaction mixture to leave a reddish oil containing a mixture of η^5-$C_5H_5Mo(CO)_3SnPh_3$ and a small amount of $[\eta^5$-$C_5H_5Mo(CO)_3]_2$. The tin derivative was separated from the dimer by fractional crystallization from CH_2Cl_2/pentane. The pale greenish crystalline derivative had m.p. 212—213°C [lit. [27] 211—214°C] and ν(CO) (CH_2Cl_2): 2000vs, 1930s, 1900vs cm^{-1} [lit. [27] (CH_2Cl_2): 2004, 1934, 1909 cm^{-1}]; the yield was not determined.

Acidification of a solution containing η^5-$C_5H_5Mo(CO)_2(Cl)COOH^-$ (III) with trifluoroacetic acid

The product presumed to be III was generated from 0.28 (1 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in the manner described above (procedure a). After the addition of η^5-$C_5H_5Mo(CO)_3Cl$ was complete, an aliquot (~5 ml) of the organic layer was removed and transferred into a 25 ml three-necked round-bottom flask under a blanket of nitrogen and treated dropwise with a dichloromethane (5 ml) solution containing 1 ml of trifluoroacetic acid at 0°C. After addition was finished, the mixture was stirred for another 5 minutes at 0°C and then warmed to room temperature. The reaction mixture was then washed with 5 ml of water and dried over $MgSO_4$. After filtration, solvent was removed on a rotary evaporator to leave a reddish oil which was crystallized from CH_2Cl_2/hexane at —15°C to afford a small amount of reddish needles, m.p. 135—137°C (dec). The product had ν(CO) (CH_2Cl_2): 2058s, 1980vs, 1968s(sh) cm^{-1}. The m.p. and spectral data were identical to those of an authentic sample of η^5-$C_5H_5Mo(CO)_3Cl$.

Reaction of η^5-$C_5H_5Mo(CO)_2(Cl)COOH^-$ (III) with triphenylphosphine

A solution containing 0.98 g (3.5 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 35 ml of CH_2Cl_2 was added slowly to a mechanically stirred mixture containing 7.98 g (35 mmol) of BTEAC, 70 ml of 5 *N* NaOH and 70 ml of CH_2Cl_2 during a period of 3 hours at room temperature. An infrared spectrum of the organic layer, when the addition of the η^5-$C_5H_5Mo(CO)_3Cl$ was finished, indicated that III was the exclusive component in the mixture. The organic layer was then separated, and treated immediately with 0.92 g (3.5 mmol) of triphenylphosphine (in 5 ml of CH_2Cl_2) at room temperature under a nitrogen atmosphere; the IR spectrum indicated that, after 15 minutes, III was completely consumed and gave a mixture containing mostly η^5-$C_5H_5Mo(CO)_2(PPh_3)H$ and a small amount of η^5-$C_5H_5Mo(CO)_3^-$. After solvent evaporation, the reddish oily residue was triturated with three 30 ml portions of benzene. The combined benzene extracts were dried over $MgSO_4$; solvent was removed under reduced pressure to leave a reddish oil which was crystallized from CH_2Cl_2/hexane at −15°C. The isolated solid (0.43 g, 45%) had PMR ($CDCl_3$): 7.38 (m, 15 H), 5.06 (s, 5 H), −5.50 (d, 1 H, J(P—H) = 50.3 Hz) [lit. [28] (THF): cyclopentadienyl protons, 5.11 and hydrido −5.49 (J(P—H) = 51.6 Hz)]. The IR spectrum of the solid showed ν(CO) (THF) at 1940 and 1865 cm^{-1} [lit. [28] (THF): 1941, 1871(sh) and 1864 cm^{-1}] and ν(CO) (CH_2Cl_2) at 1940 and 1860 cm^{-1}. Based on these spectral comparisons, we conclude that the isolated solid is *cis*-η^5-$C_5H_5Mo(CO)_2(PPh_3)H$.

Attempted reaction of $PhCH_2NEt_3^+$ η^5-$C_5H_5Mo(CO)_3^-$ *with triphenylphosphine*

To 0.46 g (1.0 mmol) of $PhCH_2NEt_3^+$ η^5-$C_5H_5Mo(CO)_3^-$, prepared by the PTC method as described above, was added 0.26 g (1.0 mmol) of triphenylphosphine in 20 ml of CH_2Cl_2 and stirred at room temperature for 1 hour. Infrared spectra indicated no evidence of reaction. The reaction mixture was then treated with 10 ml of 5 *N* NaOH followed by stirring for another hour (at room temperature). Infrared spectra again showed no evidence of reaction.

