Journal of Organometallic Chemistry, 368 (1989) 57–65
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09628

Studies on the reactivity of the halo-hydride complexes $[M(\eta^5\text{-}C_5H_5)_2HX]$ ($M = Mo, W; X = Cl, Br, I$)

C.G. De Azevedo, A.R. Dias, A.M. Martins and C.C. Romão

Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)

(Received August 8th, 1988)

Abstract

A convenient preparation of the cations $[Mo(\eta^5\text{-}C_5H_5)_2HL]^+$ and $[Mo(\eta^5\text{-}C_5H_5)_2H(L\text{–}L)]^+$ from $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ (**1**), L and $TlPF_6(BF_4)$ is described for $L = CO$, C_2H_4, PMe_2Ph, PEt_2Ph, PPh_3, NH_3, NCMe and $L\text{–}L = Ph_2PCH_2PPh_2$, (dppm), $H_2NCH_2CH_2NH_2$ (en). Complex **1** and butadiene give $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}CH_3C_3H_4)]BF_4$. The chloro and bromo analogues of **1** are less reactive, and the W analogue of **1** does not react under the conditions used for **1**. Reaction of **1** with $Ph_2PCH_2CH_2PPh_2$ (dppe) gives the cation $[Mo(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)dppe]^+$ (**18**) in the presence or absence of $TlPF_6$. The deuterido analogue of **1**, **1d**, gives **18d** having the deuterium on the *exo* face of the C_5H_5D ring.

Introduction

The bent metallocene dihydrides $[MCp_2H_2]$ * and dihalides $[MCp_2X_2]$ play a central role in the organometallic chemistry of Mo and W. The preparation [1] of the halohydrides $[MCp_2HX]$ ($M = Mo, W; X = Cl, Br, I$) allowed the study of the chemistry of these mixed complexes. Initially it might have been expected that halide substitution to give $[MCp_2HL]^+$ complexes (L = 2-electron donor) would be a dominant reaction for $[MCp_2HX]$ complexes in view of the high thermal and kinetic stability of such cations [2]. However, by analogy with the known ethyl

$$MCp_2EtCl + PR_3 \rightarrow [MCp(\eta^4\text{-}C_5H_5Et)ClPR_3]$$

migration [3] metal-to-ring hydride migration was also a possibility, and would open a path between di- and mono-cyclopentadienyl-molybdenum chemistry.

---

* $Cp = \eta^5\text{-}C_5H_5$ throughout this paper.

Chemical studies

All the new compounds described are identified by spectroscopy (^{1}H NMR and IR) and analysis. The relevant data are shown in Tables 1 and 2, respectively.

Treatment of [$MoCp_2HI$] (**1**) with CO (1 atm; 50 °C) in acetone gave the known cation [$MoCp_2H(CO)]^+$ (**2**) which was isolated as the PF_6^- salt after work-up with aqueous NH_4PF_6. The yield (80%) is not affected by the presence of $TlPF_6$ in the reaction mixture. However, in toluene, **1** reacted with CO (1 atm) only at reflux temperature, and the only tractable product, isolated in 10% yield, was [$MoCpI(CO)_3$], identified from its IR spectrum [4].

