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Reactions of metallophosphide anions $[(CO)_xM'PPh_2]^-$ ($M' = Cr, W, Fe$) with Cp'_2MCl_2 ($Cp' = \eta^5$-C_5H_4–*tert*-Bu; M = Mo, W): diastereogenic syntheses of bimetallic systems

Virginie Comte, Sandrine Rigny, Claude Moïse*

Laboratoire de synthèse et d'électrosynthèse organométallique, UMR 5632, Faculté des sciences Gabriel, 21000 Dijon, France

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Summary — Reactions of metallophosphide anions $[(CO)_xM'PPh_2]^-$ with molybdenocene and tungstenocene dichlorides Cp'_2MCl_2 (M = Mo, W; $Cp' = \eta^5$-C_5H_4–*tert*-Bu) give Cp-ring 1,3-disubstituted products. Due to planar chirality associated with an asymmetric metallic center, diastereoisomers are produced but a fast interconversion process occurs allowing the isolation of only one isomer. Molybdenum complexes do not transform into orthometallated products as was previously observed for their C_5H_5 or C_5H_4–Me analogs. Chemical reactions have been performed on the complexes **3′** and **4′**. Therefore reduction into dihydrides leads to μ-hydrido structures.

nucleophilic substitution / metallophosphide anion / bimetallic complex / stereochemistry / molybdenocene / tungstenocene

Résumé — Réactions d'anions métallophosphorés $[(CO)]_xM'PPh_2]^-$ (M′=Cr, W, Fe) avec Cp'_2MCl_2 ($Cp' = \eta^5$-C_5H_4–*tert*-Bu ; M = Mo, W) : synthèses diastéréogènes de systèmes bimétalliques. Les réactions d'anions métallophosphorés $[(CO)_xM'PPh_2]^-$ avec les dichlorures de molybdénocène et de tungsténocène donnent des produits de disubstitution 1,3 sur le cycle cyclopentadiénique. Des diastéréoisomères sont formés par suite de la présence d'un plan de chiralité associé à l'asymétrie métallique ; un processus d'interconversion rapide se produit ne permettant d'isoler qu'un seul stéréoisomère. Les complexes du molybdène ne se transforment pas en complexes orthométallés comme le font leurs analogues C_5H_5 ou C_5H_4–Me. Des transformations chimiques ont été réalisées : ainsi la réduction en dihydrure conduit à des structures avec pont hydruro.

substitution nucléophile / anion métallophosphoré / complexe bimétallique / stéréochimie / molybdénocène / tungsténocène

Introduction

Despite the wide range of electrophilic substitutions concerning cyclopentadienyl ligands in transition metal complexes, only a few examples of nucleophilic substitutions are mentioned in the litterature. Cooper et al reported reactions with anionic nucleophiles on Cp rings in cationic tungstenocene derivatives [1], but in these cases the electrophilic activation of aromatic ligands clearly results from the positive charge borne by the metal atom. Our research team has recently shown that metallophospide anions $[(CO)_xM'PPh_2]^-$ are able to achieve Cp substitution in neutral molybdenocene [2] and tungstenocene [3] dichlorides; the molybdenum complexes undergo a subsequent orthometallation reaction giving new heterobimetallic complexes with the $(\eta^5$-$C_5H_4)P(Ph)[M'(CO)_x]C_6H_4^-$ framework as bidentate ligand (scheme 1).

These results show that the group 6 metallocene dichlorides contain two potential electrophilic zones located on the Cp ligands and on the metal center respectively, and suggest that both steric and electronic factors must be considered in the orientation of the substitution reaction. This has led us to investigate the reaction of metallophosphide anions with Cp-substituted molybdenocene and tungstenocene dichlorides, and for this purpose we have selected the sterically hindered and electron donor *tert*-butyl group.

Results and discussion

The disubstituted precursors Cp'_2MCl_2 ($Cp' = \eta^5$-C_5H_4-*tert*-Bu; M = Mo (**1**), W (**2**)) are prepared from MCl_4L (M = Mo, L = $(OEt_2)_2$; M = W, L = dme) and Li[C_5H_4-*tert*-Bu] according to the procedure recently reported by Green et al for ansa complexes [4]. They are isolated in moderate yields (40%) as solids of poor solubility in common solvents.