Reactions of η^5-$C_5H_5Mo(CO)_3Cl$ *with quaternary ammonium hydroxides in* CH_2Cl_2

a) A quantity of solid $PhCH_2N(CH_3)_3^+OH^-$ was prepared by concentrating a commercial 40% methanolic $PhCH_2N(CH_3)_3^+OH^-$ on a rotary evaporator followed by crystallization from CH_2Cl_2/hexane. After filtration, the white solid was dried overnight in a desiccator. A solution containing 0.56 g (2.0 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 20 ml CH_2Cl_2 was added, during 30 minutes, to a stirred (magnetic) mixture containing (0.33 g) of $PhCH_2N(CH_3)_3^+OH^-$ in 40 ml of CH_2Cl_2 ($PhCH_2N(CH_3)_3^+OH^-$ was not all dissolved in CH_2Cl_2) at room temperature and then stirred for an additional hour. Infrared spectral data indicated no noticeable reaction during this time. The mixture was then refluxed for an hour and, again, no reaction was observable. The mixture was then cooled to room temperature, 10 ml of 5 *N* NaOH was added and stirring was continued. Anion II, η^5-$C_5H_5Mo(CO)_3^-$, was slowly formed; reaction was complete after 3 hours with a small amount of dimer, $[\eta^5$-$C_5H_5Mo(CO)_2]_2$, and anion II being the only detectable products (as determined by IR).

b) A solution containing 0.56 g (2 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 20 ml of CH_2Cl_2 was added dropwise over 8 hours to a stirred mixture of 1.81 g (10 mmol) of $(CH_3)_4NOH \cdot 5\ H_2O$ and 1.74 ml (20 mmol) of allyl bromide in 85 ml of CH_2Cl_2 at 40—45°C. After addition was complete, stirring and heating were continued for 18 hours. After this time, the mixture consisted of 39% η^5-C_5H_5-$Mo(CO)_3Cl$, 38% η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_3$ and 23% η^5-C_5H_5-η^3-$C_3H_5Mo(CO)_2$ as determined from IR and PMR spectra. The reaction was stopped at this point.

c) A solution containing 0.28 g (1 mmol) of η^5-$C_5H_5Mo(CO)_3Cl$ in 10 ml of CH_2Cl_2 was prepared and added to a dropping funnel. About half of this solution was added dropwise, during 4 hours, to a stirred mixture containing 0.90 g (5 mmol) of $(CH_3)_4NOH \cdot 5\ H_2O$, 20 ml of 5 *N* NaOH and 0.87 ml (10 mmol) of allyl bromide in 43 ml of CH_2Cl_2 at 40—45°C. No reaction took place during this time as evidenced by an IR spectrum of the mixture. At this point, 0.23 g (1 mmol) of BTEAC was added to the mixture and within a few minutes the η^1-allyl complex was evident in spectra of the mixture. Reaction was stopped after an additional 3 hours (after all the metal halide had been consumed) and the product mixture consisted of a 3 : 1 mixture of η^1 and η^3 products.

Reaction of η^5-$C_5H_5Fe(CO)_2Cl$ with base in the presence of BTEAC

A sample of η^5-$C_5H_5Fe(CO)_2Cl$, 0.11 g (0.5 mmol) was dissolved in 10 ml of benzene and added dropwise to a stirred solution containing 0.06 g (0.25 mmol) of BTEAC in 10 ml 5 *N* NaOH at room temperature. After the addition was finished, the mixture was stirred for another 5 minutes, and the infrared spectrum of the organic layer indicated that the dimer, $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, was the only carbonyl-containing compound detected (identified by comparison with an authentic sample). The reaction was stopped at this point and discarded.

Comparison of the reactivities of η^5-$C_5H_5Fe(CO)_2X$ (X = Cl, Br, I) toward allyl bromide under PTC conditions