Table 1

Spectroscopic data

Compound	^{1}H NMR δ (multiplicity, area, assignment) [a]	IR (cm^{-1})
[$Mo(Cp)_2H(NH_3)$]I (**3**)	5.21(S,10,C_5H_5), −9.30(S,1,Mo−H)	Mo−H 1825
[$Mo(Cp)_2H(en)$]I (**4**)	5.23(S,10,C_5H_5), 3.25(S(br),2,Mo−NH_2), 2.65(S(br),2,CH_2NH_2), 2.31(T,2,CH_2CH_2), 2.03(T,2,CH_2CH_2), −9.48(S,1,Mo−H)	Mo−H 1830
[$Mo(Cp)_2H(NCMe)$]BF_4 (**7**)	5.25(S,10,C_5H_5), −9.45(S,1,Mo−H) [b]	
[$Mo(Cp)_2H(PMe_2Ph)$]I (**10**)	~ 7.6(M,5,PC_6H_5), 5.07(D[$J(^{31}P–H)$ 2.9 Hz), 10(C_5H_5), 1.8(D[$J(^{31}P–H)$ 9 Hz],6PCH_3), −8.93(D[$J(^{31}P–H)$ 36 Hz]),1,Mo-H)	Mo−H 1852
[$Mo(Cp)_2I(PEt_2Ph)$][PF_6] (**15**)	~ 7.8(M,5,PC_6H_5), 6.62(D[$J(^{31}P–H)$ 1.7 Hz],10,C_5H_5), 2.76(M,4PCH_2CH_3), 1.16(M,6,PCH_2CH_3)	
[$Mo(Cp)_2H(PEt_2Ph)$][PF_6] (**16**)	~ 7.7(M,5,PC_6H_5), 5.22(D[$J(^{31}P–H)$ 2.4 Hz],10,C_5H_5), ~ 2.2(M, ~ 4,PCH_2CH_3), 1.04(M,6,PCH_2CH_3), −8.5(D[$J(^{31}P–H)$ 33 Hz],1,Mo−H)	Mo−H 1840
([$Mo(Cp)_2H]_2$dppe)[$PF_6]_2$ (**21**)	~ 7.6(M,20,PC_6H_5), 5.1(D[$J(^{31}P–H)$ 1.9 Hz],20,C_5H_5) 2.54(S,4,CH_2CH_2), −8.54(D[$J(^{31}P–H)$ 36 Hz],2,Mo−H)	Mo−H 1840

[a] δ relative to enternal TMS; Me_2CO-d_6 as solvent; S, singlet; D, doublet; T, triplet; M, multiplet, br = broad. [b] The resonance of the coordinated $NCCH_3$ is under the solvent multiplet at 1.93 ppm.

Table 2

Analytical data

Compound	Colour	Analysis (found (calc.)(%))		
		C	H	N
3	Orange	31.9 (32.4)	3.8 (3.8)	3.4 (3.8)
4	Orange	35.0 (34.8)	4.5 (4.6)	6.9 (6.8)
10	Yellow	43.6 (43.9)	5.0 (4.5)	–
15	Green	36.6 (36.2)	3.9 (3.8)	–
16	Yellow	44.9 (44.6)	5.0 (4.9)	–

In tetrahydrofuran (THF), complex **1** reacts quantitatively with NH_3 (1 atm; room temperature) within a few minutes. The orange cation, identified as $[MoCp_2H(NH_3)]^+$, was formed, and was isolated as its salts with I^- (**3**) and PF_6^- counter-ions. In toluene the yield is significantly lower. In pure ethylenediamine(en) **1** dissolves to give $[MoCp_2H(en)]I$ (**4**) in quantitative yield. In hot water **4** slowly reforms **1** ca. 50% of the latter being produced in 90 minutes. Solutions of **4** in wet acetone give the known dication $[MoCp_2(en)]^{2+}$ (**5**), identified as the I^- salt from its ^1H NMR and IR spectra [5]. In contrast, **3** is sufficiently stable in wet acetone to be recrystallized from this solvent.

A solution of **1** in acetonitrile turns orange. Upon addition of $TlBF_4$, TlI separated out immediately, but no solid product could be recovered from the bright orange filtrate after concentration and addition of diethyl ether. However, treatment of this solution with $CHBr_3$ gave the known $[MoCp_2Br(NCMe)]PF_6$ (**6**) [6,7]. This result suggests that $[MoCp_2H(NCMe)]^+$ (**7**) is formed by reaction between **1** and NCMe [7]. The ^1H NMR spectrum of **1** in d^3 NCMe, recorded ca. 5 min after dissolution, showed two singlets in the Cp region (5.27 and 5.05 ppm; relative integrals 2.0/1.0) and two singlets in the hydride region (−9.43 and −9.48 ppm; relative integrals 2/1). This integrals ratio remained constant at room temperature for 5 h. Addition of $TlBF_4$ to the solution gave a precipitate, TlI, and only one signal removed in each region (5.25 and −9.45 ppm). We interpret these observations in terms of a rapidly established equilibrium between **1** and its solvolysis product $[MoCp_2H(NCMe)]I$ (**7**). Removal of I^- with $TlBF_4$ completely shifts the equilibrium to the right, favouring the formation of **7** as the BF_4^- salt. Accordingly, the resonances of **1**, at slightly lower field from the corresponding resonances of the cation **7**, disappear.

