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Methyl–iodine exchange in (η^5-iodocyclopentadienyl)metallo methyl derivatives of iron(II), tungsten(II), and molybdenum(II) in the presence of palladium

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Abstract

A new and unexpected interchange reaction has been discovered during an attempt to make fulvalene-linked heterobimetallic complexes by palladium-catalyzed coupling between η^5-(iodo)cyclopentadienyl and η^5-(trimethyltin)cyclopentadienyl metal complexes. In the presence of Pd the (η^5-iodocyclopentadienyl)metallo methyl derivatives of general formula (η^5-IC_5H_4)M(CO)$_n$$CH_3$ (M = Fe, $n = 2$; M = W, $n = 3$; M = Mo, $n = 3$) undergo methyl–iodine exchange, to give the corresponding (η^5-$CH_3C_5H_4$)M(CO)$_n$I complexes. The palladium(0) catalysis of the reaction apparently involves an intramolecular transmetallation.

Introduction

In line with the common use of palladium-catalyzed coupling for the preparation of biscyclopentadienyl-framed polymetallic dimers [1] we attempted the direct coupling of two appropriately functionalized cyclopentadienyl metal complexes in the expectation of obtaining the corresponding fulvalene heterobimetallic species. We found that in presence of palladium catalyst the η^5-iodocyclopentadienyl derivatives (η^5-IC_5H_4)M(CO)$_n$$CH_3$ [**1**, M = Fe, $n = 2$; **2**, M = W, $n = 3$; **3**, M = Mo, $n = 3$] did not couple with the η^5-(trimethyltin)cyclopentadienyl complex [η^5-$(CH_3)_3SnC_5H_4$]$TiCl_2$(η^5-C_5H_5) (**4**) to give the heterobimetallic complex **5**, and an unusual rearrangement of the η^5-iodocyclopentadienyl derivatives **1–3** took place (Scheme 1).

The first report [2] of a transfer of an organic group from a metal to a cyclopentadienyl ring involved the thermally induced shift of an ethyl group in (η^5-C_5H_5)Mo(CO)$_3$$CH_2CH_3$ with accompanying dimerization to give [(η^5-$CH_3CH_2C_5H_4$)Mo(CO)$_3$]$_2$. Later the migration of a phenyl was reported, from a benzoyl group, attached to a Mo center, to a Cp ring, again with accompanying formation of dimeric species. A radical process was suggested to account for this

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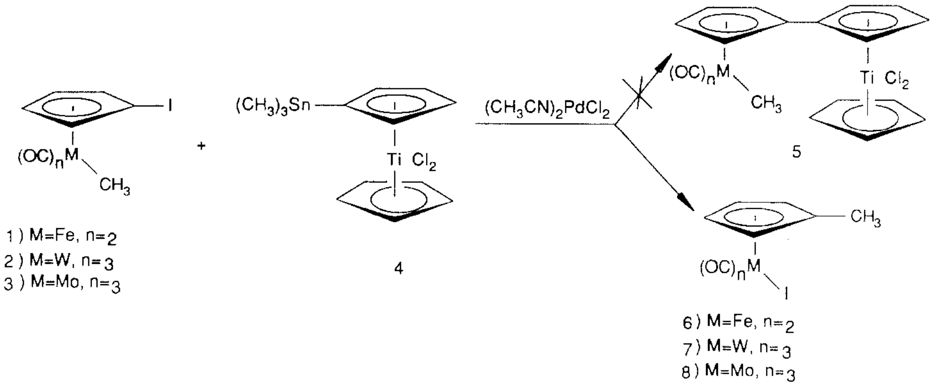


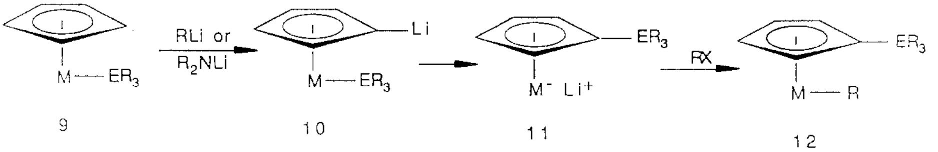
Scheme 1

transformation [3]. Following these early reports several authors have reported a number of metal-to-Cp migrations in cyclopentadienyl metal complexes, after deprotonation of the Cp ring by a strong base (LDA or BuLi) (Scheme 2).

