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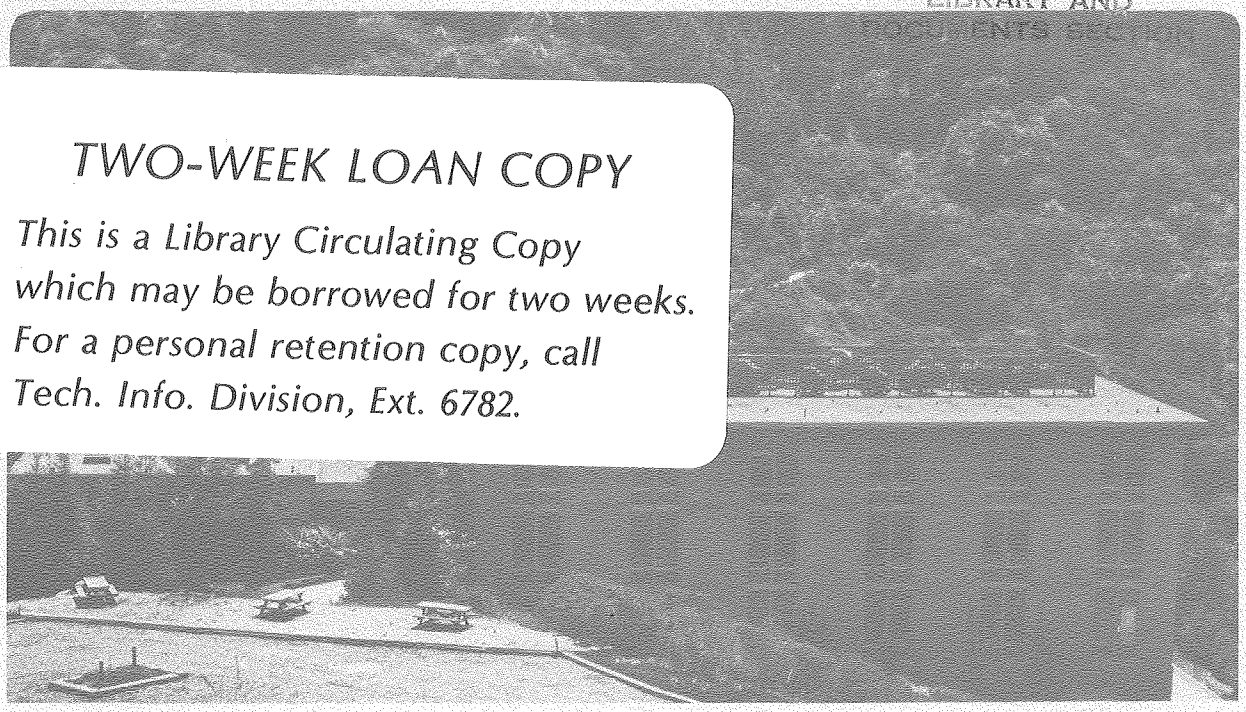

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REACTIONS OF η^5-CYCLOPENTADIENYLCOBALT(III) ALKYLS WITH COBALT(I) PHOSPHINES AND IRON CARBONYLS. EVIDENCE FOR DIRECT η^5-CYCLOPENTADIENYL AND TRIMETHYLPHOSPHINE GROUP TRANSFER BETWEEN METAL CENTERS.

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Abstract: We have found that η^5-methylcyclopentadienyl-(triphenylphosphine)dimethylcobalt(III) (1) undergoes intermolecular cyclopentadienyl ligand exchange with η^5-cyclopentadienylbistriphenylphosphinecobalt(I). The unsubstituted cyclopentadienyl(triphenylphosphine)dimethylco-balt(III) undergoes exchange of phosphine for carbon monoxide with both $Fe(CO)_4$ and $Fe(CO)_5$ by two different mechanisms. The first involves electrophilic displacement of coordinated phosphine by unsaturated $Fe(CO)_4$ and the second takes place by electrophilic displacement of CO from $Fe(CO)_5$ by the unsaturated $CpCoMe_2$ fragment (generated by phosphine dissociation from the saturated starting material).

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Introduction

Alkyl groups are easily transferred between many types of metal centers, apparently by a number of different mechanisms. The best understood of these processes are those in which a metal alkyl interacts with a second metal in a higher oxidation state, and are usually thought of as involving electrophilic attack of the high-oxidation-state center upon the metal-carbon bond[1].

