



# Synthesis of bis-cyclopentadienyl, bis-indenyl and mixed-ring indenyl halides of tungsten

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## Abstract

A convenient route to the tungstenocene derivatives  $Cp_2WX_2$  from  $CpW(\eta^3-C_5H_5)(CO)_2$  via  $[Cp_2W(CO)_2]^{2+}$  or  $[Cp_2W(NCMe)(CO)]^{2+}$  is described. Similar preparations, starting from  $CpW(\eta^3-C_9H_7)(CO)_2$ , lead to the mixed-ring indenyl analogues of tungstenocene,  $IndCpWI_2$  [ $Ind = (\eta^3-C_9H_7)$ ]. A stepwise route to bis-indenyl derivatives of tungsten is reported, based on the novel W(IV) complex  $IndWCl_3(CO)_2$  which is synthesized by the reaction of  $IndW(\eta^3-C_9H_7)(CO)_2$  with HCl gas in dichloromethane. Treatment of  $IndWCl_3(CO)_2$  with KInd in THF gives  $IndW(\eta^3-Ind)(CO)_2$  in high yield. This complex is a convenient starting material for the preparation of some bis-indenyl analogues of tungstenocene,  $Ind_2WI_2$ . The molecular structures of  $[IndW(\eta^4-C_5H_6)(CO)_2]BF_4$  (**7a**) and  $[IndCpWH(CO)]BF_4$  (**7b**) were characterized by single-crystal X-ray diffraction. The crystals belong to the triclinic and monoclinic space group  $P\bar{1}$  and  $P2_1/c$  with  $a = 729.98(3)$  and  $715.0(3)$  pm;  $b = 783.06(3)$  and  $1484.0(6)$  pm;  $c = 1419.20(4)$  and  $1389.2(6)$  pm;  $\alpha = 100.210(2)$  and  $90^\circ$ ;  $\beta = 104.557(2)$  and  $99.18(3)^\circ$ ;  $\gamma = 93.441(2)$  and  $90^\circ$ , respectively. The final refinements of **7a** and **7b** converged at  $R_1 = 0.0236$  and  $0.0680$ ;  $wR_2 = 0.0581$  and  $0.1378$ , respectively. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Tungstenocene; Cyclopentadienyl; Mixed-ring indenyl and bis-indenyl halides complexes; Hydride; X-ray diffraction

## 1. Introduction

Investigations in our laboratory have recently focused on the chemistry of ring substituted analogues of molybdenocene and tungstenocene [1,2]. The synthetic approach uses  $[Cp'M(\eta^4\text{-diene})(CO)_2]^+$  complexes to provide a high yield route to metallocenes as well as differently substituted chiral and pro-chiral molybdenocene and tungstenocene analogues, namely the indenyl congeners  $[IndCpML_2]^n+$ . According to Scheme 1, CO loss followed by H migration, or, alternatively,  $H^-$  abstraction lead directly to cationic derivatives of the  $Cp'_2M$  fragment. Deprotonation of the diene leads

to ring-slipped complexes of the type  $(\eta^5-Cp')(\eta^3-Cp')M(CO)_2$  which can be oxidized to  $[(\eta^5-Cp')_2M(CO)_2]^{2+}$  in a chemically and electrochemically reversible redox process [1e].

Of course, these general methods also apply for the synthesis of the unsubstituted parent metallocenes. However, the higher stability of the complexes  $[Cp'W(\eta^4-C_5H_6)(CO)_2]^+$  compared to the molybdenum analogues blocks the synthesis of the tungstenocene derivatives via H migration, as depicted in Scheme 2 [1b,2a] (see below).

On the other hand, the methods in Scheme 1 are difficult to apply to the synthesis of bis-indenyl complexes,  $Ind_2MX_2$  because the indene complex  $[IndM(\eta\text{-IndH})(CO)_2]^+$  is not a stable entity that can be isolated and further manipulated. In this contribution, we re-

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port improved routes for the preparation of the tungsten complexes  $Cp_2WX_2$  and present a new independent method for the synthesis of the indenyl tungstenocenes,  $IndCp'WX_2$  ( $Cp' = Cp, Ind$ ). The structural characterization of the diene  $[IndW(\eta^4-C_5H_6)(CO)_2]BF_4$  and the hydride  $[IndCpWH(CO)]BF_4$  are also presented.