When ethylene was bubbled through a solution of **1** in CH_2Cl_2 in the presence of $AgBF_4$ a colourless solution was formed and from this the known [8] off-white $[MoCp_2H(C_2H_4)]BF_4$ (**8**) was isolated in good yield. Reaction of **1** with butadiene, in the presence of $TlBF_4$ gave the known crotyl cation $[MoCp_2(\eta^3\text{-}C_3H_4CH_3)]BF_4$ (**9**) in moderate yield (65%) [9].

Treatment of **1** with an excess of PMe_2Ph in toluene gave a yellow precipitate. After work-up in aqueous NH_4PF_6 the complex was identified as $[MoCp_2H(PMe_2Ph)]PF_6$ (**10**). The similar reactions of $[MoCp_2HCl]$ (**11**) and $[MoCp_2HBr]$ (**12**) with PMe_2Ph and PPh_3 gave **10** and $[MoCp_2H(PPh_3)]PF_6$ (**13**) [2], respectively, whereas the W analogue of **1** does not react with PPh_3 under these conditions.

In order to detect in the reaction of **1** with PMe_2Ph, the possible intermediate $[MoCp(\eta^4\text{-}C_5H_6)XPR_3]$ (**14**), which would result from metal-to-ring hydrogen migration, the reaction was monitored by ^1H NMR spectroscopy in d^6-Me_2CO and in d^6-C_6H_6. In the former solvent at room temperature the reaction is slow. In the high-field region of the spectrum the initial hydride signal of **1** is cleanly replaced by the characteristic doublet of **10** ($J(^{31}PH)$ 36 Hz), and no other signal is observed in this region. Similarly, the initial Cp singlet is replaced by the expected doublet of the Cp in **10** resulting from coupling of the Cp hydrogens to one coordinated phosphine ($J(^{31}PH)$ 2.9 Hz). No peaks assignable to a C_5H_6 ligand can be seen. At 50 °C the reaction is complete within ca. 15 min in d^6-Me_2CO, but in d^6-C_6H_6 it is slower, requiring ca. 30 min for completion at 70 °C. A different course of reaction was observed for the reaction of **1** with PEt_2Ph in refluxing THF. A light brown precipitate was isolated, and after work-up with aqueous NH_4PF_6 this gave

$[MoCp_2I(PEt_2Ph)]PF_6$ (**15**) in good yield. However, the same reaction in refluxing acetone in the presence of $TlPF_6$ gave the expected $[MoCp_2H(PEt_2Ph)]PF_6$ (**16**), also in high yield. In accord with known patterns for halide substitution reactions, the diphosphine bis(diphenylphosphino)methane (dppm) reacts with **1**, in acetone, to give the known cation $[MoCp_2H(dppm)]^+$ (**17**) [10] in which the dppm acts as a monodentate ligand. Use of bis(diphenylphosphino)ethane (dppe) in place of under the same reaction conditions gave $[MoCp(\eta^4\text{-}C_5H_6)(dppe)]PF_6$ (**18**), isolated in 70–80% yields [10]. The reaction is not affected by the presence of $TlPF_6$.

Monitoring of the reaction by ^1H NMR at 50 °C, in d^6-Me_2CO, gave no evidence for the formation of the possible intermediate, or side-product, $[MoCp_2H(dppe)]^+$ (**19**). The products are **18** and a small amount of the dication $[MoCp_2(dppe)]^{2+}$ (**20**) [10] which is always formed in the reaction of **1** with dppe in small amounts (ca. 5–10%). In dry toluene the reaction of **1** or its chloride analogue **11** with dppe gives $[(MoCp_2H)_2dppe][PF_6]_2$ (**21**). Since the blue complex $[MoCp_2Br(dppm)]PF_6$ (**22**), readily prepared from **17** and $CHBr_3$, reacts with $Na[BH_4]$ to give **17**, the preparation of **19** was attempted in the same way through reaction of $[MoCp_2Br(dppe)]PF_6$ (**23**) [2] with sodium borohydride. To our surprise **18** was the only product formed, and was isolated in high yield. On the other hand **17** remains unchanged after 4 h reflux in NCMe.