Treatment of **1** at room temperature in THF with a stoichiometric amount of freshly prepared

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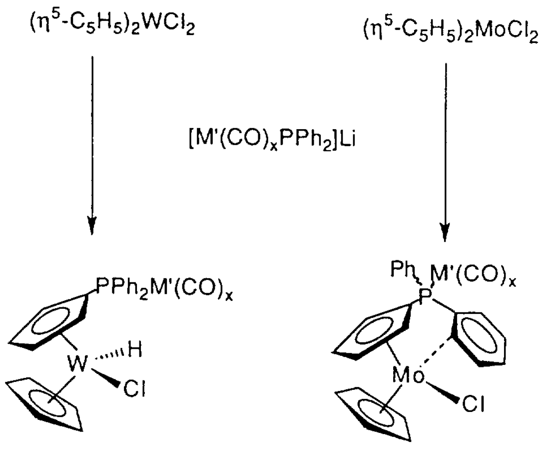
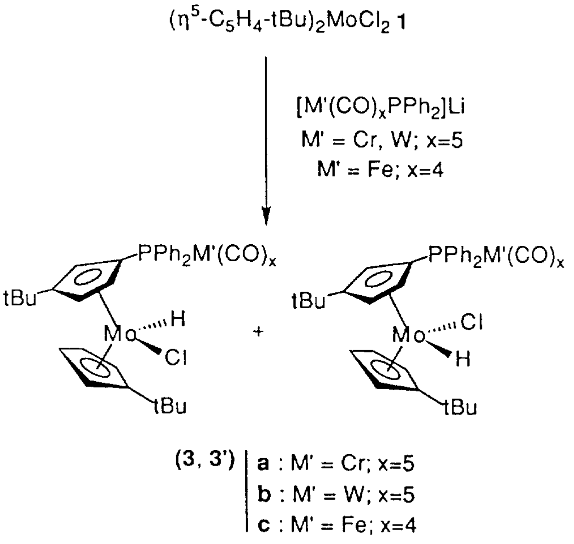
[*] Correspondence and reprints



Scheme 1

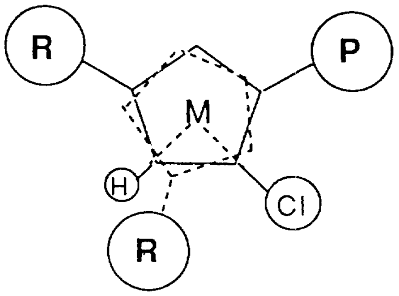
$Li[(CO)_xM'PPh_2]$ ($x = 5$, M' = Cr, W; $x = 4$, M' = Fe) resulted in the formation of bimetallic complexes according to scheme 2.

The ^{31}P and ^{1}H NMR spectra of the crude material revealed the presence of two isomers **3** and **3'** in a 3:1 ratio; each component exhibits a pattern of seven signals for the cyclopentadienyl protons in accordance with a substitution reaction occurring on the Cp ligand. This structural feature together with the generation of the chiral metallic center is responsible for the formation of diastereoisomers **3** and **3'**. As shown by NMR analysis a noticeable selectivity was observed during this diastereogenic reaction. Attempts to perform separation of diastereoisomers **3** and **3'** by chromatography were unsuccessful; however, a complete transformation in one unique isomer **3'** took place when a THF solution of the mixture **3** + **3'** was allowed to stand for 12 h at room temperature. The same evolution needed 24 h in toluene. This interconversion phenomenon which leads to the more thermodynamically stable product probably proceeds via a rearrangement of the H and Cl σ-bonded ligands. The possibility to inverse the configuration of the chiral plane of the disubstituted Cp ligand through a reversible $\eta^5 \rightarrow \eta^1$ ring slippage process seems unlikely. The 1 and 3 positions in the disubstituted Cp ligand were unambigously established by 2D ^{1}H NMR COSY experiments performed on the complex **4'b**.