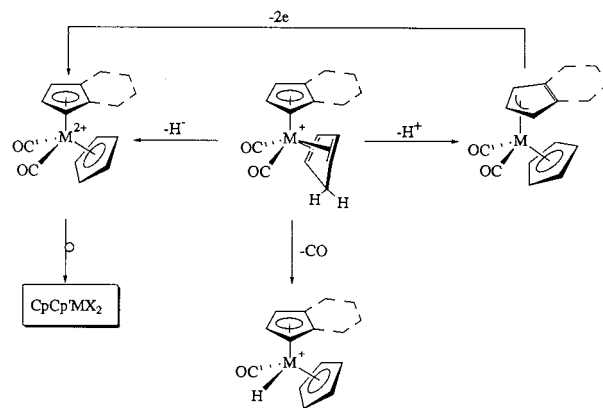
## 2. Results and discussion

### 2.1. Preparation of tungstenocene complexes $Cp_2WX_2$

The synthetic route used is based on the transformations of the cationic cyclopentadiene complex  $[CpW(\eta^4-C_5H_6)(CO)_2]^+$ . As depicted in Schemes 2 and 3, two possibilities are conceivable: (i) CO loss followed by Hendo migration to the metal to give  $[Cp_2WH(CO)]^+$  followed by addition of  $CHI_3$  and then excess of  $(n-Bu)_4NI$  under irradiation and reflux. (ii) Preparation of the dicationic tungstenocene derivative  $[Cp_2W(CO)_2]^{2+}$  and reaction with excess of  $(n-Bu)_4NI$  under irradiation and reflux.

As mentioned above, all attempts to prepare  $[Cp_2WH(CO)]BF_4$  according to Scheme 2, by use of irradiation with a 60 W tungsten lamp were unsuccessful, although they readily occur for the Mo analogues. This is certainly due to the stronger W–CO bond, compared to the Mo–CO bond, which needs to be cleaved prior to the H migration step. As a matter of fact,  $[Cp_2WH(CO)]BF_4$  is a perfectly stable compound that has been isolated in the decomposition of  $CpW(\eta^3-C_5H_5)(CO)_2$  (**1**) [1b]. According to Scheme 3, oxidation of **1** with  $(n-Bu)_4N[Br_3]$  in dichloromethane, at room temperature, forms the off-white salt  $[Cp_2W(CO)_2]Br_2$  (**2**) in almost quantitative yield. Anion metathesis to the more soluble  $BF_4^-$  salt can be performed by quick dissolution in water and precipitation with a saturated aqueous solution of  $NH_4BF_4$ . This method of preparation of **2** is much more convenient than the previously reported  $H^-$  abstraction reaction, from  $[CpW(\eta^4-C_5H_6)(CO)_2]^+$ , with the less stable reagent  $Ph_3CBF_4$  [2a].

Irradiation of a solution of **2** in NCMc with a 60 W tungsten lamp for 12 h gives the yellow crystalline complex  $[Cp_2W(NCMe)(CO)][BF_4]_2$  (**3**). The increased, but still not very high substitutional inertia of the W complex relative to its Mo congener is obvious, for the simple dissolution of the dication  $[Cp_2Mo(CO)_2][BF_4]_2$  in acetonitrile forms  $[Cp_2Mo(CO)(NCMe)][BF_4]_2$  very rapidly [1a,b]. The known halide complexes  $[Cp_2WX(CO)]^+$  [3] [ $X = Br$  (**4**),  $I$  (**5**)] are formed from  $[Cp_2W(NCMe)(CO)]^{2+}$  or  $[Cp_2W(CO)_2]^{2+}$  with one equivalent of  $(n-Bu)_4NX$  in dichloromethane/*N*-methylformamide (NMF). Disubstitution to the di-iodide complex  $Cp_2WI_2$  (**6**) [4] is performed from **3**, in good yield, by treatment with excess of  $(n-Bu)_4NI$  in reflux-



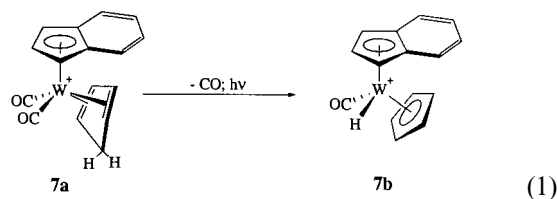
Scheme 1.

ing dichloromethane after 48 h under a 60 W tungsten lamp irradiation.

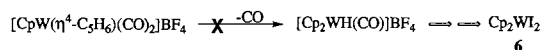
This method can be extended to the preparation of other dihalide complexes, in particular tungstenocenes with mixed-ring indenyl and bis-indenyl ligands.