Method A was adopted in these reactions. Thus, 0.23 g (1 mmol) of BTEAC was dissolved in 20 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.52 ml (6 mmol) of allyl bromide and 0.52 g (2 mmol) of η^5-C_5H_5-$Fe(CO)_2Br$ in 30 ml of benzene. The reaction was complete after stirring at room temperature for 4 hours as judged by the disappearance of the carbonyl bands of η^5-$C_5H_5Fe(CO)_2Br$. After work-up, 0.25 g of brownish yellow oily residue was obtained which consisted of a mixture of 68% η^5-C_5H_5-η^1-C_3H_5Fe-$(CO)_2$ [2], 16% of η^5-C_5H_5-η^3-C_3H_5-$Fe(CO)$ [2] and 16% of dimer, $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ (determined by PMR). In the same manner, the corresponding chloride, η^5-$C_5H_5Fe(CO)_2Cl$, required 3 hours for the completion of the reaction and gave 0.23 g of brownish yellow oil containing 42% of η^5-C_5H_5-η^1-$C_3H_5Fe(CO)_2$, 30% η^5-C_5H_5-η^3-$C_3H_5Fe(CO)$ and 28% $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. The iodide, η^5-$C_5H_5Fe(CO)_2I$, required 54 hours for the completion of the reaction and provided 0.1 g of brownish yellow oil containing 60% of η^5-C_5H_5-η^1-C_3H_5-$Fe(CO)_2$ and 40% of η^5-C_5H_5-η^3-$C_3H_5Fe(CO)$. These results are summarized in Table 2 (entries 1, 2, 6).

Preparation and derivatization of Na^+ η^5-$C_5H_5Ru(CO)_2^-$ [29]

Sodium amalgam was prepared, using approximately 0.5 g of sodium metal and about 25 ml of mercury, in the manner described previously [30]. This was transferred to a three-necked reaction vessel under nitrogen and then a solution containing 0.89 g (2 mmol) of η^5-cyclopentadienylruthenium dicarbonyl dimer in 50 ml of THF was added quickly with stirring to the amalgam. The progress of the reaction was monitored over time by IR; it was complete after about $3\frac{1}{2}$ hours. The solution showed ν(CO) (THF) 1906s and 1825s cm^{-1} for η^5-$C_5H_5Ru(CO)_2^-$ (spectra not previously reported). The amalgam was drawn off and the THF solution of the anion was filtered through glass wool under nitrogen and added dropwise with stirring to a solution containing 1.54 g (4 mmol) triphenyltin chloride dissolved in 20 ml of THF. The reaction was complete as soon as reagents could be mixed; conversion of the anion to the triphenyltin derivative was evidenced by an IR spectrum of the mixture: ν(CO) 2016s and 1956s cm^{-1} (not previously reported). Solvent was removed on a rotary evaporator and the crude product was purified by recrystallization from CH_2Cl_2/hexane. The pure white product (62% yield) had the following properties: m.p. 143.5—144°C and IR ν(CO) (hexane): 2018s and 1966s cm^{-1}. The elemental analysis is as follows: Found: C, 52.43; H, 3.52; O, 5.68. calcd for $C_{25}H_{20}O_2RuSn$: C, 52.48; H, 3.52; O, 5.59%.

Reaction of η^5-$C_5H_5Ru(CO)_2Br$ with base in the presence of BTEAC

A solution containing 0.3 g (1 mmol) of η^5-$C_5H_5Ru(CO)_2Br$ [31] in 10 ml of CH_2Cl_2 was added slowly to a mechanically stirred mixture containing 2.28 g (10 mmol) of BTEAC, 20 ml of 5 *N* NaOH and 20 ml of CH_2Cl_2 during a period of an hour at room temperature. At the end of the addition of halide (1 hour), the infrared spectrum of the organic layer showed three carbonyl bands [ν(CO): 1925s, 1740m, 1710s cm^{-1}]. An aliquot (10 ml) of the organic layer was then removed and washed with water. The infrared spectrum indicated that water washing did not significantly affect the composition of the organic layer. A second PTC reaction was done in the manner described above; from this one, an aliquot of the reaction mixture was treated dropwise, with trifluoroacetic acid until the mixture was neutral; an IR spectrum of this mixture showed the following major bands in the carbonyl region: 2025m, 1962s, 1938m, 1788s, 1740m and 1690s cm^{-1}. The IR spectral bands centered at 1962, 1938 and 1788 cm^{-1} are probably due in part to the cyclopentadienylruthenium dicarbonyl dimer; the other bands cannot be assigned with certainty.

Another aliquot of the reaction mixture was treated with a slight excess of triphenylphosphine and allowed to stand for 1 hour. The IR spectrum of this mixture showed carbonyl bands at 1950m, 1740s, 1730s(sh), 1680m cm^{-1} (the expected band [12] for η^5-$C_5H_5Ru(CO)(PPh_3)H$ is at 1937 cm^{-1} and ν(Ru—H) reported [13] for η^5-$C_5H_5Ru(PPh_3)_2H$ is 1950 cm^{-1}). Although η^5-$C_5H_5Ru(CO)(PPh_3)H$ and η^5-$C_5H_5Ru(PPh_3)_2H$ are both solids, we have not been able to obtain a crystalline product from this mixture.