Scheme 2

X-ray analysis is needed to determine the structural features of complexes **3'** but we were unable to isolate single crystals for X-ray diffraction. However, taking into account the most probable spatial disposition of the two *tert*-butyl groups in the bent metallocenic structure, a relative configuration as **I** might be assigned to the isolated complexes (fig 1).



(I)

Fig 1

As can be seen, this spatial arrangement seems the most adequate to minimize the steric interactions between the ring substituents and the σ-bonded ligands. Tungstenocene dichloride **2** exhibited the same behaviour when opposed to metallophosphide anions; substitution also occurred on the Cp ring but NMR monitoring revealed the presence of one single isomer in the crude material. This complete diastereoselectivity may in fact be due to a very fast epimerisation process between the two expected isomers **4** and **4'**; the relative configuration **I** is also reasonable for the isolated complexes **4'**.

Somewhat surprising is the lack of evolution to orthometallated structures exhibited here by complexes **3'**; this contrasts markedly with the behaviour of products obtained by opposing the dichlorides Cp_2MoCl_2 or Cp'_2MoCl_2 ($Cp' = \eta^5$-C_5H_4-Me) to metallated phosphide anions [5]. The question is whether steric or electronic considerations are responsible for this behaviour. As we have suggested in a previous paper [5], the orthometallation reaction probably involves the formation of a molybdocene-type intermediate which provides an insertion in an aromatic C–H bond owing to its carbenoid character. The structure of the 16-electron species Cp_2Mo or Cp_2W is assumed to exist with a parallel ring position [6]; steric strains arising from the hindered Cp substituents should make this required parallel structure difficult to attain for complexes **3'**.

Some chemical transformations were carried out on monohydride monochloride complexes **3′** and **4′**. By stirring a chloroform–carbon tetrachloride solution of **3′a** or **4′b** the corresponding green dichlorides **5** and **6** were obtained in good yields. Attempts were made to introduce a second metallophosphido group but no reaction took place when these dichlorides were opposed to $[(CO)_xM'PPh_2]^-$ anions. Noteworthy is the fact that a second ring substitution yielding Cp'_2WHCl quickly occurred when dichlorides $Cp'CpWCl_2$ were allowed to react with $[(CO)_xM'PPh_2]^-$ anions ($Cp' = \eta^5$-$C_5H_4PPh_2M'(CO)_x$) [3]. The sharp contrast manifested here by **5** and **6** is probably caused by steric factors.

The reduction of monochlorides **3′** and **4′** was readily achieved by $LiAlH_4$; however, for the molybdenum compound **3′** the reaction was surprisingly accompanied by the loss of the metallophosphido substituent leading to the dihydride (η^5-C_5H_4-*tert*-Bu)$_2MoH_2$ while the metallophosphine $HPPh_2M'(CO)_x$ was characterized in the reactional medium. An *ipso* nucleophilic substitution can be put forward as the cause of this result. The expected dihydrides **7** were formed from complexes **4′**; planar chirality is evidenced by the set of seven multiplets for the Cp protons and by the two distinct resonance signals for the diastereotopic hydride ligands. As mentioned earlier for closely related complexes [7], dihydrides are able to give easily hydrido-bridged compounds. Complexes **8** were thus obtained by photochemical exposure of precursors **7** in THF solution with a lamp (scheme 3); this easy evolution precluded satisfactory analytical data of dihydrides **7** which always contain some amounts of μ-hydrido compounds.