However, in all these cases the groups moving from the metal to the Cp are substituted organometallic groups such as $-ER_3$ (E = Ge [4], Sn [4], Pb [4], Si [5,6]; R = Me, Ph). In some cases migration of hydrogen [6] (–H) or a formyl group [7] (–CHO) has been observed. The metals involved in these transformations were Fe, Mo, W, and Re. Under these conditions an attempt to bring about migration of an alkyl group from the metal to the Cp by deprotonation of the ring did not lead to the expected product [5,6]. Other examples of metal-to-Cp transfer have been reported in the case of η^5-coordinated fluorenyl [8] and indenyl [9] derivatives of chromium which also bear carbonyls and a methyl group as ancillary ligands. Such complexes undergo η^5–η^6 thermal rearrangement with transfer of the methyl from the metal atom to the five-membered ring and shift of the metal group from the five- to the six-membered ring.

A metal-to-ring transfer of an ethyl group has been observed for compounds such as $(\eta^5\text{-}C_5H_5)_2M(C_2H_5)Cl$ (M = Mo, W) upon treatment with phosphines or carbon monoxide. However, in this case the transfer of the ethyl group is followed by loss of the Cp ring that receives the alkyl group [10]. More recently, a metal-to-Cp transfer of a σ^1-bonded cyclopentadienyl group induced by oxidation has been reported for a titanium complex, and used for synthetic purposes in the preparation of bimetallic complexes [11].

Although these reports show that it is fairly easy to induce migration of groups from a metal to the η^5-coordinated Cp ring, to our knowledge the shift of an organic group and a halogen with simultaneous interchange of their positions has not



Scheme 2

previously been observed. Moreover, in the migrations mentioned above, severe conditions were required to induce the rearrangement, such as use of strong bases or high temperatures, whereas in the reactions we observed, the process takes place smoothly under mild conditions. Interestingly, the process we observed has been predicted by theoretical calculations to be forbidden. Thus, following a study on orbital symmetry, it was stated that "the prediction about the reason why the methyl ligand *does not migrate* has been proved correct by analysis of the molecular orbital diagrams..." [12].

Results and discussion

Although iodo-aromatics and trimethyltin-derivatives are among the best choices as coupling partners in carbon–carbon bond formation catalyzed by palladium, under the conditions that generally lead to high yield of coupled products [13], the iron, tungsten, and molybdenum complexes **1**–**3** undergo methyl–iodine scrambling upon treatment with the coupling partner in presence of 5% bis(acetonitrile)(dichloro)palladium(II) in *N*,*N*-dimethylformamide (DMF). The yields of the isolated product in which the iodine and the methyl exchanged their position ranged from 18 to 53% depending on the substrate and the reaction conditions. The rearranged products **6**–**8** were identified by comparison with authentic samples prepared by published procedures [14]. The NMR spectra of each of the three compounds **6**, **7** and **8** are markedly different from those of their precursors **1**, **2** and **3**, respectively, in both the ^1H and ^{13}C spectra. The proton resonances of the methyl group move from 0.29, 0.51, and 0.47 ppm to 2.16, 2.37, and 2.28 ppm, respectively. For the same group, the carbon resonances move from −17.30, −29.58, and −16.00 ppm to 13.88, 22.98, and 14.88 ppm, respectively. Very diagnostic for the rearrangement are the mass spectra of products **6**–**8**. All three products show the parent ion and the ions from its characteristic fragmentation, and the base peak is that of the fulvene ion at *m/e* 78.