### 2.2. Preparation of tungstenocene complexes $IndCp'WX_2$ ( $Cp' = Cp, Ind$ )

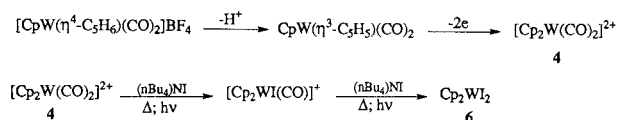
In keeping with the well established increased lability of indenyl complexes relative to their Cp congeners, one might expect the H migration reaction in Eq. (1) to take place readily. This is indeed the case. When a solution of  $[IndW(\eta^4-C_5H_6)(CO)_2]BF_4$  (**7a**) [2a] in dichloromethane/acetone is stirred for 19 h and irradiated with a 60 W tungsten lamp  $[IndCpWH(CO)]BF_4$  (**7b**) is formed in good yield. Compound **7b** is quite stable to CO loss under ordinary daylight and was recrystallized from acetone/ $CH_2Cl_2$ / $Et_2O$ , during 1 week, to give yellow crystals.



For this asymmetric hydride  $[IndCpWH(CO)]BF_4$  (**7b**) the  $^1H$ -NMR spectrum in  $CD_3COCD_3$  shows the typical pattern for the resonances of the planar  $\eta^5$ -indenyl: two sets of signals for the  $C_6$  ring protons ( $H^{5-8}$ ) at  $\delta$  7.79 and 7.47 ppm, two singlets at  $\delta$  6.17 and 6.15 ppm ( $H^{1/3}$ ) and a triplet at  $\delta$  6.13 ppm ( $H^2$ ) (see Scheme 4 for the numbering). The hydride signal appears at  $\delta$



Scheme 2.



Scheme 3.

−9.05 ppm. The IR spectrum of **7b** shows one medium  $\nu(\text{W}-\text{H})$  absorption at  $1840\text{ cm}^{-1}$  and one strong  $\nu(\text{C}\equiv\text{O})$  absorption at  $2009\text{ cm}^{-1}$ . This value is similar to the ones found for  $[\text{Cp}_2\text{WH}(\text{CO})]^+$  ( $\nu(\text{C}\equiv\text{O})\ 2015\text{ cm}^{-1}$ ) [5],  $[\text{IndCpMoH}(\text{CO})]^+$  ( $\nu(\text{C}\equiv\text{O})\ 2019\text{ cm}^{-1}$ ) [1b] and  $[\text{Cp}_2\text{MoH}(\text{CO})]^+$  ( $\nu(\text{C}\equiv\text{O})\ 2020\text{ cm}^{-1}$ ) [1b,6] suggesting little back-bonding to  $\text{M}(\text{IV})$  in these complexes.

Compounds **7a** and **7b** were crystallographically characterized by single crystal X-ray diffraction. Key bond distances and angles together with the characteristic slip and geometry parameters are listed in Table 1. Both monocationic complexes (Figs. 1 and 2) are monomeric. The geometry around the tungsten atom is best described by a distorted tetrahedron. A projection on the W, C1, C2 and W, C, H plane (Figs. 1 and 2) shows that the Cp rings adopt approximately staggered conformation.

Complex **7a** is another example of the extensive list of diene complexes of the general type  $[\text{CpM}(\eta^4\text{-diene})\text{L}_2]$  that we have recently studied by molecular mechanics and molecular orbital methods. In this respect, and according to the definitions given in that work [9], the crystal structure of **7a** corresponds to the *exo* conformer (the bridgehead  $\text{CH}_2$  being *trans* to the indenyl or Cp as in Eq. (1) with a  $\beta$  angle of  $73.8^\circ$  (see Table 1) which is a normal value for other cyclopentadiene complexes of this family [9]. The general results of the molecular mechanics calculations and the experi-

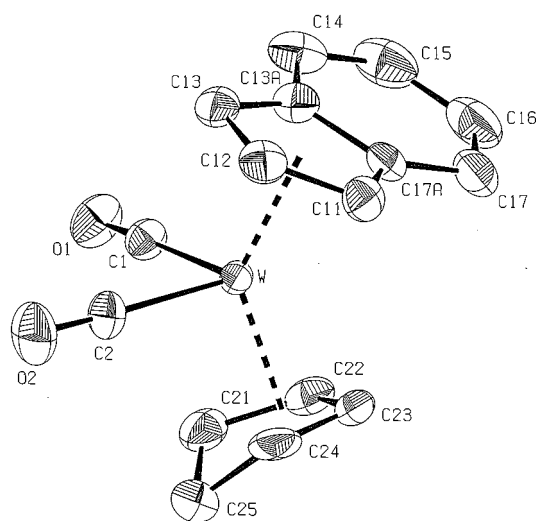


Fig. 1. ORTEP style plot of **7a** with the atomic labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

