The practical[a] preparation of $C_6H_5HgCHCl_2$ opens the possibility of CHCl transfer by the mercurial route. Preliminary experiments have shown that phenyl(dichloromethyl)mercury reacts with cyclohexene in a sealed tube at 145° (60 h) to give a mixture of both 7-chlorobicyclo[4.1.0]heptane isomers[4] in *ca.* 60% yield. The chemistry of $C_6H_5HgCHX_2$ compounds is under intensive investigation in these Laboratories.

It should be noted especially that all experiments described above were carried out under an atmosphere of prepurified nitrogen.

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[a] The Reutov-Lovtsova procedure[5] obviously is to be preferred over the tin hydride reduction method.

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Cyclobutadiene–metal complexes

Part III*. Cyclopentadienylation by ligand transfer

We recently described[1,2] the preparation of some cyclobutadiene–metal complexes by transfer of the tetraphenylcyclobutadiene ligand from (tetraphenylcyclobutadiene)palladium halides (I) onto other metals by reaction of (I) with metal carbonyls. We now report examples of the transfer of the cyclopentadienyl ligand from iron to palladium, nickel, cobalt and titanium, as well as the reverse reaction from titanium to iron. The compounds used as the cyclopentadienylating agents are the readily prepared[3] cyclopentadienyliron dicarbonyl dimer (II) or cyclopentadienyliron dicarbonyl bromide (III). Preliminary results indicate that this reaction proceeds

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* The previous papers in this series are those in refs. 1 and 2.

particularly well when the reactant has a π-bonded hydrocarbon ligand such as tetraphenylcyclobutadiene, and we have used it to prepare a number of π-cyclopentadienyl-π-(tetraphenylcyclobutadiene)metal sandwich complexes[a].

$$\begin{array}{l}
(\pi\text{-}C_5H_5)Fe(CO)_2X + \underset{(I)}{(\pi\text{-}Ph_4C_4)PdBr_2} \longrightarrow \underset{(IV)}{[(\pi\text{-}C_5H_5)Pd(\pi\text{-}Ph_4C_4)]^+Fe^{III}Br_4^-} \\
\qquad\qquad\qquad\qquad\qquad\qquad\quad \Big\uparrow \scriptstyle HBr \\
(II),\ X = (\pi\text{-}C_5H_5)Fe(CO)_2 \\
(III),\ X = Br \\
(IV) + K_4Fe(CN)_6 \longrightarrow \underset{(V)}{[(\pi\text{-}C_5H_5)Pd(\pi\text{-}Ph_4C_4)]^+Br^-} + 3KBr + KFeFe(CN)_6
\end{array}$$

Reaction of (I) with (II), or preferably with two moles of (III), in refluxing benzene for two hours gave, after crystallization of the insoluble product from dichloromethane, π-cyclopentadienyl-π-(tetraphenylcyclobutadiene)palladium tetrabromoferrate[b], (IV). (IV) is a paramagnetic[c], purple, crystalline ionic, air-stable compound which on reaction with potassium ferrocyanide in water–dichloromethane was converted into the stable, diamagnetic, orange bromide, (V), in 83% yield[d]. The PMR spectrum of (V) showed two sharp resonances at 2.39 τ (C_6H_5 protons) and 3.66 τ (C_5H_5 protons) with the expected intensity ratio of 4:1. (V) reacted with hydrogen bromide in dichloromethane to give (I) in 80% yield, indicating that the cyclobutadiene ring was still intact in (V).