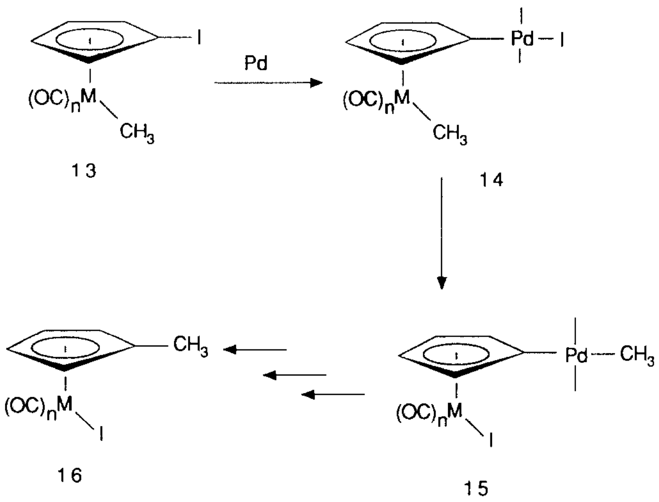
The large differences between the ^1H NMR resonances of the rearranged products and those of their precursors enabled us to use NMR spectroscopy to monitor the progress of the reaction under various conditions of solvent, catalyst and reducing agent for the Pd^{II} to Pd^0 reduction.

A systematic study of the reaction was undertaken in order to account for the unexpected observed rearrangement. Firstly, the coupling partners were stirred together in DMF without a catalyst, but no rearrangement was noticed. Similarly the η^5-iodocyclopentadienyl derivatives **1**–**3** remained unchanged when their solutions in DMF were stirred in presence of $(CH_3CN)PdCl_2$ only. The absence of rearrangement in these latter cases shows that Pd^0 is the only active species that can promote the exchange. In fact, complexes **1**–**3** gave the rearranged products **6**–**8** when their solutions were stirred in presence of a catalytic amount of $(CH_3CN)PdCl_2$ and two equivalents (relative to the Pd) of $(CH_3)_4Sn$. The role of the tin compound is to bring about the *in situ* reduction [15,16] of Pd^{II} to Pd^0. Complexes **1**–**3** also undergo rearrangement in the presence of tetrabutyltin as the reducing agent, although to a lesser extent. This shows that the methyl group transferred to the cyclopentadienyl ring comes from the metal and not from the tin reagent. The rate and extent of the conversion are strongly dependent on solvent and on the identity of the substrate. The iron complex **1** in DMF at room temperature gives 22% of **6** in

12 h, whereas under the same conditions in chloroform the conversion is complete. The effects of these two solvents are completely reversed for the tungsten complex **2**. In DMF the reaction to give **7** is complete in 2 h, while in $CHCl_3$ it is only 28% complete after 20 h. When longer reaction times were used in order to increase the extent of conversion, loss of material by decomposition was observed in both cases.

These experiments suggested that use of a Pd^0 catalyst might avoid the addition of the reducing agent, and so reactions were carried out with tetrakis(triphenylphosphine)palladium(0), $Pd[P(C_6H_5)_3]_4$. Monitoring of the reaction by ^1H NMR spectroscopy revealed that although in some cases the substrate was consumed, the reaction was more complex than under the conditions used previously. At 25 °C the iron complex $(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_3$ in $CDCl_3$ in the presence of 5% of $Pd[P(C_6H_5)_3]_4$ reacts very slowly; after 2 h the only change observable in the spectrum is the appearance of two new signals, at 5.25 and 5.50 ppm, for the Cp protons, but relative to the signals of the starting material at 4.69 and 4.87 ppm their intensity is only 3–6%. No new signals appear for the methyl group. Reaction at 40 °C gives the same result. The tungsten complex $(\eta^5\text{-}C_5H_4I)W(CO)_3CH_3$ does not react at all in $CDCl_3$ at 25 °C. In the reaction in DMF-d_7 at 25 °C most of the starting material remains unchanged, and alongside the Cp resonances at 5.49 and 5.28 ppm two new small signals appear at 6.52 and 6.39 ppm. No formation of the usual product is observed. In C_6D_6 at 50 °C the substrate is completely consumed within 20 minutes; the original Cp resonances at 4.64 and 4.20 ppm disappear and new resonances appear at 5.07 and 4.73 ppm. No signals for the methyl group are detectable in the spectrum. The new species formed does not change to the rearranged product, and within one hour complexes have completely decomposed.

The detailed mechanism of the interchange has not yet been elucidated. A reasonable hypothesis is that after the oxidative addition of the cyclopentadienyl iodide to the Pd, the tin complex **4** is for some reason unable to transmetallate the cyclopentadienyl group (bearing also the metal and its ancillary ligands) on the Pd-adduct. Therefore, the only possible pathway open to the Pd-adduct is an



Scheme 3

intramolecular transmetallation in which the methyl is transferred from the metal to the palladium and the iodine migrates from the Pd to the metal. Subsequently this new adduct undergoes the usual reactions [13], *trans* to *cis* isomerization and reductive elimination, to give the final product (Scheme 3).