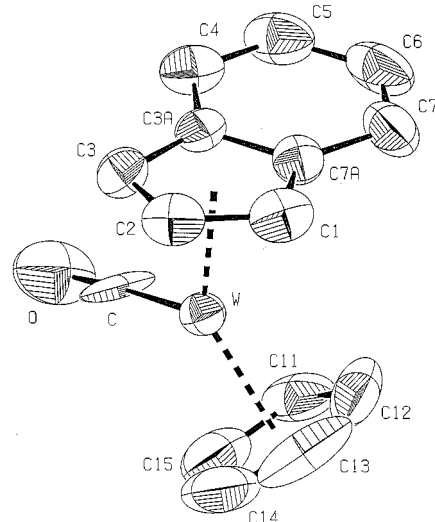


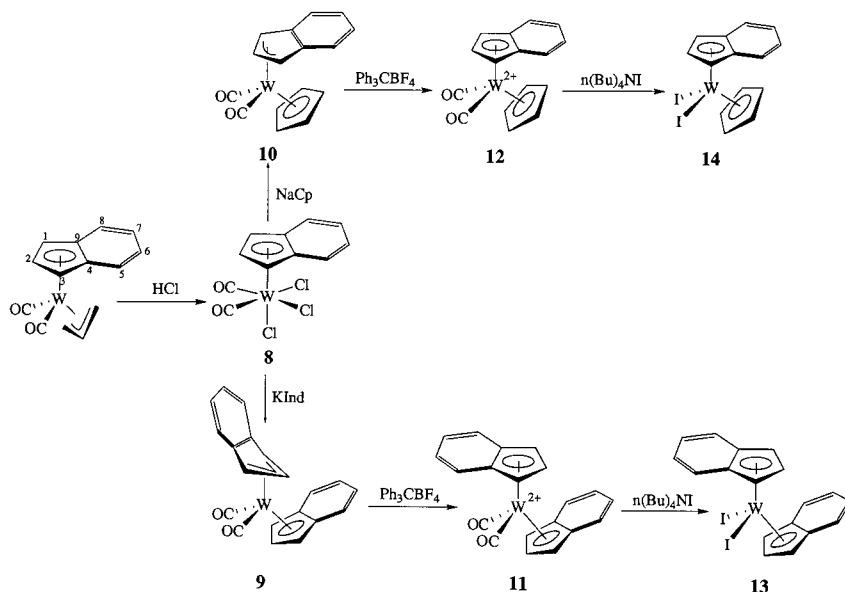
Fig. 2. ORTEP style plot of **7b** with the atomic labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

mental facts taken from crystallographic data show that the *exo* conformation in these complexes is exceptional and, indeed, a search in the Cambridge Structural Database [10] for all transition metal complexes of type  $[\text{CpM}(\eta^4\text{-diene})\text{LL}']$  revealed  $[\text{CpW}(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$  as the only other one of this type [11]. It is, therefore, rather interesting to note that the molecular mechanics calculations performed for a value of  $\beta = 79^\circ$  predicted that the complex  $[\text{CpMo}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})_2]^+$  prefers the *exo* conformation, that is, the same conformation experimentally observed for complex  $[\text{IndW}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})_2]^+$ , (**7a**) [9]. However, the value of these predictions must still be taken with some precautions due to the low energy differences between both *exo* and *endo* conformations [9].

All crystals of  $[\text{IndCpWH}(\text{CO})]\text{BF}_4$  (**7b**) were twinned. The fact that the twinning problem could not be resolved properly during the refinement prevents us from discussing in detail the bonding parameters. However, the overall core geometry of the cationic moiety corresponds (Table 1) to the related compound  $[\text{Cp}_2\text{WH}(\text{CO})][\text{Co}(\text{CO})_4]$  reported by Ito et al. [5].

In general, the observed values for the ring-slippage parameters are typical for  $\eta^5$ -coordination in **7a** and **7b** and are consistent with those given in the literature [1b,8]. Faller et al. introduced a ‘rule of thumb’ [8] which states that the preferred ring orientation of an indenyl ligand coordinated to a  $\text{ML}_2\text{L}'$  fragment will place the six-membered ring *trans* to the ligand with the higher *trans* influence. This rule predicts the situation in **7b** with the hydride atom *trans* to C3A and C7A. Likewise, the prediction also holds for  $[\text{IndCpMo}(\text{CO})(\text{NCMe})]^{2+}$  where the benzene ring lies *trans* to the CO [1a,b].