Attempted conversion of η^1-$C_3H_5Mn(CO)_5$ in the PTC media

BTEAC, 0.18 g (0.75 mmol), was dissolved in 20 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.35 g (1.5 mmol) of η^1-$C_3H_5Mn(CO)_5$ [32] in 30 ml of benzene at room temperature. After 1 hour, an infrared spectrum showed the complete disappearance of η^1-$C_3H_5Mn(CO)_5$; however, η^3-$C_3H_5Mn(CO)_4$ was not observable. Stirring was continued for another hour;

again, no η^3-complex could be detected. Addition of allyl bromide (0.26 ml, 3 mmol), however, resulted in immediate formation of η^3-$C_3H_5Mn(CO)_4$ (from an IR spectrum taken 15 minutes after addition of allyl bromide). After this, there was no noticeable change in the infrared spectra of the organic layer during an additional hour (at room temperature). After work-up (separating the organic layer, washing, drying and evaporating the solvent as described above), 0.12 g (58%, based on η^1-$C_3H_5Mn(CO)_5$) of yellow solid, η^3-$C_3H_5Mn(CO)_4$, was obtained (the properties of this solid were identical with those of an authentic sample [2] of the η^3 complex).

PTC reaction of $CH_3Mn(CO)_5$ with allyl bromide

BTEAC, 0.06 g (0.25 mmol), was dissolved in 10 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.11 g (0.5 mmol) of $CH_3Mn(CO)_5$ [33] in 20 ml of benzene at room temperature. After stirring for 30 minutes, (infrared spectra indicated that a small amount of $CH_3Mn(CO)_5$ had been consumed), 0.1 ml (1.1 mmol) of allyl bromide was added and the stirring was continued for another hour. Infrared indicated the complete disappearance of $CH_3Mn(CO)_5$, and η^3-$C_3H_5Mn(CO)_4$ was the only observable compound in the organic layer. Stirring for a further 30 minutes provided only a very small increase of η^3-$C_3H_5Mn(CO)_4$. After work-up in the usual manner (as in Method A), the yellow oily residue was identified as η^3-$C_3H_5Mn(CO)_4$ (yield not determined).

PTC reactions of $PhCH_2NEt_3^+$ $Mn_2(CO)_9Br^-$ with allyl bromide *

a) BTEAC, 0.11 g (0.5 mmol), was dissolved in 15 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.44 ml (5 mmol) of allyl bromide and 0.33 g (0.5 mmol) of $PhCH_2NEt_3^+$ $Mn_2(CO)_9Br^-$ [2] in 15 ml of CH_2Cl_2. The η^3-allyl complex, η^3-$C_3H_5Mn(CO)_4$, was gradually formed upon refluxing, and after an hour the reaction was approximately 20% complete with respect to formation of η^3-$C_3H_5Mn(CO)_4$. This was estimated from the intensity of the carbonyl band at 2075 cm^{-1} in η^3-$C_3H_5Mn(CO)_4$ after an hour as compared to its intensity after 5 hours at the end of reaction. After work-up, a yellow waxy solid, η^3-$C_3H_5Mn(CO)_4$, was obtained (yield not determined).

b) The reaction was conducted in the manner described above in (a) except that benzene was used as solvent and the reaction temperature was 60°C. The formation of η^3-$C_3H_5Mn(CO)_4$ was complete after 3 hours of stirring at this temperature. The reaction mixture was not worked-up and the yield was not determined.

c) A solution containing 0.33 g (0.5 mmol) of $PhCH_2NEt_3^+$ $Mn_2(CO)_9Br^-$ in 10 ml of CH_2Cl_2 was added slowly to a stirred mixture containing 0.11 g (0.5 mmol) of BTEAC, 15 ml of 5 *N* NaOH, 0.44 ml (5 mmol) of allyl bromide in 15 ml of CH_2Cl_2 during a period of 45 minutes at 45°C. In this case, the formation of η^3-$C_3H_5Mn(CO)_4$ seemed to be faster than in reaction (a) described above. After a total of one hour, the reaction was approximately 50% complete

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* Et_4N^+ $Mn_2(CO)_9Br^-$ has also been prepared from Et_4NBr and $BrMn(CO)_5$ by PTC. The complex had m.p. 153—155°C (dec) and the following elemental analysis: Found: C, 35.71; H, 3.69; Br, 14.25. calcd. $C_{17}H_{20}NO_9BrMn_2$: C, 35.69; H, 3.52; Br, 13.97%. The IR (ν(CO)) bands were identical to those of the $PhCH_2NEt_3$ salt reported previously [2].

with respect to the formation of η^3-$C_3H_5Mn(CO)_4$ (estimated from the intensity of carbonyl band at 2075 cm^{-1} in η^3-$C_3H_5Mn(CO)_4$). The reaction was stopped after an hour and not investigated any further.