A number of formally symmetrical alkyl transfer reactions have also been uncovered recently. In the majority of these, alkyl transfer is assisted by transfer of halogen or another electronegative group in the opposite direction[2], but cooperative transfer of two alkyl groups (as well as examples of stable dialkyls in which the alkyl groups bridge two metal centers) are now known[3,4].

Transfer of an alkyl group from a metal center to a second center in a <u>lower</u> oxidation state (i.e. attack at metal-bound carbon by a second, nucleophilic, metal center) is less common[5]. During a recent study of pairwise exchange of methyl groups between the Co(III) centers in $CpCoLR_2$ complexes[4], we considered the possibility that traces of a cobalt (I) complex, $CpCo(PPh_3)_2$, might contribute to the alkyl transfer reactivity of the system. We have now examined the possibility directly by examining reactions such as that shown in eq. (1). We have found that this reaction occurs easily. However, the mechanism surprisingly involves <u>cyclopentadienyl</u>, rather than alkyl and phosphine, transfer. We report here the details of this study, as well as some observations on reactions of Co(III) dimethyl complexes with

several other low-valent metal complexes.

Results and Discussion

Reaction of $CpCo(PPh_3)Me_2$ (1) with $CpCo(PPh_3)_2$. When a solution of 1 and $CpCo(PPh_3)_2$ (2) in THF-d_8 was heated in a sealed NMR tube at 62°C new methyl resonances arising from the unsubstituted methyl analog 3 were observed in the ^1H NMR spectrum; AA'BB' Cp resonances corresponding to $MeCpCo(PPh_3)_2$ (4) were also seen (cf. eq.(1)). After 48 hours the reaction had apparently reached equilibrium, with NMR observations showing a 67:33 ratio of 1 and 3. The cobalt(III) complexes could be removed from this mixture by chromatography under air-free conditions, and recrystallized together from benzene/hexane solvent. Because 1 and 3 could not be separated in this way, each pure complex was prepared independently, and synthetic mixtures were shown to be identical with the material isolated from the exchange reaction.

Reaction of $MeCpCo(PMe_3)Me_2$ (5) with $CpCo(PPh_3)_2$ (6). Reaction (1) might take place by either phosphine and methyl, or cyclopentadienyl ring, exchange. Previous studies have shown that phosphine substitution lability in these complexes is highly dependent upon both cobalt oxidation state and the nature of the phosphine involved[6]. For example, 2 undergoes dissociation of PPh_3 rapidly even at -60°C[6a]; in the presence of PMe_3 this gives the less reactive $CpCo(PPh_3)(PMe_3)$, and ultimately the still less reactive $CpCo(PMe_3)_2$ is formed. Cobalt(III) complex 1 dissociates PPh_3 at a reasonable rate at 60°C[6b,c], but the

corresponding PMe_3 complex 5 is quite inert under these conditions. Thus it is possible to in effect "label" the cobalt(III) atom in a $MeCpCo(L)Me_2$ complex with the tightly bound PMe_3 ligand. Accordingly, complex 5 was heated in THF-d_8 with cobalt(I) PPh_3 complex 2. Surprisingly, this reaction (eq. (2)) proceeded at a rate similar to that of reaction (1) at 62°C, and the products were found to be 6 and 4, again by comparison with independently prepared samples. Simple methyl exchange would be expected to have given 3 and the mixed phosphine complex $MeCpCo(PMe_3)(PPh_3)$ (7). The observed products suggest that cyclopentadienyl ligand exchange has taken place.

Reaction of 1 with $CpCo(PPh_3)(PMe_3)$ (7). One possible way reaction (2) might be occuring without Cp ligand transfer is illustrated in eqs. (3) and (4). Here it is postulated that phosphine/methyl transfer occurs to give transient amounts of 7 and 1, and these complexes react rapidly, (perhaps by PPh_3 dissociation from 1 and some sort of direct bimolecular PMe_3 transfer) to give 4 and 6. In order to see whether such a direct reaction could occur we heated the analogous complexes 1 and 8 under conditions where both reactions (1) and (2) took place. No reaction was observed, indicating that eq. (4) does not take place. At higher temperatures (80°C) slow thermal decomposition of 1 was observed, but no phosphine exchange was noted. On the basis of this information Cp exchange is strongly implicated as being responsible for reactivity in this Co(I)/Co(III) system.

Reaction of 3 with low-valent complexes. Although methyl exchange in reaction (1) has been ruled out, the question of

whether such an exchange is possible in cases where some thermodynamic driving force favors that type of process is still an interesting one. To briefly survey this type of reaction, 3 was allowed to react with several unsaturated transition metal complexes which normally undergo facile two electron oxidations.