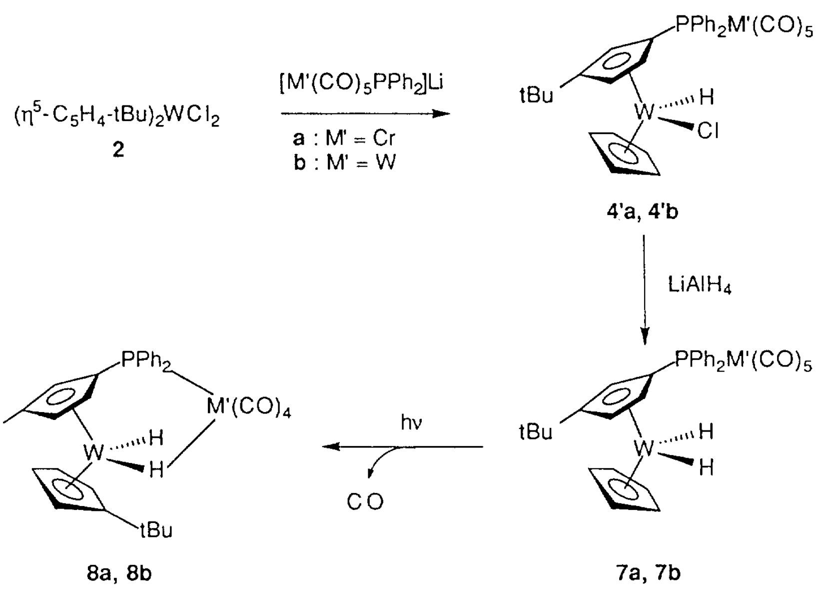
The ^1H NMR spectra of **8** show characteristic upfield signals of bridging hydrides with a shielding depending on the nature of the metal, Cr or W; the non-bridged hydride resonances remain practically unchanged.

No significative variation in $J(^{183}WH)$ values is found after hydrido bridging; therefore the interaction with the metallocenic tungsten atom remains strong, suggesting that no noticeable variation in the W–H bond length occurs in the W–H$\cdots$M′ moiety.

In conclusion, this work shows that Cp rings bearing *tert*-butyl substituents undergo nucleophilic substitutions as the unsubstituted ligands do; nevertheless a striking difference is found with molybdenocene derivatives which do not give the expected orthometallation reaction. Both steric and electronic considerations might explain these results but the balance between these two factors remains difficult to estimate; further studies are needed to rationalize these results and we are now focusing our efforts on studying the behaviour of ansa-bridged molybdenocene and tungstenocene complexes.

Experimental section

All reactions were carried out under an atmosphere of purified argon. The solvents were dried by the appropriate procedure and distilled under argon prior to use. Standard Schlenk techniques and conventional glass vessels were employed. Column chromatography was performed under argon with silica gel (70–230 mesh). Elemental analyses were performed by the CNRS microanalytical laboratory. Field desorption and electron ionization mass spectra were run respectively on a Finnigan MAT 311 instrument and a Kratos Concept 32S. ^1H and ^{31}P spectra were recorded on a Bruker AC 200 spectrometer; chemical shifts are given in ppm relative to TMS (^1H) or external H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet 205 IR-FT. The lithium reagent, $Li[(CO)_xM'PPh_2]$ (x = 5, M′ = Cr, W; x = 4, M′ = Fe), was prepared according to the literature method [8] using low-chloride methyllithium (Janssen).



Scheme 3

Synthesis of $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2MCl_2$ *(M = Mo)* **1**, *(M = W)* **2**

The complexes $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2MoCl_2$ **1** and $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2WCl_2$ **2** were all prepared from MCl_4L (M = Mo, L = $(OEt_2)_2$; M = W, L = dme) [9] by adapting the published procedures described by Green et al for ansa complexes [4]. A further purification by chromatography with silica silanized (eluent: chloroform) gave a dark green powder in 30% yield for **1** and 40% for **2**.

- $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2MoCl_2$ **1**

^1H NMR (200 MHz, $CDCl_3$): δ 1.15 (s, 18H, *t*Bu), 5.32 (m, 4H, C_5H_4), 5.81 (m, 4H, C_5H_4).

MS (EI) *m/z*: 409.2 [M^+].

Anal calc for $C_{18}H_{26}Cl_2Mo$: C, 52.83; H, 6.40. Found: C, 51.86; H, 6.27.

- $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2WCl_2$ **2**

^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (s, 18, *t*Bu), 5.04 (m, 4H, C_5H_4), 5.92 (m, 4H, C_5H_4).

MS (EI): *m/z*: 496 [M^+].

Anal calc for $C_{18}H_{26}Cl_2W$: C, 43.49; H, 5.27. Found: C, 40.10; H, 5.10.