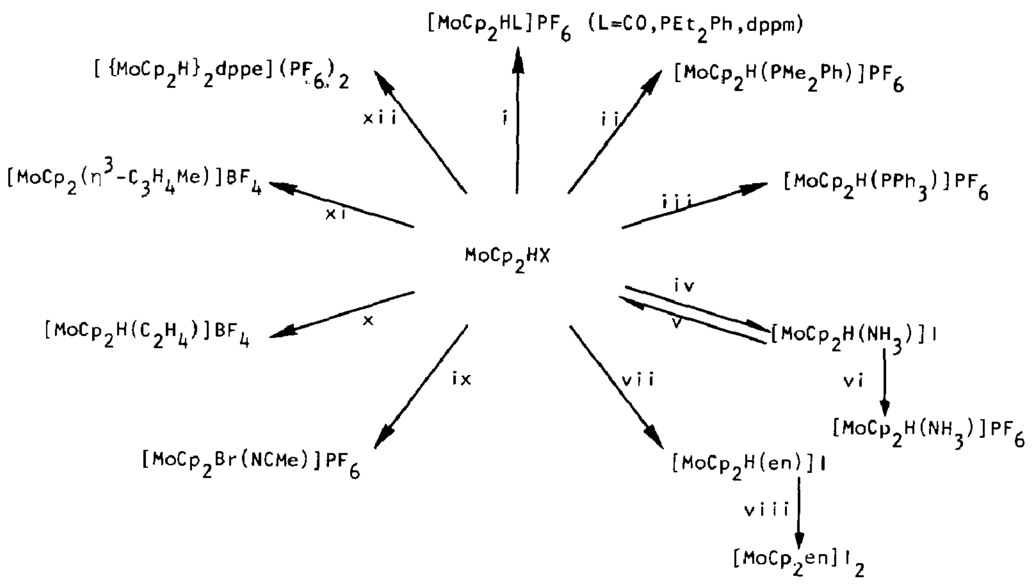
When $[MoCp_2DI]$ (**1d**) obtained by reaction of $[MoCp_2D_2]$ with 1 molar equivalent of MeI, is treated with dppe in carefully dried d^6-Me_2CO, the product, **18d**, is shown by IR and ^1H NMR to have the deuterium at the *exo* position of the methylene group of the C_5H_5D ligand; the **18d** obtained gives spectra identical with those of the compounds from the reaction of $[MoCp_2(dppe)]^{2+}$ (**20**) with $Na[BD_4]$ [10].

Discussion

From the results described above it is clear that the halohydrides $[MoCp_2HX]$ react with neutral 2-electron donors, L, by replacement of halide as shown in Scheme 1.

The presence of $TlPF_6$ as halide abstractor in some cases leads to higher yields and cleaner reactions. The stronger W–X bond may be responsible for the lower reactivity of $[WCp_2HX]$ complexes than of their Mo analogues. The type of reaction described seems to provide the easiest and most general route to hydride derivatives of the general formula $[MoCp_2HL]^+$ many of which are already known [2]. However, three observations fall outside this general pattern (see Scheme 2) and deserve further comment.

Reaction 1 (Scheme 2) and the formation of $[MoCp_2(dppe)]^{2+}$ in reaction 3 represent overall hydride replacement. The decomposition of $[MoCp_2H(en)]^+$ in wet acetone to give $[MoCp_2(en)]^{2+}$ and the reported preparation of $[MoCp_2(dppe)]^{2+}$ from $[MoCp_2H_3]^+$ and dppe in cold acetone [10] are other examples of the same type of reaction. In no case has the fate of the hydride been established. It is plausible that acetone reduction is involved, but the origin and scope of the reaction remains unclear; the contrasts with the absence of hydridic character in the parent $[MoCp_2H_2]$ is noteworthy.