Given the known similarities that seem to exist



Scheme 4.

between the chemistry of the mixed-ring molybdenocenes [IndCpMoL<sub>2</sub>]<sup>n+</sup> bis-cyclopentadienyl congeners, [Cp<sub>2</sub>MoL<sub>2</sub>]<sup>n+</sup> in the Mo(IV) oxidation state, **7b** is expected to open the way to a large number of other hydride derivatives of the type [IndCpWHL]<sup>+</sup>.

As we mentioned in the introduction, the impossibility of isolating [IndW(η-IndH)(CO)<sub>2</sub>]<sup>+</sup> precludes the synthesis of the symmetric hydride complex [Ind<sub>2</sub>WH(CO)]<sup>+</sup> by the H migration route, as in Scheme 2. This prompted us to find an alternative method to prepare the complexes of the symmetric Ind<sub>2</sub>W fragment.

An attractive alternative would be complex IndW(CO)<sub>2</sub>Cl<sub>3</sub>, which might be expected to react like its Mo analogue to give Ind<sub>2</sub>W(CO)<sub>2</sub> complexes [12].

Reaction of IndW(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> [2a] with excess of HCl gas in CH<sub>2</sub>Cl<sub>2</sub> at room temperature produces IndWCl<sub>3</sub>(CO)<sub>2</sub> (**8**) ca. 80% yield, according to Eq. (2):



The IR spectrum of **8** shows two strong ν(CO) absorptions at 2065 and 2002 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum in NCCD<sub>3</sub> is compatible with the η<sup>5</sup>-coordination mode of the indenyl ligand, the spectrum presents one multiplet in the aromatic region at δ 7.58–7.45 (H<sub>5–8</sub>), a doublet at δ 5.90 (H<sub>1/3</sub>), and a triplet at δ 5.62 ppm for H<sub>2</sub>. However, decomposition of this solution takes place after a short period of time.

Reaction of IndWCl<sub>3</sub>(CO)<sub>2</sub> (**8**) with KInd in THF at low temperature affords IndW(η<sup>3</sup>-Ind)(CO)<sub>2</sub> (**9**) in high yield (Scheme 4). This well known product was the first bent η<sup>3</sup>-indenyl complex to be structurally characterized but had been produced in a minute 1.5% yield [13]. The same kind of reaction takes place with NaCp

giving the mixed-ring complex CpW(η<sup>3</sup>-Ind)(CO)<sub>2</sub> (**10**) that we reported earlier as the result of the deprotonation of [IndW(η<sup>4</sup>-C<sub>5</sub>H<sub>6</sub>)(CO)<sub>2</sub>]BF<sub>4</sub> [2a]. The IR and <sup>1</sup>H-NMR spectra of both **9** and **10** are very similar to the spectra of the molybdenum analogues CpMo(η<sup>3</sup>-Ind)(CO)<sub>2</sub> [1b] and IndMo(η<sup>3</sup>-Ind)(CO)<sub>2</sub> [1b,12a].

Reaction of **9** and **10** with two equivalents of Ph<sub>3</sub>CBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature give the dicationic [Ind<sub>2</sub>W(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**11**) and the known [IndCpW(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**12**) [2a], respectively.

The complex **11** was characterized by ν(CO) stretching vibrations at 2118 and 2077 cm<sup>-1</sup>. The rather high wavenumbers are expected for a dicationic high oxidation state complex with a weak W–CO back-bonding. The <sup>1</sup>H-NMR spectrum of **11** can be measured in CD<sub>3</sub>CN without signs of CO substitution by NCMc solvent, again in contrast with the Mo analogue where such substitution is facile and gives [Ind<sub>2</sub>Mo(NCMc)(CO)]<sup>2+</sup> [12]. As expected for this type of dication, the indenyl protons are rather deshielded appearing as two multiplets in the aromatic region at δ 7.74 and 7.58 (H<sub>5–8</sub>), a doublet at δ 6.37 (H<sub>1/3</sub>), and a triplet at δ 6.03 ppm for H<sub>2</sub> (four resonances with a 4:4:4:2 ratio).