Synthesis of $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2M'(CO)_x][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3** *and* **3′**

5 mL of a THF solution of $Li[(CO)_xM'PPh_2]$ (1 mmol) ($x = 5$, M′ = Cr, W; $x = 4$, M′ = Fe) was rapidly added to $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]_2MoCl_2$ **1** (410 mg, 1 mmol) in suspension in THF (20 mL). The mixture was stirred at room temperature for 4 h. THF was removed in vacuo, the residue was washed with pentane (2 × 30 mL) to give a beige powder. Analysis of the NMR spectrum of the crude product indicated clearly the presence of two diastereoisomers **3** and **3′** in 3:1 ratio. When this mixture is again dissolved in THF (or toluene) and stirred at room temperature for 12 h (24 h in toluene), only the thermodynamically stable complex **3′** was obtained after removal of the solvent. A further purification by chromatography (eluent: toluene) and a recrystallisation from toluene gave an orange crystalline powder in 20% yield for **3′a** (150 mg), in 25% for **3′b** (220 mg) and in 15% for **3′c** (110 mg).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_5][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3a**

IR (ν_{CO}, THF): 2 063 (m), 1 937 (S + sh) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.57 (s, 1H, Mo–*H*), 1.06 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu), 3.43 (m, 1H), 3.96 (m, 1H), 4.12 (m, 1H), 4.81 (m, 1H), 4.98 (m, 1H), 5.02 (m, 1H), 5.43 (m, 1H), C_5H_4 or C_5H_3, 7.40–7.79 (m, 10H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 47.3 (s).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_5][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3′a**

IR (ν_{CO}, THF): 2 063 (m), 1 937 (S + sh) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.77 (s, 1H, Mo–*H*), 1.25 (s, 9H, *t*Bu), 1.43 (s, 9H, *t*Bu), 3.29 (m, 1H), 3.43 (m, 1H), 3.60 (m, 1H), 4.06 (m, 1H), 4.83 (m, 1H), 4.92 (m, 1H), 5.31 (m, 1H), C_5H_4 or C_5H_3, 7.40–7.79 (m, 10H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 46.2 (s).

MS (FD): (*m/z*): 752.1 [M^+].

Anal calc for $C_{35}H_{36}ClCrMoO_5P$: C, 55.97; H, 4.83. Found: C, 55.0; H, 4.5.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_5][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3b**

IR (ν_{CO}, THF): 2071 (m), 1943 (S + sh) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.65 (s, 1H, Mo–*H*), 1.09 (s, 9H, *t*Bu), 1.22 (s, 9H, *t*Bu), 3.56 (m, 1H), 3.97 (m, 1H), 4.25 (m, 1H), 4.81 (m, 1H), 4.99 (m, 2H), 5.43 (m, 1H), C_5H_4 or C_5H_3, 7.41–7.59 (m, 6H, C_6H_5), 7.62–7.78 (m, 4H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 9.74 (s + d, $^1J(^{183}WP) = 253$ Hz).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_5][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3′b**

IR (ν_{CO}, THF): 2 071 (m), 1943 (S + sh) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.79 (s, 1H, Mo–*H*), 1.25 (s, 9H, *t*Bu), 1.44 (s, 9H, *t*Bu), 3.31 (m, 1H), 3.45 (m, 1H), 3.67 (m, 1H), 4.09 (m, 1H), 4.83 (m, 1H), 4.87 (m, 1H), 5.29 (m, 1H), C_5H_4 or C_5H_3, 7.41–7.59 (m, 6H, C_6H_5), 7.62–7.78 (m, 4H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 8.39 (s + d. $^1J(^{183}WP) = 245$ Hz).

