Journal of Organometallic Chemistry, 135 (1977) 115–124
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A CYCLOPENTADIENYL RING EXCHANGE METHOD FOR THE ATTACHMENT OF EARLY TRANSITION METAL METALLOCENE DICHLORIDES TO A POLYMER SUPPORT

John Guo-shuh Lee and Carl H. Brubaker, Jr.*
Department of Chemistry, Michigan State University, East Lansing,
Michigan 48824 (U.S.A.)

(Received March 1st, 1977)

SUMMARY

PMR and mass spectral analysis have been used to study the interchange of π-bonded cyclopentadienyl rings with σ-bonded cyclopentadienyl rings in the compounds $(C_5H_5)_4M$ (M = Ti, Zr, Hf, Nb, Ta, Mo and W) and $(C_5H_5)_3V$ or σ-bonded benzylcyclopentadienyl rings in the compounds $(C_6H_5CH_2C_5H_4)(C_5H_5)_2MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo and W). As soon as the Cp_4M species are generated (indicated by a color change), the interchange occurs and the equilibrium is established. As reported, no such interchange was observed in $(C_5H_5)_4Mo$ in the PMR time scale; however, it does occur after a longer time. By using this interchange behavior of the cyclopentadienyl ring, metallocene dichlorides of Ti, Zr, Hf, V, Nb, Ta, Mo and W have been attached to polystyrene-divinylbenzene beads.

INTRODUCTION

Interchange of η^5-C_5H_5 and η^1-C_5H_5 rings in $M(C_5H_5)_x$ complexes was first observed in temperature-dependent PMR studies of $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5$ Ti.[1,2]. This work and subsequent investigation of three other Cp_4M (M=Z Hf and Mo)[3] systems demonstrated that only the molybdenum complex does not undergo rapid ring interchange at ambient temperatures. By using labelled Cp compounds (C_5D_5 in Cp_4M and $C_6H_5CH_2C_5H_4$ in Cp_3MCl systems), the interchange reactions in some d^0 to d^2 metallocenes were investigated.

The results show the interchange of monohapto and pentahaptocyclopentadienyl rings occurs in all the systems studied.

Recently we have been investigating ways of attaching transition metal catalysts to polystyrene-divinylbenzene beads [4] and since lithiated cyclopentadiene rings have been attached to these polymers, their reactions with metallocene dichlorides would be expected to lead to a ring interchange. Thus the metallocene dichlorides of T, Zr, Hf, V, Nb, Ta, Mo and W have been attached to the polymer.

RESULTS AND DISCUSSION

The compounds $(C_5H_5)_{2-n}(C_5D_5)_{2+n}M$, where n = 0, 1, 2; M = Ti, Zr, Hf, Nb, Ta, Mo, and W; were prepared from the corresponding $(C_5H_5)_2MCl_2$, and two moles of NaC_5D_5 (or TlC_5D_5 for Mo system). Excess NaC_5D_5 was used for the Nb and Ta compounds. When the resulting products were treated with gaseous HCl, σ-bonded Cp was replaced by Cl^-, and $(C_5H_5)_{2-n}(C_5D_5)_nMCl_2$, was isolated. The ratio of the peak areas $(C_5H_5)_2MCl_2/(C_5H_5)_{2-n}(C_5D_5)MCl_2$ (M = Ti, Zr, and Hf) for two different equimolar solutions based on absolute ^1H nmr intergration was _ca._ 2 and suggests that essentially half of the C_5H_5 rings were replaced by C_5D_5 rings. The mass spectrographic data of $(C_5H_5)MCl_2$ and $(C_5H_5)_{2-n}(C_5H_5)_nMCl_2$ (M = Ti, Zr, Hf, Nb, Ta, Mo and W) were consistent with the presence of a mixture of $C_{10}D_{10}MCl_2$, $(C_5H_5)(C_5D_5)MCl_2$ and $C_{10}H_{10}MCl_2$ as expected if the initially σ-bonded C_5D_5 rings were interchanged with π-bonded C_5H_5 rings. Our results confirm the fast ring exchange expected in d^0 systems. With the intermediately bonded ring concept proposed by Cotton [2], fast ring interchange in d^1 systems also can be explained. As reported, no such interchange was observed in $(C_5H_5)_4Mo$ on the PMR time scale, since it has an eighteen electron configuration in its ground state and would have to go through a high-energy, intermediately bonded state in order to exchange the rings. However, this interchange is observed in our experiment that encompasses a longer period of time. The PMR spectrum of