The di-iodides IndCp'WI<sub>2</sub>, [Cp' = Ind (**13**); Cp (**14**)] are prepared in a good yield from the dicationic **11** and **12**, respectively, by treatment with excess of (n-Bu)<sub>4</sub>NI in acetone for ca. 30 h under reflux and visible light irradiation. Like Cp<sub>2</sub>WI<sub>2</sub> (**6**), solution spectroscopic methods can not be applied to the compound characterization due to their high insolubility in the common organic solvents. However, the IR of all these di-iodides are very similar and the analytical data agrees with the proposed formulation.

Table 1  
Selected interatomic distances (pm) and angles (°) for [IndW( $\eta^4$ -C<sub>5</sub>H<sub>6</sub>)(CO)<sub>2</sub>]BF<sub>4</sub> (**7a**), [IndCpWH(CO)]BF<sub>4</sub> (**7b**) and [Cp<sub>2</sub>WH(CO)][Co(CO)<sub>4</sub>] (**7c**)

	<b>7a</b> <sup>a</sup>	<b>7b</b> <sup>b</sup>	<b>7c</b> [5] <sup>c</sup>			
W–C(m1)	236.8(5)	225(2)	231			
W–C(m2)	225.6(4)	225(2)	228			
W–C(m3)	224.5(4)	230(2)	226			
W–C(m4)	232.9(5)	230(2)	231			
W–C(m5)	292.7(7)	225(2)	232			
W–C(n1)	233.1(5)	230(2)	225			
W–C(n2)	230.0(5)	227(1)	229			
W–C(n3)	227.8(5)	223(1)	230			
W–C(n3A)	240.3(5)	239(1)	228			
W–C(n7A)	241.9(4)	239(2)	228			
W–C(1)	202.5(4)	198(2)	198			
W–C(2)	198.0(5)					
C(n1)–C(n2)	140.8(6)	141(2)	145			
C(n1)–C(n7A)	142.0(7)	142(2)	139			
C(n2)–C(n3)	143.1(7)	142(2)	133			
C(n3)–C(n3A)	144.7(7)	143(2)	145			
C(n3A)–C(n4)	141.7(8)	142(2)				
C(n3A)–C(n7A)	143.3(7)	141(2)	139			
C(n4)–C(n5)	135.7(9)	134(3)				
C(n5)–C(n6)	141.9(10)	144(3)				
C(n6)–C(n7)	137.2(10)	135(3)				
C(n7)–C(n7A)	141.1(6)	143(2)				
C(1)–W–C(2)	87.9(2)					
C(1)–W–Cind	107.9	105	105			
C(1)–W–Cp	99.0	102	106			
C(2)–W–Cind	114.5					
C(2)–W–Cp	80.0					
Cind–W–Cp	149.5	144	144			
	indenyl	CpH-part	indenyl	Cp-part	CpC <sub>1–5</sub>	CpC <sub>6–10</sub>
<i>D</i> =   <i>S</i>   (pm)	14.2		15.8	7.6	4.7	10.2
<i>s</i> (°)	22.5		19.2	19.5	36.6	52.3
<i>Y</i> (°)	4.1		4.6	2.2	1.4	3.0
$\overline{\text{DM-C}}$ (pm)	10.8		12.3	5.0	2.5	3.2
<i>W</i> (°)	4.8		5.4	1.4	3.4	1.6
$\alpha$ (°)		149.5				
$\beta$ (°)		73.8				

<sup>a</sup> *m* = 2, *n* = 1; Cind denotes centroid C(11–17A); Cp denotes midpoint of C(21) and C(24).

<sup>b</sup> *m* = 1, *n* = 0; Cind denotes centroid C(1–7A); Cp denotes centroids C(11–15); C(1) eq. C.

<sup>c</sup> *m* = C(6–10), *n* = C(1–5); Cind denotes centroid C(1–5); Cp denotes centroids C(6–10); C(1) eq. C(11). Slip and geometry parameters are defined in [7–9].

Following a similar approach, it could be shown that the known CpWCl<sub>3</sub>(CO)<sub>2</sub> (**15**) [14] could also be prepared by reaction of CpW( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> with excess gaseous HCl. However, treatment of **15** with KInd in THF, at low temperature, affords the CpW(CO)<sub>3</sub>Cl [15a] (53% yield) instead of the expected mixed ring complex CpW( $\eta^3$ -Ind)(CO)<sub>2</sub> (**10**). This large difference in the reactivity between CpWCl<sub>3</sub>(CO)<sub>2</sub> and IndWCl<sub>3</sub>(CO)<sub>2</sub> is difficult to explain. We believe that the stabilization of the reduced oxidation state provided by the ring-slippage of the indenyl ligand at some point along the reaction pathway is responsible for the formation of the products **9** and **10**. Such stabilization

might not be available when the reaction starts from CpWCl<sub>3</sub>(CO)<sub>2</sub>. Indeed, the latter complexes are very reactive and unpredictable species and earlier results on the reaction of CpWCl<sub>3</sub>(CO)<sub>2</sub> [14] and CpMoCl<sub>3</sub>(CO)<sub>2</sub> [14] with NaCp also show a different pattern of reactivity whereby ring substituted products, e.g. CpW( $\eta^3$ -C<sub>5</sub>H<sub>5</sub>Cp<sub>2</sub>)(CO)<sub>2</sub> were obtained [15b,c].