Anal. calc for $C_{35}H_{36}ClWMoO_5P$: C, 47.62; H, 4.11. Found: C, 47.20; H, 4.02.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Fe(CO)_4][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3c**

IR (ν_{CO}, THF): 2 046 (m), 1 970 (S), 1 941 (S) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.29 (s, 1H, Mo–*H*), 1.08 (s, 9H, *t*Bu), 1.15 (s, 9H, *t*Bu), 3.70 (m, 1H), 3.81 (m, 1H), 4.14 (m, 1H), 4.32 (m, 1H), 4.68 (m, 1H), 4.74 (m, 1H), 5.48 (m, 1H), C_5H_4 or C_5H_3, 7.23–7.69 (m, 10H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 69.7 (s).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Fe(CO)_4][3\text{-}tert\text{-}Bu]\}Mo(H)(Cl)$ **3′c**

IR (ν_{CO}, THF): 2 046 (m), 1 970 (S), 1 941 (S) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ −7.59 (s, 1H, Mo–*H*), 1.26 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 3.61 (m, 1H), 4.06 (m, 2H), 4.20 (m, 1H), 4.85 (m, 1H), 4.96 (m, 1H), 5.04 (m, 1H), C_5H_4 or C_5H_3, 7.23–7.69 (m, 10H, C_6H_5).

^{31}P $\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 69.07 (s).

Synthesis of $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2M'(CO)_x][3\text{-}tert\text{-}Bu]\}W(H)(Cl)$ **4′**

To 15 mL of a THF suspension of $(\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu)_2WCl_2$ **2** (500 mg,1 mmol), 5 mL of a THF solution of $Li[(CO)_xM'PPh_2]$ (1 mmol) ($x = 5$, M′ = Cr, W: $x = 4$, M′ = Fe) was added rapidly. The mixture was stirred at room temperature for 3 h. THF was removed in vacuo, the residue was washed with 40 mL of pentane and chromatographed (eluent: toluene/THF, 9:1) to give **4′** as a beige powder. **4′** was recrystallised from toluene as orange needles in 30% yield for **4′a** (250 mg), in 35% yield for **4′b** (340 mg) and in 20% yield for **4′c** (160 mg).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_5][3\text{-}tert\text{-}Bu]\}W(H)(Cl)$ **4′a**

IR (ν_{CO}, THF): 2 063 (m), 1 944 (S + sh) cm^{-1}.

^1H NMR (200 MHz, C_6D_6): δ −9.78 (s + d, $^1J(^{183}WH) =$ 59 Hz, 1H, W–*H*), 0.90 (s, 9H, *t*Bu), 1.23 (s, 9H, *t*Bu), 2.85 (m, 1H), 3.80 (m, 2H), 4.68 (m, 1H), 4.71 (m, 1H), 4.91 (m, 1H), 5.02 (m, 1H), C_5H_4 or C_5H_3, 6.83–7.57 (m, 10H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 48.2 (s).

Anal calc for $C_{35}H_{36}ClCrO_5PW$: C, 50.11; H, 4.33. Found: C, 49.78; H, 4.28.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_5][3\text{-}tert\text{-}Bu]\}W(H)(Cl)$ **4′b**

IR (ν_{CO}, THF): 2 071 (m), 1 943 (S), 1 934 (S) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −9.86 (s + d, $^1J(^{183}\mathrm{WH})$ = 57 Hz, 1H, W-*H*), 0.91 (s, 9H, *t*Bu), 1.22 (s, 9H, *t*Bu), 2.92 (m, 1H), 3.79 (m, 1H), 3.88 (m, 1H), 4.65 (m, 1H), 4.72 (m, 1H), 4.85 (m, 1H), 4.99(m, 1H), C_5H_4 or C_5H_3, 6.91–7.28 (m, 4H, C_6H_5), 7.51–7.77 (m, 4H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 10.8 (s + d, $^1J(^{183}\mathrm{WP})$ = 246 Hz).

MS (EI): (*m/z*): 970 [M$^+$], 858 [M$^+$ − 4CO], 830 [M$^+$ − 5CO].

Anal calc for $C_{35}H_{36}ClO_5PW_2$: C, 43.3; H, 3.74. Found: C, 44.6; H, 3.87.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Fe(CO)_4][3\text{-}tert\text{-}Bu]\}W(H)(Cl)$ **4′c**

IR (ν_{CO}, THF): 2 047 (m), 1 943 (S), 1 934 (S) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −9.36 (s + d, $^1J(^{183}\mathrm{WH})$ = 61 Hz, 1H, W-*H*), 0.91 (s, 9H, *t*Bu), 1.24 (s, 9H, *t*Bu), 3.47 (m, 1H), 4.01 (m, 1H), 4.17(m, 1H), 4.62 (m, 1H), 4.821 (m, 2H), 4.87 (m, 1H), C_5H_4 or C_5H_3, 7.77–8.11 (m, 4H, C_6H_5), 7.0–7.13 (m, 6H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 69.91 (s).