PTC reaction of $Mn(CO)_5Br$ with allyl bromide (via Method B)

A solution containing 0.28 g (1 mmol) of $Mn(CO)_5Br$ in 10 ml of CH_2Cl_2 was added slowly to a stirred mixture containing 0.11 g (0.5 mmol) of BTEAC, 15 ml NaOH, 0.44 ml (5 mmol) of allyl bromide in 5 ml of CH_2Cl_2 during 45 minutes at 45°C. In this case, the formation of η^3-allyl product was faster than in the reaction where all reactants were rapidly mixed (Method A [2]): after a total of an hour of reaction time, an IR spectrum indicated that the formation of η^3-$C_3H_5Mn(CO)_4$ was approximately 90% complete, whereas only about 75% completion was observed when the reaction was conducted by Method A in CH_2Cl_2. The reaction was stopped at this point and discarded.

Attempted reaction of $PhCH_2NEt_3^+$ $Mn_2(CO)_9Br^-$ [2] with allyl bromide

Allyl bromide, 0.26 ml (3.0 mmol) and 0.3 g (0.5 mmol) of $PhCH_2NEt_3^+$ $Mn_2(CO)_9Br^-$ were dissolved in 20 ml of CH_2Cl_2 and the solution was heated, at reflux, for 5 hours. Infrared spectra indicated that the starting anion was slowly consumed and gave some new bands (ν(CO): 2110, 2010, 1940 cm^{-1}); however, there was no evidence for the formation of η^3-$C_3H_5Mn(CO)_4$ during 5 hours of refluxing (from IR). After solvent evaporation, a reddish oil was obtained which appeared to contain some unreacted starting anion. Hexane extraction of this reddish oil gave a pale yellow oil having very complicated IR absorptions [ν(CO) (hexane): 2010vw, 2058w, 2017s, 1997m, 1980w, 1968w cm^{-1}] which, however, do not match those of η^3-$C_3H_5Mn(CO)_4$.

Attempted reaction of $Mn(CO)_5Br$ with allyl bromide

Allyl bromide, 0.87 mmol (10 mmol), and 0.55 g (2 mmol) of $Mn(CO)_5Br$ were dissolved in 30 ml of CH_2Cl_2 and the solution was stirred at room temperature for 5 hours. Infrared spectra indicated no evidence of reaction.

Reaction of $Mn(CO)_5X$ ($X = Cl, Br$) with base in the presence of $PhCH_2NEt_3Cl$ in benzene

BTEAC, 0.11 g (0.5 mmol), was dissolved in 15 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.28 g (1 mmol) of $Mn(CO)_5Br$ or 0.23 g (1 mmol) of $Mn(CO)_5Cl$ in 15 ml of benzene at room temperature. The starting halide was completely consumed in 5 minutes and the color of the organic layer changed from yellow to reddish and some reddish emulsion was formed in the interface. After work-up in the usual manner (as described in Method A), a small amount of yellow oil was obtained which was identified to be $Mn_2(CO)_{10}$. The reddish emulsion obtained from the reaction mixture was very soluble in CH_2Cl_2 and showed a complicated infrared absorption pattern [ν(CO) (CH_2Cl_2): 2080w, 2010s, 1980vs, 1970vs, 1950m(sh), 1905s, 1862s cm^{-1}]. This material appears to be the same as that isolated and characterized from the reaction in CH_2Cl_2 [2].

Attempted reactions of cis-Et_4N^+ $Mn(CO)_4Br_2^-$ [34] with allyl bromide

(a) *cis*-Et_4N^+ $Mn(CO)_4Br_2^-$ (0.23 g, 0.5 mmol) and allyl bromide (0.22 ml, 2.5 mmol) were refluxed in 20 ml of CH_2Cl_2 for $1\frac{1}{2}$ hours. Infrared spectra indicated no evidence of reaction.