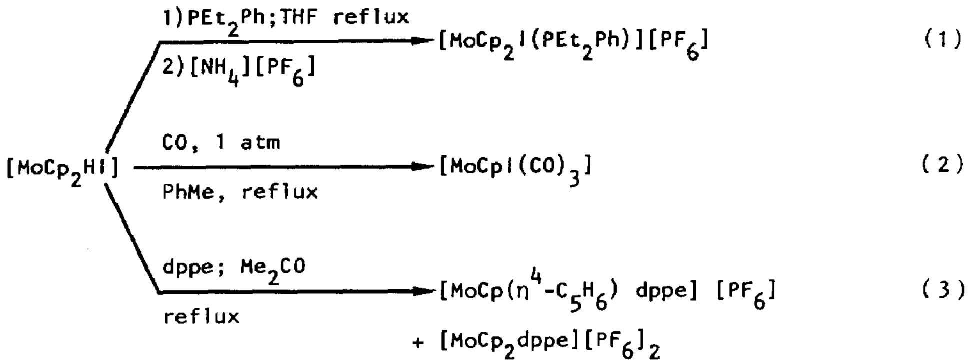
Scheme 1. i: $X = I$; $Me_2CO/TlPF_6$, reflux, CO (1 atm), PEt_2Ph and dppm; ii: $X = Cl$, I; $PhCH_3$ at reflux then aq. NH_4PF_6; iii: $X = Br$; $PhCH_3$ at reflux then aq. NH_4PF_6; iv: $X = I$; THF, r.t., 5 min. NH_3 1 atm; v: H_2O reflux 90 min; vi: aq. NH_4PF_6; vii: $X = I$; neat en, r.t., 5 min; viii: in Me_2CO/H_2O, reflux 10 min, KI; ix: $X = I$; NCMe, $TlPF_6$, r.t., 24 h then $CHBr_3$; x: $X = I$; $AgBF_4$ and C_2H_4 in CH_2Cl_2, r.t. 4 h; xi: $X = I$; $TlBF_4$ and C_4H_6 in CH_2Cl_2, r.t. 4 h; xii: $X = Cl$, I; PhMe, reflux, 24 h, aq. NH_4PF_6 10%.

Reaction 2 is similar to the known carbonylations of $[MoCp_2(CH_3)_2]$ and $[MoCp_2H_2]$ [3,11], e.g.

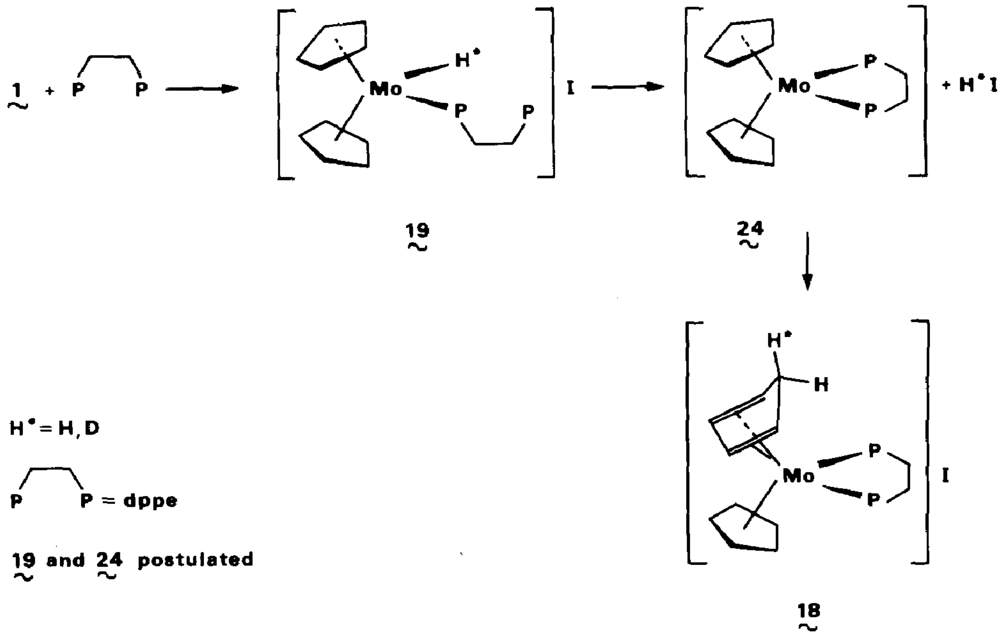
$$[MoCp_2(CH_3)_2] + CO \rightarrow Mo(CO)_6 + C_5H_5CH_3$$

$$[MoCp_2H_2] + CO \rightarrow [MoCp(C_5H_7)(CO)_2]$$

For the packing a mechanism involving intramolecular metal-to-ring R migration ($R = H, CH_3$) was suggested. Though it may be regarded as yet another metal-to-ring H migration, the formation of **18** in reaction 3 poses some mechanistically interesting questions.