Anal calc for $C_{34}H_{36}ClFeO_4PW$: C, 50.12; H, 4.45. Found: C, 50.80: H, 4.50.

Synthesis of $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2M'(CO)_5][3\text{-}tert\text{-}Bu]\}MCl_2$ $(M = Mo, M' = Cr)$ **5** *and* $(M = W, M' = W)$ **6**

500 mg of **3′a** or **4′b** were dissolved in 20 mL of $CHCl_3/CCl_4$. The mixture was stirred for 5 h at room temperature. After removal of the solvent and purification chromatography with silanized silica (eluent: chloroform) a green powder was obtained.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_5][3\text{-}tert\text{-}Bu]\}MoCl_2$ **5**

IR (ν_{CO}, THF): 2 065 (m), 1 938 (S) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): 1.07 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 3.92 (m, 1H), 4.57 (m, 1H), 4.94 (m, 1H), 5.19 (m, 1H), 5.37 (m, 1H), 5.64 (m, 1H), 5.71 (M, 1H), C_5H_4 or C_5H_3, 7.46–7.53 (m, 10H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, $CDCl_3$): δ 51.5 (s).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_5][3\text{-}tert\text{-}Bu]\}WCl_2$ **6**

IR (ν_{CO}, THF): 2 072 (m), 1 940 (S) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): 1.14 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu), 3.79 (m, 1H), 4.78 (m, 1H), 4.85 (m, 1H), 4.95 (m, 2H), 5.60 (m, 1H), 5.84 (m, 1H), C_5H_4 or C_5H_3, 7.44–7.60 (m, 10H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, $CDCl_3$): δ 16.8 (s + d, $^1J(^{183}\mathrm{WP})$ = 240 Hz).

Anal calc for $C_{35}H_{35}W_2PO_5Cl_2$: C, 41.82; H, 3.51. Found: C, 41.27; H, 3.81.

Synthesis of $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2M'(CO)_5][3\text{-}tert\text{-}Bu]\}WH_2$ **7**

To 20 mL of a THF solution of **4′** (2 mmol), $LiAlH_4$ was slowly added at 0 °C. The resulting mixture was stirred for 3 h at room temperature. Excess of $LiAlH_4$ was filtered off. After hydrolysis of the filtrate, the solvent was removed in vacuo and in each case after extraction with ether, **7** was always obtained in mixture with **8** and was never found pure. Its spectroscopic characteristics are obtained from the spectrum of the crude material.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_5][3\text{-}tert\text{-}Bu]\}WH_2$ **7a**

IR (ν_{CO}, THF): 2 062 (s), 1 940 (S + sh) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −11.45 (d + dd, ^2J(HH) = 9.6 Hz, $^1J(^{183}\mathrm{WH})$ = 68 Hz, 1H, W-*H*), −10.50 (d + dd, ^2J(HH) = 9.6 Hz, $^1J(^{183}\mathrm{WH})$ = 78 Hz, 1H, W-*H*), 1.08 (s, 9H, *t*Bu), 1.22 (s, 9H, *t*Bu), 3.41 (m, 1H), 3.48 (m, 1H), 4.06 (m, 1H), 4.16 (m, 1H), 4.40 (m, 1H), 4.47 (m, 1H), 4.54 (m, 1H), C_5H_4 or C_5H_3, 7.48–7.61 (m, 4H, C_6H_5), 6.98–7.15 (m, 6H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 49.1 (s).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_5][3\text{-}tert\text{-}Bu]\}WH_2$ **7b**