$(C_5H_5)_2(C_5D_5)_2Mo$ (prepared from either $(C_5H_5)_2MoI_2$ and two moles of TlC_5D_5 or from $(C_5D_5)_2MoI_2$ and two moles of TlC_5H_5, was measured. The spectrum (toluene-d^8) consisted of two very sharp singlets at δ 3.83 and δ 3.94 with equal intensities. With no interchange, only one of these two singlets should be observed in the PMR spectra [3]. After 6 hr. the Cp_4Mo species were generated (indicated by a violet color), the interchange had occurred and the equilibrium had been established. Because of the insolubility of Cp_2MoI_2, the formation rate of Cp_4Mo is less than its σ-π exchange rate.

Since Cp_4V cannot be prepared [5], the interchange reactions of Cp_2V and Cp_3V were chosen for study. The compound, $(C_5H_5)_2(C_5D_5)V$, was prepared from $(C_5H_5)_2VCl$ and one mole of NaC_5D_5. When Cp_2V and Cp_3V were heated, σ-bonded Cp was eliminated and exchange products $(C_5H_5)_2V$, $(C_5H_5)(C_5D_5)V$, and $(C_5D_5)_2V$ were isolated by sublimation. Mass spectrometric data confirmed the exchange. When vanadocene was treated with NaC_5D_5 in excess, ring substitution to give mostly $(C_5D_5)_2V$ was confirmed, as indicated by the mass spectra of the final products.

$(C_5H_5)_2(C_6H_5CH_2C_5C_4)MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo and W) were prepared from the corresponding metallocene dichlorides and one mol of sodium (or lithium) benzylcyclopentadienide. The interchange follows reaction scheme below.

REACTION SCHEME 1

$$\begin{tikzcd}
C_6H_5CH_2C_5H_4^- + (C_5H_5)_2MCl_2 \arrow[d] & \\
(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_6H_5CH_2C_5H_4)MCl \arrow[r, leftrightharpoons] \arrow[d, "HCl"] & (\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_6H_5CH_2C_5H_4)MCl \arrow[dl, "HCl"'] \\
(\eta^5\text{-}C_5H_5)_{2-n}(\eta^5\text{-}C_6H_5CH_2C_5H_4)_nMCl_2 \quad (n = 0, 1, 2) &
\end{tikzcd}$$

The $(C_5H_5)_{2-n}(C_6H_5CH_2C_5H_4)_nMCl_2$ compounds were isolated and the

PMR spectral data for M = Ti, Zr, and Hf are listed in Table 1. The presence of C_6H_5- and -CH_2- protons is a good indication of the ring exchange reactions. The mass spectrometric data for M = Ti, Zr, Hf, Nb, Ta, Mo and W revealed the presence of either the parent peaks of $(C_5H_5)(C_6H_5CH_2C_5H_4)MCl_2$ or of their fragments. These data suggest that interchange of the rings had occurred. By the same scheme, when vanadocene dichloride was tested, no ring interchange was detected by the PMR and mass spectra, nor was any vanadocene dichloride recovered -- spectra showed that the starting material had disappeared (decomposed).

TABLE 1
PMR DATA FOR Ti, Zr and Hf in $(C_5H_5)_{2-n}(C_6H_5CH_2C_5H_4)_nMCl_2$
THE SOLVENT IS TOLUENE-d^8

M	Cp-	δ (rel.int.) C_6H_5-	-CH_2-
Ti	6.48(18)	7.2(9)	4.1(1)
Zr	6.2(3.2)	7.05(1)	3.95(0)
Hf	6.35(12)	7.15(7)	4.05(1)