Scheme 2.



Scheme 3.

Taking account of the usual nature of the reactions of $[MoCp_2HI]$ (1) with ligands in acetone or acetone/$TlPF_6$, the expected result of reaction 3 would be the formation of $[MoCp_2H(dppe)]^+$ (**19**) as was found in the case of the reaction with the similar diphosphine dppm, in which $[MoCp_2Hdppm]^+$ (**17**) was formed in high yield. Since we could not isolate **19**, nor detect it spectroscopically (^1H NMR), we suggest that it probably rearranges quickly, to give **18** as the major reaction product. The result obtained with $[MoCp_2DI]$, giving *exo*-**18d**, shows that the mechanism of the migration is not analogous to that of ethyl migration [3], since this would result in the formation of *endo*-**18d**. We have insufficient data on which to base a mechanistic explanation for this unexpected result, and we are studying these migration reactions further.

Experimental

All reactions were carried out under N_2 or Ar by Schlenk techniques. Solvents were dried over Na wire in the presence of benzophenone (toluene, THF and diethyl ether) and distilled before use. CH_3CN was refluxed over CaH_2 and distilled. Deuterated solvents were vacuum distilled into the NMR sample tubes. $[MCp_2HX]$ (M = Mo, W) was prepared as described previously [1].

Preparation of $[MoCp_2H(CO)][PF_6]$ *(2).* A solution of $[MoCp_2HI]$ (0.25 g; 0.71 mmol) in 30 ml of acetone was treated with a 10% excess of $TlPF_6$ and the mixture was refluxed under 1 atm CO for 45 min. The solution was filtered to remove TlI and 10 ml of water added. Upon slow evaporation of the acetone, crystals of $[MoCp_2H(CO)]PF_6$ separated. These were filtered off, washed with water, and dried in vacuum. Yield 80%.

Preparation of [MoCpI(CO)$_3$]. A solution of [MoCp$_2$HI] (0.13 g; 0.37 mmol) in 30 ml of dry toluene, was refluxed for 19 h under 1 atm of CO. The solution was then filtered and the intractable precipitate discarded. The filtrate was evaporated, and the residue extracted with cyclohexane. Concentration gave [MoCpI(CO)$_3$] in 10% yield.

Preparation of [MoCp$_2$H(NH$_3$)]I (3). NH$_3$ was gently bubbled through a solution of [MoCp$_2$HI] (0.3 g; 0.86 mmol) in THF (40 ml). An orange precipitate began to separate immediately, and after 5 min the solution was colourless. The precipitate was filtered off, washed with THF, and recrystallized from water by slow evaporation under vacuum. The orange crystals were isolated in 95% yield.

*Reaction of **3** with H$_2$O.* Refluxing a solution of **3** in H$_2$O (10 ml) for 1.5 h gave a brown solution. This was evaporated to dryness and the residue was extracted with THF. Concentration gave crystals of [MoCp$_2$HI] in 50% yield.

Preparation of [MoCp$_2$H(NH$_3$)]PF$_6$. A sample of **3** (0.1 g) was suspended in Me$_2$CO (5 ml) and excess TlPF$_6$ added. After 16 h the solution was filtered and the same volume of ethanol added. Upon slow evaporation orange crystals separated, and were shown to be the PF$_6^-$ salt of **3** by IR spectroscopy.

Preparation of [MoCp$_2$H(en)]I (4). Solid [MoCp$_2$HI] (0.25 g; 0.71 mmol) was added to ethylenediamine (2 ml). The solid rapidly turned orange and after 15 min of vigorous stirring the mixture was evaporated to dryness. The residue was washed with THF (5 × 5 ml) and dried in vacuum. The yield was quantitative.

*Reaction of **4** with Me$_2$CO/H$_2$O.* A solution of **4** (0.1 g) in a 1/1 water/acetone mixture was refluxed for 30 min and the brown solution was then slowly evaporated under vacuum. When most of the acetone had been removed the solution became deep red, and addition of excess KI gave red crystals of [MoCp$_2$en]I$_2$ (**5**) in 80% yield.