IR (ν_{CO}, THF): 2 071 (m), 1 943 (S), 1 930 (S) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −11.40 (d + dd, ^2J(HH) = 8.8 Hz, $^1J(^{183}\mathrm{WH})$ = 67 Hz, 1H, W-*H*), −10.50 (d + dd, ^2J(HH) = 8.8 Hz, $^1J(^{183}\mathrm{WH})$ = 78 Hz, 1H, W-*H*), 1.07 (s, 9H, *t*Bu), 1.22 (s, 9H, *t*Bu), 3.36 (m, 1H), 3.45 (m, 1H), 4.02 (m, 1H), 4.18 (m, 1H), 4.47 (m, 2H), 4.52 (m, 1H), C_5H_4 or C_5H_3, 7.18–7.50 (m, 4H, C_6H_5), 6.80–6.96 (m, 6H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 15.6 (s + d, $^1J(^{183}\mathrm{WP})$ = 250 Hz).

Synthesis of $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2M'(CO)_4][3\text{-}tert\text{-}Bu]\}W(H)(\mu\text{-}H)$ **8**

A solution of the mixture of **7** and **8** in THF (100 mL) was irradiated with a Hanau TQ 150 lamp for 3 h at room temperature. After removal of the solvent, the crude product was chromatographed with toluene as eluent. **8** was recrystallised from toluene as red needles in 25% yield for **8a** (390 mg) and 30% yield for **8b** (540 mg).

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2Cr(CO)_4][3\text{-}tert\text{-}Bu]\}W(H)(\mu\text{-}H)$ **8a**

IR (ν_{CO}, THF): 2 003 (m), 1 901 (S), 1 850 (vS) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −22.60 (d + dd, ^2J(HH) = 8 Hz, $^1J(^{183}\mathrm{WH})$ = 68 Hz, 1H, W-*H*), −12.05 (d + dd, ^2J(HH) = 8 Hz, $^1J(^{183}\mathrm{WH})$ = 66 Hz, 1H, W-*H*), 0.82 (s, 9H, *t*Bu), 1.15 (s, 9H, *t*Bu), 3.56 (m, 1H), 3.66 (m, 2H), 4.46 (m, 2H), 4.56 (m, 2H), C_5H_4 or C_5H_3, 7.58–7.85 (m, 4H, C_6H_5), 6.82–7.15 (m, 6H, C_6H_5).

^{31}P {^{1}H} NMR (81 MHz, C_6D_6): δ 49.1 (s).

Anal calc for $C_{34}H_{37}CrO_4PW$: C, 52.59; H, 4.80. Found: C, 53.83; H, 5.18.

- $[\eta^5\text{-}C_5H_4\text{-}tert\text{-}Bu]\{\eta^5\text{-}C_5H_3[1\text{-}PPh_2W(CO)_4][3\text{-}tert\text{-}Bu]\}W(H)(\mu\text{-}H)$ **8b**

IR (ν_{CO}, THF): 2 008 (m), 1 890 (S), 1 846 (vS) cm^{-1}.

^{1}H NMR (200 MHz, C_6D_6): δ −17.43 (dd + dddd, ^2J(HH) = 8 Hz, ^2J(PH) = 1.5 Hz, $^1J(^{183}\mathrm{WH})$ = 72 Hz,

$^1J(^{183}WH)$ = 27 Hz, 1H, W–*H*), −11.52 (dd + ddd, $^2J(HH)$ = 8 Hz, $^2J(PH)$ = 1.5 Hz, $^1J(^{183}WH)$ = 62 Hz, 1H, W–*H*), 0.79 (s, 9H, *t*Bu), 1.03 (s, 9H, *t*Bu), 3.68 (m, 1H), 4.02 (m, 1H), 4.22 (m, 1H), 4.40 (m, 1H), 4.52 (m, 2H), 4.62 (m, 1H), C_5H_4 or C_5H_3, 7.95–8.00 (m, 4H, C_6H_5), 6.93–7.15 (m, 6H, C_6H_5).

^{31}P {^1H} NMR (81 MHz, C_6D_6): δ 5.1 (s + d, $^1J(^{183}WP)$ = 233 Hz).

Anal calc for $C_{34}H_{37}O_4PW_2$: C, 44.93; H, 4.11. Found: C, 46.03; H, 4.67.

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