### 3. Conclusions and prospects

A convenient stepwise preparation of tungstenocene derivatives Cp'<sub>2</sub>WX<sub>2</sub> (Cp' = Cp, Ind) and their mixed-

ring indenyl substituted analogues, IndCpWX<sub>2</sub> has been achieved and the first indenyl modified hydride, [IndCpWH(CO)]BF<sub>4</sub> was crystallographically characterized. An alternative strategy had to be developed in order to achieve the high yield synthesis of complexes of the symmetric Ind<sub>2</sub>W fragment. This strategy, which comprises the reaction of IndWCl<sub>3</sub>(CO)<sub>2</sub> with KInd to give Ind<sub>2</sub>W(CO)<sub>2</sub> was extended to the preparation of IndCpW(CO)<sub>2</sub>. This method opens the door to the synthesis of other metallocene analogues containing fluorenyl and related ligands, which may provide a fine modulation of the electronic and stereochemical properties of these modified metallocenes.

Still in keeping with the existing parallel between the chemistry of Cp<sub>2</sub>M(IV) and IndCpM(IV) derivatives (M = Mo, W), the relatively straightforward synthesis of several di-iodides, Cp'<sub>2</sub>WI<sub>2</sub> (Cp' = Cp, Ind) foresees the possibility of the synthesis and study of a number of alkyl and hydride derivatives, e.g. Cp'<sub>2</sub>WR<sub>2</sub>, that may have enhanced insertion reactivity in comparison with their well known Cp<sub>2</sub>M counterparts [16].

## 4. Experimental

### 4.1. Materials and procedures

All preparations and manipulations were carried out under an atmosphere of dinitrogen/argon with standard Schlenk-line and glovebox techniques. Solvents were dried by standard procedures (THF, Et<sub>2</sub>O, toluene and hexane over Na/benzophenone ketyl; CH<sub>3</sub>COCH<sub>3</sub> over anhydrous K<sub>2</sub>CO<sub>3</sub>; CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, NCMe and triethylamine over P<sub>2</sub>O<sub>5</sub>), distilled under argon and kept over 4 Å molecular sieves (3 Å for NCMe).

Microanalyses were performed at the ITQB. <sup>1</sup>H-NMR spectra were measured on a Bruker CXP 300. <sup>1</sup>H and <sup>13</sup>C chemical shifts were reported on the scale relative to SiMe<sub>4</sub> (δ 0.0). Infrared spectra were obtained using a Unicam Mattson model 7000 FTIR spectrometer.

The following reagents were prepared as published: [IndW(η<sup>4</sup>-C<sub>5</sub>H<sub>6</sub>)(CO)<sub>2</sub>]BF<sub>4</sub> [2a], Cp'W(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> [Cp' = Cp, Ind] [2a], Ph<sub>3</sub>CBF<sub>4</sub> [17].

### 4.2. Preparation of [Cp<sub>2</sub>W(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (2)

Addition of a solution of *n*-Bu<sub>4</sub>[Br<sub>3</sub>] (0.21g, 0.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> to a solution of CpW(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> (0.16 g, 0.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> caused immediate precipitation of a white solid. After stirring for 1 h the precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (10 ml), Et<sub>2</sub>O and dried. Quick dissolution of this compound in the minimum amount of water and addition of a saturated solution of [NH<sub>4</sub>][BF<sub>4</sub>] gave an abundant white precipitate, which was filtered off, washed with

water and dried under vacuum. Yield: >90%. IR (KBr) and <sup>1</sup>H-NMR data are in agreement with Ref. [2a].