(b) Et_4NBr (0.06 g, 0.25 mmol) was dissolved in 10 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.23 g (0.5 mmol) of *cis*-Et_4N^+ $Mn(CO)_4Br_2^-$ and 0.22 ml (2.5 mmol) of allyl bromide in 20 ml of CH_2Cl_2 at room temperature. After 5 minutes, the IR spectrum of the organic layer showed the complete consumption of *cis*-Et_4N^+ $Mn(CO)_4Br_2^-$ and carbonyl absorptions at 2020m, 1910s cm^{-1}. The IR absorptions of the organic layer did not significantly change thereafter and the reaction was stopped after an hour of stirring (at room temperature). After work-up in the normal way (as described in Method A [2]) a small amount of yellow solid was obtained which had $\nu(CO)$ (CH_2Cl_2): 2025s, 1925s(br) cm^{-1}. There was no evidence for the formation of η^3-$C_3H_5Mn(CO)_4$.

Attempted oxidative addition of allyl bromide to $BrMn(CO)_5$ and PTC synthesis of an η^1,η^3-allyl product mixture

Allyl bromide (0.44 ml, 5 mmol) and $BrMn(CO)_5$ (0.28 g, 1 mmol) were stirred in 20 ml of benzene at room temperature for 12 hours. IR spectra indicated no evidence of reaction. A solution of 0.046 g (0.2 mmol) of BTEAC in 4 ml of 5 *N* NaOH was then added dropwise during 30 minutes; 15 minutes after this addition was complete an IR spectrum indicated that all $BrMn(CO)_5$ had been consumed and showed both η^1 and η^3 allyl products. Stirring was continued for an additional $1\frac{1}{4}$ hours but the concentration of allyl products remained constant. After work-up, the crude yellow oil was shown to contain (by IR) η^1-$C_3H_5Mn(CO)_5$, η^3-$C_3H_5Mn(CO)_4$ and a small amount of $Mn_2(CO)_{10}$; the η^1 to η^3 ratio was 50 : 50 (determined by PMR). The yields were not determined.

Attempted preparation of η^3-$C_3H_5Re(CO)_4$ [35] from $Re(CO)_5Br$ [36]

a) BTEAC, 0.23 g (1 mmol), was dissolved in 30 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.87 ml (10 mmol) of allyl bromide and 0.82 g (2.0 mmol) of $Re(CO)_5Br$ in 50 ml of CH_2Cl_2. The mixture was then heated at a reflux for 12 hours. The starting bromide, $Re(CO)_5Br$, was completely consumed after 30 minutes to give an unidentified compound [$\nu(CO)$ (CH_2Cl_2): 2085w, 1993s, 1980m(sh), 1945m, 1875s cm^{-1}] which was, however, unreactive thereafter. There was no IR spectral evidence for the formation of η^3-$C_3H_5Re(CO)_4$; however, after work-up, trituration of the crude yellow oily residue with hexane gave a small amount (~0.03 g, 5% yield) of pale yellow oil which was identified as η^3-$C_3H_5Re(CO)_4$; $\nu(CO)$ (hexane): 2090m, 1996s, 1982vs, 1962s cm^{-1} [lit. [35] (hexane): 2094s, 1994vs, 1980vs, 1959vs].

b) A solution of 0.82 g (2.0 mmol) of $Re(CO)_5Br$ in 60 ml of CH_2Cl_2 was added slowly at 45°C to a stirred solution containing 0.23 g (1 mmol) of BTEAC, 30 ml of 5 *N* NaOH, 0.87 ml (10 mmol) of allyl bromide and 20 ml of CH_2Cl_2 over a period of 8 h. The mixture was then heated at reflux for an additional 17 h. The starting bromide, $Re(CO)_5Br$, was completely consumed as quickly as it was added to the PTC media. After work-up and solvent removal, 0.2640 g of pale yellow oil was obtained [$\nu(CO)$ (CH_2Cl_2): 2090vw, 1995vs, 1950m, 1875vs cm^{-1}]. The oil was extracted with hexane and a very small amount (0.004 g) of η^3-$C_3H_5Re(CO)_4$ was obtained; ν(CO) (hexane): 2095m, 1995s, 1985s, 1965s cm^{-1}.