This proposed mechanism accounts also for the NMR spectral changes observed in the case of the $Pd[P(C_6H_5)_3]_4$ catalyst. In this case the new Cp resonances observed may be those of the complex obtained by insertion of Pd between the Cp and the iodine (structure **14** in Scheme 3). The presence of the bulky triphenylphosphine ligands attached to Pd prevents the shift of the methyl and the formation of the rearranged product, and so decomposition occurs.

Further studies aimed at a detailed elucidation of the mechanism of the reaction and its use for synthetic purposes are in progress.

Experimental section

All reactions and manipulations were carried out under argon (deoxygenated with copper-based BTS catalyst (Fluka) and dried with 4 Å molecular sieves) by standard procedures [17]. Chromatographic separations were effected on columns packed with silica gel (70–230 mesh; Merck). Infrared (IR) spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode. ^1H NMR spectra and broad-band proton-decoupled ^{13}C NMR spectra were recorded in the Fourier transform mode on a Bruker WP-270 spectrometer, operating at 270 MHz for (^1H NMR) and 67.5 MHz (^{13}C NMR). The NMR chemical shifts are reported in ppm relative to Me_4Si and were determined by reference to the peak from the ^1H impurity in the solvent ($CDCl_3$) at 7.24 ppm. The ^{13}C spectral chemical shifts are reported to the ^{13}C triplet ($CDCl_3$) at 77.00 ppm. Low resolution mass spectra (LRMS) were obtained on a VG70 instrument.

N,N-Dimethylformamide (DMF) was distilled under vacuum from CaH_2 and stored over activated molecular sieves (4 Å). Cyclopentadienyl complexes and reagents were prepared by known methods: $(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_3$ [1a], $(\eta^5\text{-}C_5H_4I)W(CO)_3CH_3$ [1a], $(\eta^5\text{-}C_5H_4I)Mo(CO)_3CH_3$ [1a], $(CH_3CN)_2PdCl_2$ [18]. $[\eta^5\text{-}(CH_3)_3SnC_5H_4]Ti(\eta^5\text{-}C_5H_5)Cl_2$ was prepared by reaction of $[\eta^5\text{-}(CH_3)_3SnC_5H_4]TiCl_3$ [19] and $(\eta^5\text{-}C_5H_5)Tl$ [20]. Tetramethyltin, tetrabutyltin, and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich and used without purification

General procedure for the reaction of $(\eta^5\text{-}C_5H_4I)M(CO)_nCH_3$ *(1–3) with* $[\eta^5\text{-}(CH_3)_3SnC_5H_4]M'L_n$ *(4,5) in presence of* $(CH_3CN)_2PdCl_2$

To a Schlenk tube under argon were successively introduced the catalyst, the solvent, the iodocyclopentadienyl complex, and the trimethyltincyclopentadienyl complex. After overnight stirring at room temperature, the mixture was shaken with Et_2O/water and the organic layer was dried over anhydrous magnesium sulfate then filtered and evaporated. The residue was adsorbed on Celite and chromatographed as described below.

$(\eta^5\text{-}CH_3C_5H_4)Fe(Co)_2I$ *(6)*

$(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_3$ (**1**) (1.31 g, 4.12 mmol) was treated with $[\eta^5\text{-}(CH_3)_3SnC_5H_4]Ti(\eta^5\text{-}C_5H_5)Cl_2$ (**4**) (2.03 g, 4.94 mmol) in the presence of

$(CH_3CN)_2PdCl_2$ (0.05 g, 0.20 mmol) in 50 ml of DMF. After mixing of the reactants the solution slowly darkened from red to brown. After the usual work-up, column chromatography (silica gel, benzene/EtO = 8/2), gave the rearranged product (0.24 g, 18%) and unchanged $(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_3$ (0.52 g, 40%). The spectroscopic data for the product were consistent with those previously reported [14a].