TABLE 1

Reactant	*Cyclopentadienylating agent*	*Product*	*Yield*[a]
$(\pi\text{-}Ph_4C_4)PdBr_2$	$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{}^b$	$[(\pi\text{-}C_5H_5)Pd(\pi\text{-}Ph_4C_4)]^+FeBr_4^-$	42
$(\pi\text{-}Ph_4C_4)PdBr_2$	$(\pi\text{-}C_5H_5)Fe(CO)_2Br^b$	$[(\pi\text{-}C_5H_5)Pd(\pi\text{-}Ph_4C_4)]^+FeBr_4^-$	85
$(\pi\text{-}Ph_4C_4)NiBr_2$	$(\pi\text{-}C_5H_5)Fe(CO)_2Br^b$	$[(\pi\text{-}C_5H_5)Ni(\pi\text{-}Ph_4C_4)]^+FeBr_4^{-d}$	77
$(\pi\text{-}1.5\text{-}C_8H_{12})PdBr_2{}^5$	$[(\pi\text{-}C_5H_5)Fe(CO)_2{}^b$	$[(\pi\text{-}C_5H_5)Pd(\pi\text{-}1.5\text{-}C_8H_{12})]^+FeBr_4^-$	~ 8
$(\pi\text{-}1.5\text{-}C_8H_{12})PdBr_2{}^5$	$(\pi\text{-}C_5H_5)Fe(CO)_2Br^b$	$[(\pi\text{-}C_5H_5)Pd(\pi\text{-}1.5\text{-}C_8H_{12})]^+FeBr_4^-$	54
$(\pi\text{-}Ph_4C_4)Co(CO)_2Br^c$	$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{}^b$	$(\pi\text{-}C_5H_5)Co(\pi\text{-}Ph_4C_4)^{6,1}$	73
$(\pi\text{-}Ph_4C_4)Co(CO)_2Br^e$	$(\pi\text{-}C_5H_5)Fe(CO)_2Br^b$	$(\pi\text{-}C_5H_5)Co(\pi\text{-}Ph_4C_4)$	>50
$TiCl_4$	$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{}^f$	$(\pi\text{-}C_5H_5)TiCl_3{}^g$	5
$Fe(CO)_5$	$(\pi\text{-}C_5H_5)_2TiCl_2{}^f$	$(\pi\text{-}C_5H_5)_2Fe$	~10

[a] Yield in % based on amount of reactant. [b] Refluxing benzene. [c] Kindly donated by Dr. H. H. FREEDMAN. [d] Characterized as the diamagnetic bromide $[(C_5H_5)Ni(Ph_4C_4)]^+Br^-$ obtained in 70% overall yield. [e] The preparation of this compound will be described shortly. [f] Refluxing xylene. [g] Isolated and characterized as the oxychloride[7] $[(C_5H_5)TiOCl]_4$.

As shown in the table, the cyclopentadienyl group could also be transferred onto nickel and cobalt complexes of tetraphenylcyclobutadiene, and onto the 1,5-cyclo-

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[a] These reactions differ from the well-known reactions of manganese dicyclopentadienide and other ionic cyclopentadienides with transition-metal halides in ethereal solvents to give metallocenes[4] in that both (II) and (III) contain covalently bound cyclopentadienyl groups, and that these reactions occur in non-polar solvents.

[b] All new compounds reported here gave satisfactory analyses for three or more elements.

[c] A rough magnetic susceptibility measurement on (IV) gave μ_{eff} = 6.1 Bohr Magnetons, in fair agreement with the expected value (5.92 B.M.) for tetrahedral Fe(III).

[d] The infra-red spectra of (IV) and (V) (KBr discs) were identical in the 2–16 μ region.

octadiene complex of palladium bromide. When the reactant did not possess a π-bonded hydrocarbon ligand, reaction only proceeded to a very small extent, as with titanium tetrachloride, or not at all. The reverse of this reaction, transfer from titanium onto iron, gave ferrocene in 10 % yield from titanocene dichloride and iron pentacarbonyl. However, titanocene dichloride did not react with nickel carbonyl to give nickelocene. This result is not unexpected since the only other case of the transfer of the cyclopentadienyl group from one metal to another which has been reported is that of the preparation (in unspecified yields) of cyclopentadienyliron dicarbonyl dimer, cyclopentadienylnickel carbonyl dimer and tricarbonylcyclopentadienyliron-cyclopentadienylnickel from nickelocene and iron pentacarbonyl[8].

We have also observed one case of the simultaneous transfer of a cyclopentadienyl and a cyclobutadiene ligand. Reaction of π-cyclopentadienyl-π-(tetraphenylcyclobutadiene)palladium bromide (V) with dicobalt octacarbonyl in benzene gave a 10 % yield of π-cyclopentadienyl-π-(tetraphenylcyclobutadiene)cobalt[6,1] (VI).

$$\underset{\text{(V)}}{[(\pi\text{-Ph}_4\text{C}_4)\text{Pd}(\pi\text{-C}_5\text{H}_5)]^+\text{Br}^-} + \text{Co}_2(\text{CO})_8 \longrightarrow \underset{\text{(VI)}}{(\pi\text{-Ph}_4\text{C}_4)\text{Co}(\pi\text{-C}_5\text{H}_5)}$$

While these ligand-transfer reactions are not likely to supersede the use of metal cyclopentadienides in most syntheses, these reactions promise to be useful when strongly basic conditions or the use of complexing solvents such as ethers are to be avoided. Thus, for example, we were unable to prepare (V) from (I) and sodium cyclopentadienide in tetrahydrofuran.

Full details of these reactions and proposals for their mechanisms will be published shortly.

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