Reaction of η^5-$C_5H_5Mo(CO)_2(PPh_3)Cl$ (mixture of cis and trans isomers, cis/trans >50) with allyl bromide

BTEAC, 0.35 g (1.5 mmol), was dissolved in 45 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 1.54 g (3 mmol) of η^5-$C_5H_5Mo(CO)_2(PPh_3)Cl$ [37] and 1.31 ml (15 mmol) of allyl bromide in 80 ml of CH_2Cl_2. The mixture was then heated, at reflux, for 15 hours. Infrared spectra indicated no evidence of reaction. When the reaction was performed in refluxing benzene, however, the starting chloride was slowly consumed and the reaction was complete (judged by disappearance of η^5-$C_5H_5Mo(CO)_2(PPh_3)Cl$ ν(CO) bands) after 24 hours of refluxing. After work-up, a yellow oil was obtained which yielded a 43 : 57 mixture of η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_3$ and η^5-C_5H_5-η^3-$C_3H_5Mo(CO)_2$ (a combined yield of ca. 18%) and also an unidentified compound (0.07 g) having ν(CO) 1865 cm^{-1} in hexane (the parent η^1- and η^3-allyl complexes were separated from the unidentified compound by vacuum sublimation at 45°C/0.1 mmHg). This unidentified compound was not the expected η^1-complex, η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_2PPh_3$ (it has only one carbonyl band which did not match those of a closely related compound, η^5-C_5H_5-η^1-$C_3H_5Mo(CO)_2P(OPh)_3$ [38], ν(CO) (CH_2Cl_2): 1962, 1883 cm^{-1}).

Reaction of η^5-$C_5H_5Fe(CO)PPh_3X$ (X = Br, Cl) with allyl bromide

BTEAC, 0.23 g (1 mmol), was dissolved in 30 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 1.03 g (2 mmol) of η^5-$C_5H_5Fe(CO)PPh_3Br$ [37] and 0.87 ml (10 mmol) of allyl bromide in 50 ml of benzene. The mixture was then stirred at room temperature for 3 hours. Infrared spectra indicated that no noticeable reaction occurred for η^5-$C_5H_5Fe(CO)_2Br$. As the temperature was raised to 60—70°C, however, the halide started to decompose as evidenced by the formation of a substantial amount of brown iron oxide; the starting bromide was all consumed after 3 hours at 60—70°C. After workup, 0.29 g of yellow oil was obtained which was identified (by PMR) as a mixture of ferrocene and triphenylphosphine oxide m.p. 150—154°C (lit. [39] 156°C), isolated by crystallization from CH_2Cl_2/hexane. Similarly, the corresponding chloro complex, η^5-$C_5H_5Fe(CO)(PPh_3)Cl$, was completely consumed in benzene at 60—70°C after 3 hours, it also suffered decomposition and provided no allyl product.

Reaction of η^5-$C_5H_5Ru(CO)PPh_3Cl$ with allyl bromide

BTEAC, 0.06 g (0.25 mmol), was dissolved in 10 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.25 g (0.5 mmol) of η^5-$C_5H_5Ru(CO)PPh_3Cl$ and 0.22 ml (2.5 mmol) of allyl bromide in 15 ml of benzene. The mixture was then stirred at room temperature for 5 hours followed by heating at 60—70°C for another 15 hours. Infrared spectra indicated no evidence of reaction; the starting chloride was then fully recovered unchanged.

Reaction of mer-$Mn(CO)_3(PPh_3)_2Br$ with allyl bromide

BTEAC, 0.11 g (0.5 mmol), was dissolved in 15 ml of 5 *N* NaOH and added rapidly to a stirred solution containing 0.74 g (1 mmol) of *mer*-Mn(CO)$_3$(PPh$_3$)$_2$Br [40] and 0.44 ml (5 mmol) of allyl bromide in 50 ml of CH$_2$Cl$_2$. The mixture was then heated, at reflux, for 2 hours; however, the starting bromide was completely consumed after 1 hour. An IR spectrum of the organic phase showed three new bands at 2020w, 2000m, 1900s(br) cm^{-1}. The IR absorptions did not change thereafter. After work-up, an orange oil was obtained which consisted of a small amount (0.1 g, 22% based on *mer*-Mn(CO)$_3$(PPh$_3$)$_2$Br) of η^3-C$_3$H$_5$Mn(CO)$_3$PPh$_3$ (identified, after isolation by hexane trituration, from its m.p. and IR spectrum) and an unidentified carbonyl-containing compound [ν(CO) (CH$_2$Cl$_2$): 2020m, 2000m, 1915s, 1898s cm^{-1}]. This unidentified compound, however, was not the expected product, η^3-C$_3$H$_5$Mn(CO)$_2$(PPh$_3$)$_2$, since the IR data did not match those of a closely related compound, η^3-C$_3$H$_5$Mn(CO)$_2$[P(C$_2$H$_5$)$_3$]$_2$ [41] [ν(CO) (hexane): 1905, 1840 cm^{-1}]. No further work has been done with this system.