Preparation of [MoCp$_2$Br(NCMe)]PF$_6$ (6). A solution of [MoCp$_2$HI] (0.15 g; 0.43 mmol) in dry acetonitrile (30 ml) was stirred with an excess of TlPF$_6$ for 24 h at room temperature. The resulting orange solution was filtered, concentrated to ca. 15 ml, and treated with 2 ml of CHBr$_3$. After 12 h the solution was evaporated, and the purple residue recrystallized from acetone/ethanol to give **6** in 85% yield.

Preparation of [MoCp$_2$H(C$_2$H$_4$)]BF$_4$ (8). A solution of [MoCp$_2$HI] (0.13 g; 0.38 mmol) in CH$_2$Cl$_2$ was saturated with C$_2$H$_4$ at −10 °C. An excess of AgBF$_4$ was then added and the temperature allowed to rise as ethylene was continuously bubbled through the solution. When the solution became colourless, the AgI was filtered off, and the filtrate concentrated. Addition of diethyl ether produced a white compound, which was filtered off, and dried in vacuum. Yield 50%.

Preparation of [MoCp$_2$(η^3-C$_3$H$_4$CH$_3$)]BF$_4$ (9). A solution of [MoCp$_2$HI] (0.19 g; 0.54 mmol) in CH$_2$Cl$_2$ was treated with a saturated solution of butadiene in CH$_2$Cl$_2$ and then with TlBF$_4$ (0.16 g; 0.54 mmol). After 4 h stirring the mixture was filtered. Concentration and addition of diethyl ether gave an orange powder. Yield 65%.

Preparation of [MoCp$_2$H(PMe$_2$Ph)]PF$_6$ (10). A solution of [MoCp$_2$HCl] (0.25 g; 0.95 mmol) and PMe$_2$Ph (0.5 ml) in toluene (30 ml) was refluxed for 5 h. The yellow precipitate was filtered off from the colourless solution, washed with toluene and diethyl ether, and dried. The yellow powder thus obtained was dissolved in water (10 ml), and an aqueous solution of NH$_4$PF$_6$ added dropwise until no further precipitation was observed. The fine precipitate was filtered off and washed with water. Recrystallization from acetone/ethanol (1/1) by slow evaporation under vacuum gave yellow crystals in 95% yield.

Preparation of [MoCp$_2$H(PPh$_3$)]PF$_6$ (13). This complex was prepared as described for the PMe$_2$Ph analogue, but starting from [MoCp$_2$HBr] (0.14 g; 0.46 mmol) and PPh$_3$ (0.12 g; 0.46 mmol): after 24 h reflux the isolated yield was 80%.

Preparation of [MoCp$_2$I(PEt$_2$Ph)]PF$_6$ (15). A solution of [MoCp$_2$HI] (1 mmol) and PEt$_2$Ph (1 mmol) in THF (30 ml) was refluxed for 19 h. A yellow microcrystalline precipitate slowly separated, and was filtered off and dissolved in acetone/water (1/1). Upon addition of aqueous NH$_4$PF$_6$ the solution turned green. Evaporation of the acetone gave a green precipitate which was filtered off and washed with H$_2$O (2 × 5 ml). The green solid was recrystallized from acetone/ethanol (1/1) by slow evaporation in vacuum to give needles of **15** in 60% yield.

Preparation of [MoCp$_2$H(PEt$_2$Ph)]PF$_6$ (16). A solution of [MoCp$_2$HI] (0.35 g; 1 mmol) in acetone (40 ml) was treated with PEt$_2$Ph (0.4 ml; 2 mmol) and an excess of TlPF$_6$ then refluxed for 20 h. The solution was filtered and evaporated to dryness. The oily residue was washed with toluene and diethyl ether. Recrystallization from acetone/diethyl ether afforded orange crystals in 60% yield.

Preparation of [MoCp$_2$H(dppm)]PF$_6$ (17). This complex was prepared in the same way as **16**, starting from [MoCp$_2$HI] (0.24 g; 0.69 mmol) and dppm (0.25 g; 0.69 mmol). The yield was 60%.