When 3 was heated in solutions containing $(PPh_3)_3RhCl$ no changes in the ^1H NMR spectra were noted below 80°C. Above that temperature slow decomposition of 3 was observed but no evidence for alkyl exchange was obtained in a variety of solvents (THF-d_8, CD_2Cl_2, and C_6D_6) regardless of whether or not excess triphenylphosphine was added to the solutions. Similarly, no reaction between $(PPh_3)_3IrCl$ and 3 was noted under a variety of conditions. In C_6D_6 and THF-d_8 $(PPh_3)_3IrCl$ was found to undergo unimolecular <u>ortho</u>-metallation faster than reaction with 3, at all temperatures between 25 and 100°C. Finally, no methyl exchange between 3 and $(PPh_3)_2PtCl_2$ was observed in either THF-d_8 or CD_2Cl_2 regardless of added phosphine.

In contrast to the above observations, cobalt alkyls <u>do</u> react with iron carbonyls. When 3 was allowed to react at 25°C in THF-d_8 with excess $Fe_2(CO)_9$ high yields (>95% by NMR) of acetone and $CpCo(CO)_2$ were realized. Those compounds were identified by isolation and comparison with independently prepared samples. Infrared and NMR spectroscopy allowed us to tentatively identify the iron products as a mixture of $Fe(CO)_5$, $Fe_3(CO)_{12}$ and $(PPh_3)Fe(CO)_4$. This reaction took place in darkened solutions as well as in room light. Monitoring the reaction by ^1H NMR spectroscopy allowed detection of an unstable

intermediate whose concentration built up to a small extent during the reaction (*vide infra*). Reaction of 3 with $Fe(CO)_5$ under the same conditions led to a similar product mixture, although the reaction was *faster* and more of the aforementioned intermediate was observed in the NMR spectrum. The intermediate was identified on the basis of its NMR (single resonances in THF-d_8 at δ 0.46 and 4.95 ppm in a ratio of 6:5) and IR (single CO absorbance at 2001 cm^{-1}) spectra as $CpCo(CO)Me_2$, which was previously detected[6c,d] during the carbonylation of $[CpCo(CO)(CH_3)]_2$ and 3. This complex is known[6c,d] to produce acetone and $CpCo(CO)_2$ in the presence of CO, and to decompose thermally to acetone at 25°C.

Although $Fe(CO)_5$ effects many interesting processes, it only grudgingly exchanges PPh_3 for CO at elevated temperatures in the absence of any other catalysts. Yet clearly $Fe(CO)_5$ serves as a source of CO for (potentially) coordinatively unsaturated cobalt. A mechanism for this process (Scheme 1) involving phosphine dissociation from 3 prior to reaction with $Fe(CO)_5$ explains the observed results. This mechanism involves the known dissociation of $Fe_2(CO)_9$ into $Fe(CO)_5$ and $Fe(CO)_4$ as an initiating step[7] (a) and relies on the other previously studied steps (b)[6], (e)[8] and (f)[7] to explain the products obtained. The requirement of step (b) in this mechanism is supported by the absence of reaction between 5 and $Fe(CO)_5$ in THF-d_8; as pointed out earlier, 5 does not rapidly dissociate its phosphine ligand as 3 has been shown to do.

While Scheme 1 accounts for the acetone formed in the

reaction between 3 and $Fe(CO)_5$, it suggests that no reaction should take place when 5 is combined in THF-d_8 with $Fe_2(CO)_9$. In fact, when that reaction was undertaken, a product mixture of acetone, $CpCo(CO)_2$, $(PMe_3)Fe(CO)_4$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ was obtained. To determine whether the $Fe(CO)_4$ produced from $Fe_2(CO)_9$ was responsible for the production of acetone in the reaction of 5 with $Fe_2(CO)_9$, the iron pyridine complex, $(C_5H_5N)Fe(CO)_4$, was prepared and dissolved in THF-d_8 containing complex 5. The mixture was stable for a few hours at room temperature; heating the solution to 40°C, where the $pyFe(CO)_4$ is known to dissociate CO[9], resulted in the production of acetone, $CpCo(CO)_2$ and some $(PMe_3)(C_5H_5N)Fe(CO)_3$ as well as a complex mixture of higher iron clusters. Clearly, both $Fe(CO)_4$ and $Fe(CO)_5$ can react with these cobalt(III) complexes; the former can even remove bound phosphine from a cobalt(III) dialkyl, thus requiring a step such as c' (Scheme 1) to fully describe the reactivity of this system. We prefer to regard such a step c' as electrophilic displacement of phosphine by unsaturated iron as the other obvious pathway (electron transfer) would result in instantaneous reductive elimination of ethane from the Co(IV) species so generated[10]. Stereochemical labelling experiments with optically active phosphines are needed to further establish the nature of this displacement.