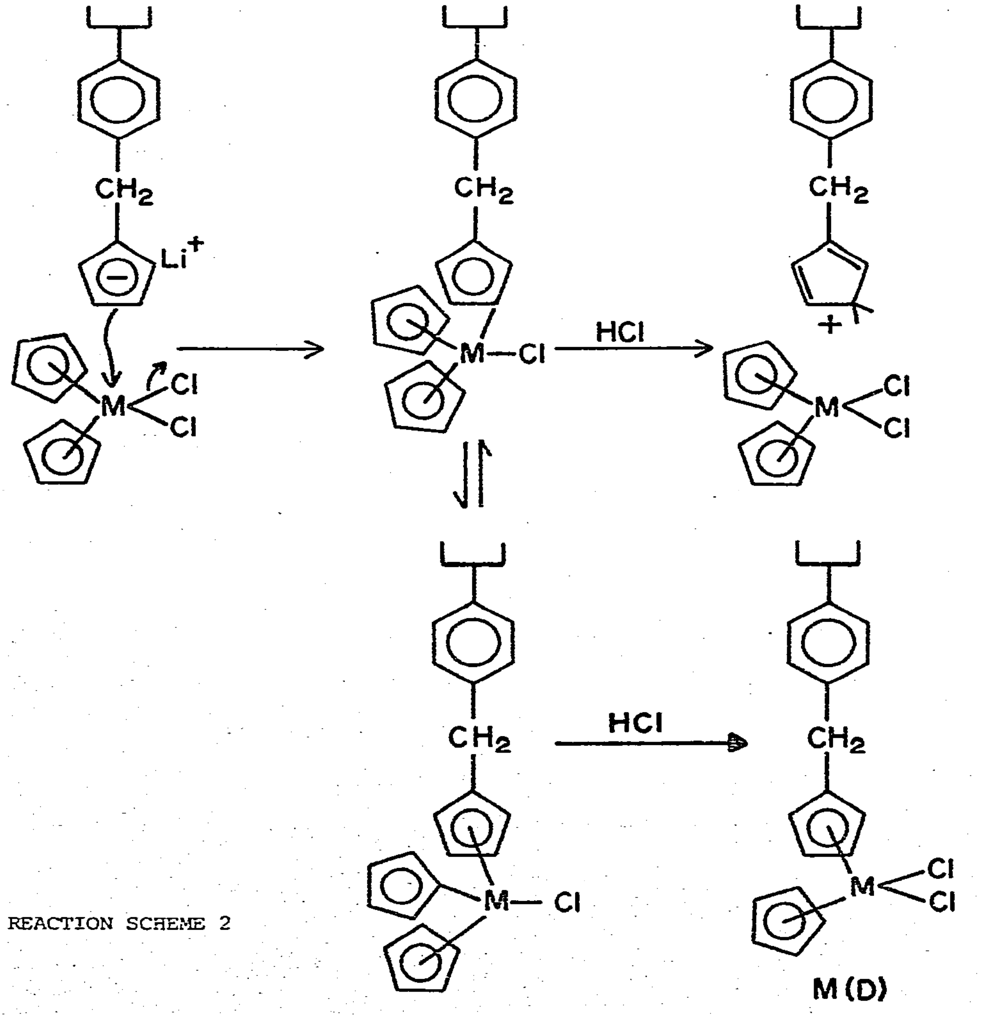
The metallocene dichlorides of Ti, Zr, Hf, Nb, Ta, Mo and W have been attached to the polymer according to the following Scheme 2.

Because there is no direct ring exchange between benzylcyclopentadienide anion and vanadocene dichloride, the attachment procedure is different. Since we do know that the cyclopentadienide anion will displace a bound ring in vanadocene, this behavior can be used to attach the complex to the beads. After the polymer-attached Cp_3VCl was treated with HCl it was then oxidized by air to vanadocene dichloride [6]. The analytical results are listed in Table 2. In general, they are in reasonable agreement with the expected results. Since the beads are not totally inert to the gaseous HCl, the metal to chloride ratio may increase if the reaction time is too long. However, usually the replacement reactions are fast and keeping the

TABLE 2

ANALYTICAL RESULTS FOR POLYMER SUPPORTED METALLOCENE DICHLORIDE

ATTACHED SPECIES $-(C_5H_4)(C_5H_5)MCl_2$	CONCENTRATION (mmol/g· beads) METAL	CONCENTRATION (mmol/g· beads) CHLORIDE	RATIO EXPECTED	RATIO FOUND
M = Ti	0.1	0.21	2	2.1
Zr	0.19	0.45	2	2.4
Hf	0.11	0.26	2	2.3
V	0.048	0.109	2	2.3
Nb	0.11	0.22	2	2.0
Ta	0.4	0.92	2	2.3
Mo	0.1	0.24	2	2.4
W	0.12	0.23	2	1.9



REACTION SCHEME 2

reaction times less than 2 hours lead to the desired products. ESR spectral data of attached vanadocene and niobocene dichloride were identical with those reported for nonattached species [7].