Preparation of [MoCp(η^4-C$_5$H$_6$)dppe]PF$_6$ (18). An equimolar mixture of [MoCp$_2$HI] (0.58 g; 1.66 mmol) and dppe in acetone (150 ml) was refluxed for 7 h. The small amount of precipitate was filtered off and discarded. Water (20 ml) and NH$_4$PF$_6$ (in excess) was added to the yellow-orange solution. Evaporation of the acetone left a yellow powder, which was filtered off, washed with water (2 × 5 ml), and vacuum dried. Recrystallization from acetone/ethanol gave **18** in 70% yield. A further small amount of [MoCp$_2$dppe](PF$_6$)$_2$ (**20**) was recovered from the mother liquor by addition of diethyl ether.

When the same reaction was carried out at room temperature for 24 h in the presence of excess TlPF$_6$, complexes **18** and **20** were isolated by the procedure described above in 40 and 15% yields, respectively.

Preparation of (18d). A solution of [MoCp$_2$D$_2$] (0.08 g; 0.35 mmol) and isopropyl iodide in dry toluene (15 ml) was kept for 3 h at 60 ° C. After concentration and addition of dry pentane, green crystals of [MoCp$_2$DI] separated. (It was possible that a little [MoCpI$_2$] was present and this was not checked.) The crystals were redissolved in d^6-Me$_2$CO (10 ml), an excess (0.1 g) of dppe was added, and the mixture was refluxed for 3 h. Addition of TlPF$_6$ gave an immediate precipitate of TlI, and the resulting solution was evaporated to dryness. The residue was chromatographed on a Al$_2$O$_3$ column made up with light petroleum, and the main yellow band eluted with CH$_2$Cl$_2$/Me$_2$CO (2/1). Recrystallization from Me$_2$CO/EtOH gave crystalline **18d**.

Reaction of [MoCp$_2$Br(dppe)]PF$_6$ with NaBH$_4$. A solution of [MoCp$_2$Br(dppe)]PF$_6$ (0.1 g; 0.14 mmol) in acetone/ethanol was stirred overnight with an excess of NaBH$_4$ at room temperature. The resulting yellow solution was filtered and concentrated, and crystals of **18** separated in ca. 80% yield.

Reaction of [MoCp$_2$Br(dppm)]PF$_6$ with NaBH$_4$. In the way described immediately above, [MoCp$_2$Br(dppm)]PF$_6$ was treated with an excess of NaBH$_4$. The product [MoCp$_2$H(dppm)]PF$_6$ (**17**) was isolated in 60% yield.

Preparation of [(MoCp$_2$H)$_2$dppe][PF$_6$]$_2$ (21). A solution of [MoCp$_2$HCl] (1 mmol) in dry toluene (40 ml) was refluxed for 24 h. The yellow precipitate was filtered off, dissolved in water (10 ml), and treated with aqueous NH$_4$PF$_6$. The yellow precipitate formed was filtered off, washed with water, and recrystallized from acetone/ethanol to give crystals of **21** in 10% yield. Most of the [MoCp$_2$HCl] was recovered unchanged, from the toluene solution.

References

1 A.R. Dias and C. Romão, J. Organomet. Chem., 233 (1982) 223.

2 R.H. Crabtree, A.R. Dias, M.L.H. Green, and P.J. Knowles, J. Chem. Soc. A, (1971) 1350.

3 F.W.S. Benfield and M.L.H. Green, J. Chem. Soc. Dalton Trans., (1974) 1324.

4 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.

5 E. Gore and M.L.H. Green, J. Chem. Soc. A, (1970) 2315.

6 M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T. Domingos, M.T.L.S. Duarte, M.H. Garcia and C.C. Romão, J. Organomet. Chem., 320 (1987) 63.

7 M.L.H. Green and P.J. Knowles, J. Chem. Soc. Perkin Trans., (1973) 989.

8 F.W.S. Benfield and M.L.H. Green, J. Chem. Soc. Dalton Trans., (1974) 1324.

9 B.R. Francis, M.L.H. Green, T. Luong-thi and G.A. Moser, J. Chem. Soc. Dalton Trans., (1976) 1339.

10 Tereza Aviles, M.L.H. Green, Alberto R. Dias and Carlos Romão, J. Chem. Soc. Dalton Trans., (1979) 1367.

11 M.A. Adams, K. Folting, J.C. Huffmann and K.G. Caulton, J. Organomet. Chem., 164 (1979) C29.