Conclusions

Several surprising phenomena have been observed in this study. Exchange of cyclopentadienyl groups between transition

metal centers, albeit slowly in this case, appears to be quite rare[11]; certainly such transfer has not previously been observed between cobalt atoms in the general class of organometallic complexes discussed here. The nature of the transition state for this ligand transfer is unknown. However, the novel bridging-Cp complexes in the palladium series (e.g. A) recently discovered by Werner[12] provide an interesting model for such a transition state. It seems reasonable that in some complexes bridging systems have a free energy lower than their non-bridging analogs and are therefore isolable. In other systems, where mononuclear Cp complexes are more stable, Cp-bridging structures may be less stable but still energetically accessible, thus becoming possible transition states or intermediates for Cp-exchange processes.

It is also clear from our results that $Fe(CO)_5$ can serve as a source of CO to unsaturated cobalt, and that the unsaturated iron fragment $Fe(CO)_4$ has the ability to abstract PMe_3 from a (normally inert) Co(III) center.

Experimental

General. All manipulations of oxygen-or water-sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Tetrahydrofuran (THF) and diethylether were distilled from purple sodium/benzophenone ketyl solutions. Benzene and hexanes were degassed and used as supplied from J. T. Baker ("Analyzed

Reagent" grade). Methylene Chloride (Baker "Analyzed Reagent" grade) was distilled from CaH_2 and degassed by freeze-pump-thaw cycles. Iron carbonyls ($Fe(CO)_5$ and $Fe_2(CO)_9$) were used as supplied from Alfa. $(PPh_3)_2PtCl_2$ (Alfa) was recrystallized from absolute ethanol, while $(PPh_3)_3RhCl$ (Alfa) was recrystallized from CH_2Cl_2/hexane. The $CpCo(PPh_3)Me_2$[4,6c], $CpCo(PMe_3)Me_2$[6c], $MeCpCo(PPh_3)Me_2$[4], $MeCpCo(PMe_3)Me_2$[4], $CpCo(PPh_3)_2$[13], $CpCo(PPh_3)(PMe_3)$[14], $Fe(CO)_4(PPh_3)$[9], $Fe(CO)_4(NC_5H_5)$[10] and $(PPh_3)_3IrCl$[15] were synthesized by previously published methods.

Infrared (IR) spectra were recorded on a Perkin-Elmer model 283 grating spectrophotometer using solutions of samples in sodium chloride cells (0.10 mm path length).

NMR Experiments. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 90 MHz spectrometer or a high field (180.09 MHz) instrument equipped with a Bruker magnet, Nicolet Technology Corp. Model 1180 data system, and electronics assembled by Mr. Rudi Nunlist (U. C. Berkeley). Spectra were recorded at probe temperatures (35°C for the 90 MHz instument and 25°C for the high field machine). Deuterated THF and benzene were vacuum transferred from sodium/benzophenone ketyl solutions while methylene chloride-d_2 was vacuum transferred from Linde 4A° molecular sieves and degassed through four freeze-pump-thaw cycles on a vacuum line.

NMR experiments were carried out as follows: a standard NMR tube fused to a 14/20 ground glass joint was loaded with the desired compounds in the dry box, capped with a teflon needle valve, placed on a vacuum line, and evacuated at -196°C. The

tube was charged with the desired amount of solvent by vacuum transfer out of a graduated tube of solvent. The NMR tube was sealed and carefully thawed before any heating cycles were undertaken. All heating was accomplished in a Precision Scientific model H-11 constant temperature bath.

After completion of a reaction, the volatile components were vacuum transferred into another tube, under inert conditions, and analyzed by standard NMR, IR, VPC and mass spectral methods. The non-volatile components were then similarly isolated and analyzed by standard methods. Non-volatile products of the iron reactions were analyzed as a mixture by NMR and IR comparrisons to known compounds. Mixtures of cobalt alkyls were purified by air free column chromatography on silica gel using benzene/hexane eluent. The mixture was recrystallized from benzene/hexane.