EXPERIMENTAL

General comments

Oxygen and moisture were excluded from the reaction mixtures by thoroughly drying the glassware and reagents, and by manipulating the reagents under dry argon or in vacuo in Schlenk-type apparatus.

Deuterum oxide was purchased from the Mallinckrodt Chemical Works. Benzyl chloride was obtained from J. T. Baker Chemical Co. Thallium(I) sulfate and the metal chlorides ($TiCl_4$, $ZrCl_4$, $HfCl_4$, VCl_4, VCl_3, $NbCl_5$, $TaCl_5$, $MoCl_5$ and WCl_6) were purchased from Alfa Products (Ventron Corp.).

Vanadocene, vanadocene monochloride [6] and the metallocene dichlorides of Ti, Zr, Hf, V, Nb, Ta, Mo and W were prepared as previously reported [7-12], as were C_5D_6 [13], $C_6H_5CH_2C_5H_5$ [14], and their lithium (or sodium) salts. $(C_5H_5)_2MoI_2$ and TlC_5D_5 were also prepared by known methods [2]. The beads contained 0.7 - 0.9 mmol C_5H_5/g.

PMR spectra were obtained by using a Varian T-60 NMR spectrometer, and by using TMS as a reference. The mass spectra were obtained by use of a Perkin Elmer model RMU-6 mass spectrometer.

The metal and chloride analysis of the polymer-attached complexes was performed as described previously [4]. Titanium, hafnium, vanadium, niobium, tantalum, molybdenum and tungsten were determined by decomposition 0.5 g of the polymer with three drops of concentrated H_2SO_4 and heating over a very low flame, and then by ignition of the metal containing polymer at 900° (600° for Mo and W) for 12 hr. The residues were weighed as the oxides. Metal complexed chloride was removed by digestion of the polymer samples in 2 N KOH solution at 100°C for 12 hr. Chloride was determined by the Volhard method following acidification of the aqueous supernant liquid.

Preparation of $(C_5H_5)_2(C_5D_5)_2M$ (M = Ti, Zr, Hf and V) and their reactions with gaseous HCl

The $(C_5H_5)_2MCl_2$ (0.01 mol) was mixed with the benzene suspension of NaC_5D_5 (0.02 mol). The reaction mixture was stirred for 15 min. The filtrate obtained after separation of the sodium chloride was evaporated to dryness. This residue of $(C_5H_5)_2(C_5D_5)_2M$ was dissolved in toluene, the flask containing the solution partially evacuated and was refilled with gaseous HCl. After 30 min stirring, the solvent was removed under reduced pressure, and the products, $(C_5H_5)_{2-n}(C_5D_5)_nMCl_2$, were purified by vacuum sublimation (145°/0.01 torr).

Preparation of $(C_5H_5)_2(C_5D_5)V$

$(C_5H_5)_2VCl$ (0.0034 mol) was mixed with 60 ml of THF at 0°, and 11.5 ml of NaC_5D_5 (ml = 0.39 mmol) in THF and stirred for 15 min. The solvent was removed *in vacuo* and then 100 ml of cold ether (0°) was added. The mixture was stirred for 15 min., filtered and concentrated to 40 ml. On slow cooling to -78°, $(C_5H_5)_2(C_5D_5)V$ separated as black crystals. When the compound was heated to 75°, *in vacuo*, the mixture of $(C_5H_5)_{2-n}(C_5D_5)_nV$ species sublimed.

Cyclopentadiene ring exchange between vanadocene and NaC_5D_5

$(C_5H_5)_2V$ in THF was treated with NaC_5D_5 in large excess for 15 min. and for 4 days with similar results. The reaction mixture was evaporated to dryness and blue crystals of $(C_5H_5)_2V$, $(C_5H_5)(C_5D_5)V$, and $(C_5D_5)_2V$ were isolated upon sublimation (70°/0.01 torr).

Preparation of $(C_5H_5)_{4-n}(C_5D_5)_nM$ (M = Nb and Ta) and their reactions with gaseous HCl

About 1 g of $(C_5H_5)_2MCl_2$ was treated with an excess of NaC_5D_5 in THF. The reaction mixtures, which became red in four hours, were stirred an additional 12 hr., the solvent was removed at reduced pressure and the residue evaporated to dryness. Dry ether was added and the mixture stirred for an additional hour. The red filtrate of $(C_5H_5)_{4-n}(C_5D_5)_nM$ was separated from the salt residue, the flask was partially evacuated and refilled with gaseous HCl, after which the mixture immediately became dark colored. Two hours later, the supernatant, clear, ethereal solut was decanted, and the residue was evaporated to dryness. The $(C_5H_5)_{2-n}(C_5D_5)_nMCl_2$ was sublimed at 280°/0.01 torr.