Synthesis of η^3-$C_3H_5Mn(CO)_3[P(OCH_3)_3]$

a) A mixture containing 2.64 g (7.11 mmol) of Mn(CO)$_4$[P(OCH$_3$)$_3$]Br [42], 4.30 g (35.54 mmol) of allyl bromide, 0.81 g (3.55 mmol) of BTEAC, 107 ml of 5 *N* NaOH and 150 ml of CH$_2$Cl$_2$ was stirred for 1 hour at room temperature under nitrogen. The organic layer was separated, washed with three 60 ml portions of water and dried over MgSO$_4$. The solvent was removed under reduced pressure to give 1.79 g of brown oil, which consisted of a mixture of η^3-C$_3$H$_5$Mn(CO)$_4$ and η^3-C$_3$H$_5$Mn(CO)$_3$P(OCH$_3$)$_3$ (18 : 82 as determined from the PMR spectrum). The mixture was separated by column chromatography on silica gel with elution by hexane followed by CH$_2$Cl$_2$ (the parent allyl complex elutes first). The crude η^3-C$_3$H$_5$Mn(CO)$_3$P(OCH$_3$)$_3$ was recrystallized from pentane at —78° C to give a pale yellow powder, m.p. 33.5—34° C; IR ν(CO) (hexane) 2018s, 1950vs, 1940sh, 1916vs, 1920sh cm^{-1}. PMR (C$_6$D$_6$): δ 1.58—1.79 (dd, 2), 2.37—2.48 (d, 2), 3.04—3.36 (m, 9), 4.28—4.73 (m, 1); Anal. Found: C, 35.56; H, 4.73; P, 10.00. calcd. for C$_9$H$_{14}$O$_6$PMn: C, 35.55; H, 4.64; P, 10.18%.

b) A mixture containing 1.12 g (3.01 mmol) of BrMn(CO)$_4$P(OCH$_3$)$_3$, 1.82 g (15.03 mmol) of allyl bromide, 0.34 g (1.51 mmol) of BTEAC, 45 ml of 5 *N* NaOH and 50 ml of C$_6$H$_6$ was stirred for 2 hours at room temperature under prepurified N$_2$. The benzene layer was then separated, washed with three 20 ml portions of water and finally dried over MgSO$_4$. After filtration, solvent was removed under reduced pressure and a brown oil was obtained; IR spectral examination of the oil showed that it contained no η^3-C$_3$H$_5$Mn(CO)$_4$. The crude product (0.75 g, 82%) was purified by crystallization at —78° C in pentane.

Synthesis of η^3-$C_3H_5Mn(CO)_2[P(OCH_3)_3]_2$

a) This compound was prepared from BrMn(CO)$_3$[P(OCH$_3$)$_3$]$_2$ [43] (0.934 g, 2 mmol), allyl bromide (1.21 g, 10 mmol), PhCH$_2$NEt$_3$Cl (0.228 g, 1 mmol) and 5 *N* NaOH (30 ml) in 80 ml of CH$_2$Cl$_2$ in the same manner described above in procedure a, except that the reaction mixture was heated with stirring at 45° C for 73 hours under prepurified N$_2$. After work-up, a pale yellow oil (0.36 g) was obtained which consisted of a mixture of η^3-C$_3$H$_5$Mn(CO)$_3$P(OCH$_3$)$_3$ and η^3-C$_3$H$_5$Mn(CO)$_2$[P(OCH$_3$)$_3$]$_2$ (32 : 68 as determined from the

PMR spectrum). Column chromatography on silica gel, with elution by hexane/CH_2Cl_2 provided the separate complexes (the disubstituted complex was obtained as a pale yellow oil, IR ν(CO) (hexane): 1940, 1870 cm^{-1}; reported [41] 1940, 1870 cm^{-1}). The crude product was taken up in hexane and cooled to —20°C; yellow-orange crystals, m.p. 43.5—44.5°C, were obtained (lit. [41] 45.5—46.1°C).

b) A mixture of $BrMn(CO)_3[P(OCH_3)_3]_2$ (1.09 g, 2.33 mmol), allyl bromide (1.41 g, 11.67 mmol), BTEAC (0.80 g, 3.50 mmol), 35 ml of 5 *N* NaOH and 100 ml of C_6H_6 was heated at 80°C for $2\frac{1}{2}$ hours under prepurified nitrogen. The benzene layer was separated, washed with three 50 ml portions of water, and dried over $MgSO_4$. After solvent removal, it gave 0.57 g (61%) of η^3-C_3H_5-$Mn(CO)_2[P(OCH_3)_3]_2$. An IR spectrum of this oil showed that it contained no η^3-$C_3H_5Mn(CO)_3P(OCH_3)_3$.

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