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Scheme 1

a) $Fe_2(CO)_9$ $Fe(CO)_4$ + $Fe(CO)_5$

b) $CpCoLMe_2$ $CpCoMe_2$ + L

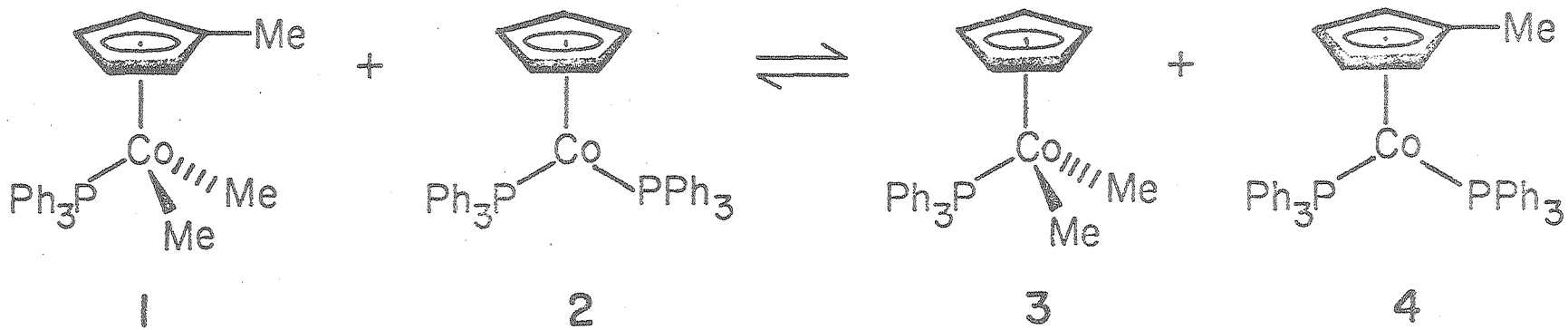
c) $CpCoMe_2$ + $Fe(CO)_5$ $CpCo(CO)Me_2$ + $Fe(CO)_4$

d) $CpCo(CO)Me_2$ + $2Fe(CO)_5$ $CpCo(CO)_2$ $+2Fe(CO)_4$ + CH_3COCH_3

e) $Fe(CO)_4$ + L $LFe(CO)_4$

f) $3Fe(CO)_4$ $Fe_3(CO)_{12}$

c') $CpCoLMe_2$ + $Fe(CO)_4$ $CpCoMe_2$ + $LFe(CO)_4$



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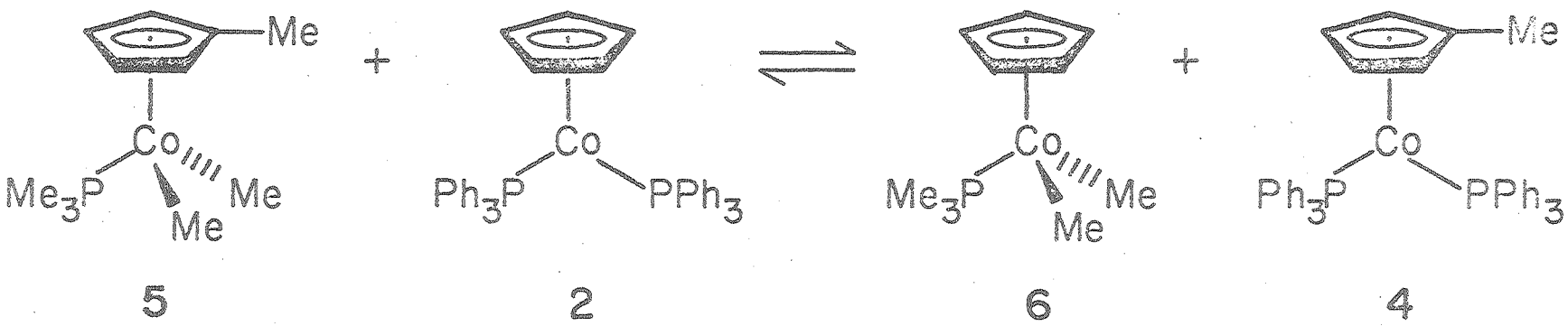