Preparation of $(C_5H_5)_2(C_5D_5)_2M$ (M = Mo and W) and their reactions with gaseous HCl

The $(C_5H_5)_2MoI_2$ (or $(C_5D_5)_2MoI_2$) (0.01 mol) was mixed with TlC_5D_5 (or TlC_5H_5) (0.02 mol) in THF. After 12 hr, a yellow precipitate of thallium(I) iodide had formed and the color of the solution changed from green to red. The resulting violet solution, which formed after additional 60 hr, was reduced to dryness in a vacuum and the dry residu extracted with 200 ml of toluene. The red filtrate of $(C_5H_5)_2(C_5D_5)_2M$ was separated and the reaction with HCl carried out as above. The gre residues of $(C_5H_5)_{2-n}(C_5D_5)_nMoCl_2$ were filtrated and dried *in vacuo*.

Preparation of $(C_6H_5CH_2C_5H_4)(C_5H_5)_2MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo and W) and their reactions with gaseous HCl

About 1 g of $(C_5H_5)_2MCl_2$ was suspended in toluene, and then a stoichiometric amount of sodium (or lithium) benzylcyclopentadienide w added. The reaction times varied: 30 min for the Ti, Zr and Hf compou 6 hr for the Nb and Ta compounds; 4 days for the Mo and W compounds. The filtrate was separated from the residue, and treated with gaseous HCl. The mixtures of $(C_5H_5)_{2-n}(C_6H_5CH_2C_5H_5)_nMCl_2$ (M = Mo and W) were precipitated and were separated and dried *in vacuo*, while those of otl (M = Ti, Zr, Hf, Nb and Ta) were simply dried *in vacuo* and purified b vacuum sublimation.

Preparation of anion beads

Two g of polymer-attached cyclopentadiene beads in THF were treat with an excess of CH_3Li in ether for 3 days at room temperature. The unconverted CH_3Li was removed by thorough washing with THF (5 x 40 ml) to give the $C_5H_5^-$ beads. For the attachment of the Ti and Hf complexe the lithium salt of the anion beads was kept in THF, but for all the others, the dry beads were stored in an argon filled dry box.

Preparation of polymer-supported metallocene dichlorides of Ti and Hf

A toluene solution of the metallocene dichloride was added to the anion beads (THF suspension), the mixture was stirred for 2 days, and the beads then were treated with HCl. The color of the beads immediately changed from dark brown to red for the Ti species and the yellow to cream for the Hf species. After being stirred for 5 hr, the solvent was removed and the beads were washed with $CHCl_3$ and THF until the washings were freed of metallocene dichloride and lithium chloride. The beads then were dried *in vacuo*.

Preparation of polymer-supported niobocene, tantalocene, molybdenocene and tungstenocene dichlorides

An excess of the metallocene dichlorides of niobium, tantalum, molybdenum and tungsten was added to the anion beads in a dry-box, and then 100 ml of THF was added to the mixture. The flask was removed from the dry-box and the mixture was stirred for 6 days. The flask then was partially evacuated and refilled with HCl as above. The color of the beads changed from red to brown-black in the case of the niobium and tantalum compounds and to green in the case of the molybdenum and tungsten species. After the washing procedures described above, the beads were dried *in vacuo*. (The Ta containing beads are air sensitive, the others are not.)

Preparation of polymer-supported vanadocene dichloride

An excess of vanadocene was mixed with the "anion beads" in 100 ml of THF, for 6 days under nitrogen. The atmosphere over the beads then was replaced with HCl gas as above. The color of the beads changed from dark to light blue within 10 min, as expected for the attached vanadocene monochloride. Five hours later, the whole mixture was exposed to the air and the attached species was oxidized to green vanadocene dichloride beads. The solution was decanted, and the beads were washed with THF as above, and dried *in vacuo*.

ACKNOWLEDGMENT

The authors acknowledge the support of the National Science Foundation under grant GP-38312, and the Petroleum Research Fund under grant 8512-AC3. Mass spectra were most ably obtained by Mrs. Lorraine Guile.

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