IR (CCl_4, cm^{-1}) 2035 vs, 1998 vs. ^1H NMR ($CDCl_3$, δ) 4.88 (t, 2H, *J* 1.56 Hz), 4.81 (t, 2H, *J* 1.56 Hz), 2.16 (3, s, 3H). ^{13}C NMR ($CDCl_3$, δ) 213.31, 102.43, 84.76, 82.50, 13.88. LRMS, 318 (M^+), 290 ($M^+ - CO$), 262 ($M^+ - 2CO$), 134 ($C_6H_6Fe^+$), 78 ($C_6H_6^+$).

$(\eta^5\text{-}C_5H_4I)W(CO)_3CH_3$ (7)

In the way described above for **6**, $(\eta^5\text{-}C_5H_4I)W(CO)_3CH_3$ (**2**) (0.63 g, 1.32 mmol) was treated with $[\eta^5\text{-}(CH_3)_3SnC_5H_4]Ti(\eta^5\text{-}C_5H_5)Cl_2$ (**4**) (0.65 g, 1.58 mmol) in the presence of $(CH_3CN)_2PdCl_2$ (0.017 g, 0.06 mmol) in 30 ml of DMF. The solution turned from red to brown within minutes. Chromatographic separation (silica gel, benzene) gave first the unreacted $(\eta^5\text{-}C_5H_4I)W(CO)_3CH_3$ (0.32 g, 51%) and then the rearranged product (0.29 g, 46%).

IR (CCl_4, cm^{-1}) 2028 vs, 1958 vs. ^1H NMR ($CDCl_3$, δ) 5.57 (t, 2H, *J* 1.96 Hz), 5.46 (t, 2H, *J* 1.96 Hz), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, δ) 207.76, 101.37, 93.92, 89.58, 22.98. LRMS, 474 (M^+), 446 ($M^+ - CO$), 418 ($M^+ - 2CO$), 390 ($M^+ - 3CO$), 78 ($C_6H_6^+$). Anal. Found: C, 22.88; H, 1.45. $C_9H_7O_3IW$ calc.: C, 22,81; H, 1.48%.

$(\eta^5\text{-}C_5H_4I)Mo(CO)_3CH_3$ (8)

In the way described above for **6**, $(\eta^5\text{-}C_5H_4I)Mo(CO)_3CH_3$ (**3**) (0.56 g, 1.45 mmol) was treated with $[\eta^5\text{-}(CH_3)_3SnC_5H_4]Ti(\eta^5\text{-}C_5H_5)Cl_2$ (**4**) (0.72 g, 1.74 mmol) in the presence of $(CH_3CN)_2PdCl_2$ (0.02 g, 0.07 mmol) in 20 ml of DMF. Within 30 minutes the solution had turned from red to deep brown. Chromatography (silica gel, benzene) afforded first unreacted $(\eta^5\text{-}C_5H_4I)Mo(CO)_3CH_3$ (0.05 g, 9%) and then the rearranged product (0.15 g, 53%).

IR (CCl_4, cm^{-1}) 2035 vs, 1972 vs. ^1H NMR ($CDCl_3$, δ) 5.46 (t, 2H, *J* 2.29 Hz), 5.35 (t, 2H, *J* 2.29 Hz), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, δ) 220.82, 114.78, 95.33, 90.95, 14.88. LRMS, 386 (M^+), 358 ($M^+ - CO$), 330 ($M^+ - 2CO$), 302 ($M^+ - 3CO$), 78 ($C_6H_6^+$). Anal. Found: C, 28.07; H, 1.84. $C_9H_7O_3IMo$ calc.: C, 28.00; H, 1.82%.

General procedure for NMR-tube reactions

A 5 ml NMR tube was charged with samples of substrates **1**–**3** ($5\text{–}7 \times 10^{-2}$ mmol) and $(CH_3CN)_2PdCl_2$ or $Pd(PPh_3)_4$ (5% by mole with respect to the substrate) and sealed with a rubber septum. The solvent ($CDCl_3$ or DMF-d_7) (0.2–0.5 ml) was injected into the tube from a syringe. When a Pd^{II} catalyst was used, pure tetramethyltin or tetrabutyltin (10% by mole with respect to the substrate) was injected into the tube through the septum with a syringe. Recording of the spectra started immediately and continued until no further significant change occurred. The extent of the conversion of the starting material into the rearranged product was determined by integration of the relative intensities of the corresponding signals.

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