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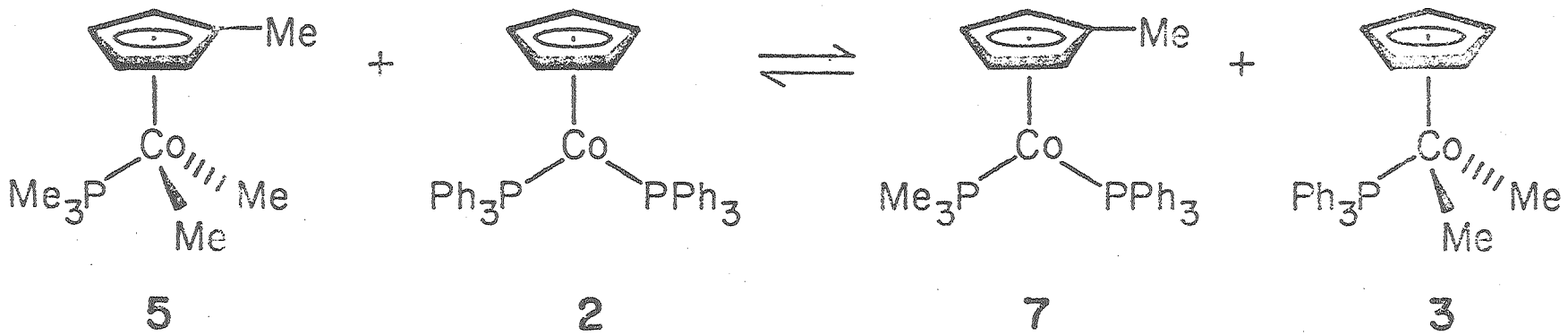
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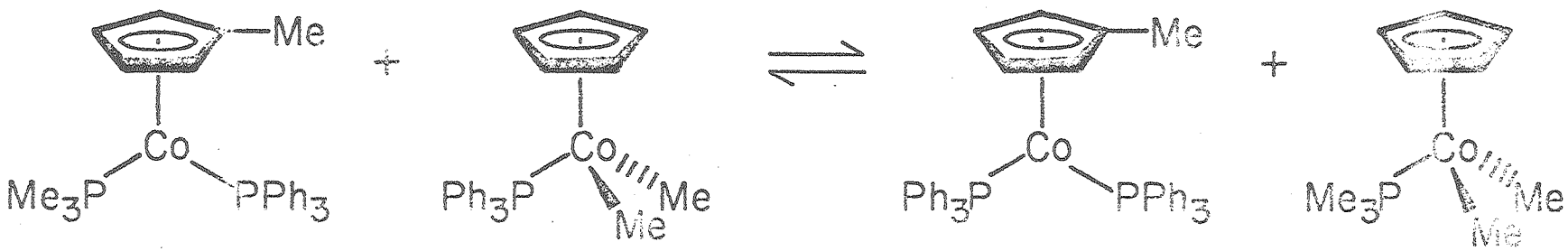
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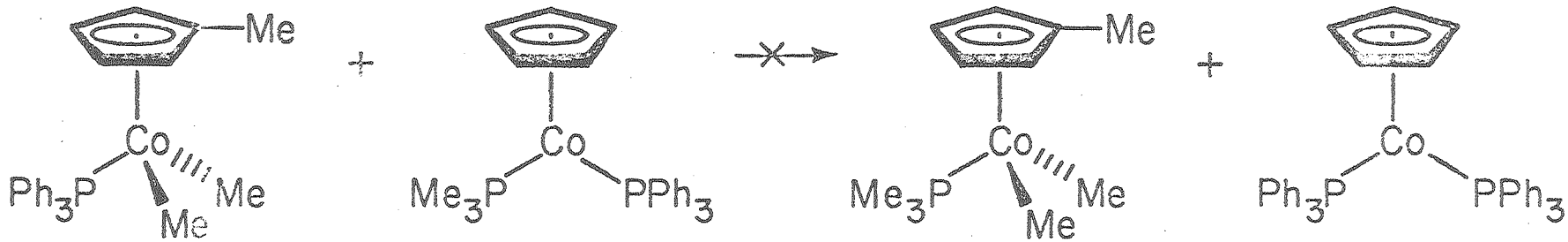
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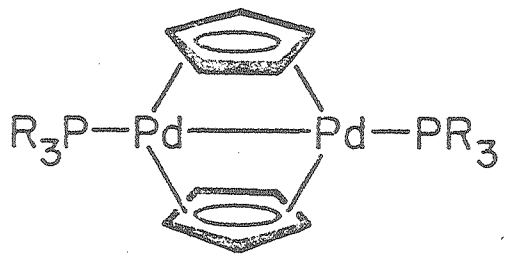
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