### 4.3. Preparation of [Cp<sub>2</sub>W(NCMe)(CO)][BF<sub>4</sub>]<sub>2</sub> (3)

A solution of [Cp<sub>2</sub>W(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (0.25 g, 0.45 mmol) in NCMe (20 ml) was irradiated with a 60 W tungsten lamp for 12 h. After concentration to ca. 5 ml and addition of ether, the yellow crystalline complex that formed was filtered off and washed with ether (10 ml). Yield: 91%. Anal. Found: C 27.89; H 2.28; N 2.40. Calc. for C<sub>13</sub>H<sub>13</sub>B<sub>2</sub>F<sub>8</sub>ONW: C 28.05; H 2.35; N 2.52%. Selected IR (KBr, ν cm<sup>-1</sup>): 2322, 2292 m, (N≡C), 2053 vs, (C≡O). Selected IR (NCMe, ν cm<sup>-1</sup>): 2066 vs, (C≡O). <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 300 MHz, r.t., δ ppm): 6.21 (s, 10H, Cp); 2.57 (s, 3H, NCMe). <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 300 MHz, r.t., δ ppm): 191.7 (CO), 117.8 (s, CD<sub>3</sub>CN and NCMe), 97.1 (Cp), 5.8 (NCMe)

### 4.4. Preparation of [Cp<sub>2</sub>WBr(CO)]<sup>+</sup> (4)

Solid (*n*-Bu)<sub>4</sub>NBr (2.71 mmol) was added to a solution of [Cp<sub>2</sub>W(CO)<sub>2</sub>]<sup>2+</sup> (2.71 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/NMF (15:2 ml) at room temperature. After 3 h the solution was concentrated to ca. 3 ml and addition of Et<sub>2</sub>O precipitated the violet product, which was filtered, washed with hot THF (5 ml), ether (10 ml) and dried in vacuum. Yield: 83%. IR (KBr) and <sup>1</sup>H-NMR data are in agreement with Ref. [3].

### 4.5. Preparation of Cp<sub>2</sub>WI<sub>2</sub> (6)

Solid (*n*-Bu)<sub>4</sub>NI (0.48 g, 1.35 mmol) was added to a solution of [Cp<sub>2</sub>W(NCMe)(CO)][BF<sub>4</sub>]<sub>2</sub> (0.25 g, 0.45 mmol) in acetone (20 ml) at room temperature. After 3 h the solution was violet due to [Cp<sub>2</sub>WI(CO)][BF<sub>4</sub>]. The solution was irradiated and refluxed for 48 h. A green precipitate formed slowly, and the solution became almost colourless. After being concentrated and cooled the precipitate was filtered, and washed CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Yield: 83%. EA, IR (KBr) and <sup>1</sup>H-NMR data are in agreement with Ref. [4].

### 4.6. Preparation of [IndCpWH(CO)]BF<sub>4</sub> (7b)

A solution of [IndW(η<sup>4</sup>-C<sub>5</sub>H<sub>6</sub>)(CO)<sub>2</sub>]BF<sub>4</sub> (0.18 g, 0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/acetone (20 ml) was stirred for 19 h and irradiated with a 60 W tungsten lamp. The volume was halved and ether added to precipitate a yellow complex which was filtered, washed with ether (2 × 10 ml) and dried in vacuum. Recrystallization from acetone/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (2:3:15) under daylight gave, in 1 week, yellow crystals. Yield: 87%. Found: C 37.40; H 2.70. Calc. for C<sub>15</sub>H<sub>13</sub>BF<sub>4</sub>OW: C 37.54; H 2.73%. Selected IR (KBr, ν cm<sup>-1</sup>) 2009 vs, (C≡O), 1840 m,

(hydride).  $^1\text{H-NMR}$  ( $d^6\text{Me}_2\text{CO}$  300 MHz, r.t.,  $\delta$  ppm): 7.79 (m, 2H,  $\text{H}^{5-8}$ ); 7.47 (m, 2H,  $\text{H}^{5-8}$ ); 6.17 (s, 1H,  $\text{H}^{1/3}$ ); 6.15 (s, 1H,  $\text{H}^{1/3}$ ); 6.13 (t, 1H,  $\text{H}^2$ ); 5.59 (s, 5H, Cp);  $-9.05$  (s, 1H, W–H).

#### 4.7. Preparation of $\text{IndWCl}_3(\text{CO})_2$ (**8**)

Gaseous HCl was bubbled through a solution of  $\text{IndW}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2$  (1.90 g, 4.82 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 ml) for 3 min, and the reaction mixture was stirred for a further 1 h to ensure completion of the reaction. After concentration to ca. 20 ml and addition of  $\text{Et}_2\text{O}$ , an orange precipitate was obtained. The solid was filtered off, washed with  $\text{Et}_2\text{O}$ , and dried under vacuum. Yield: 1.75 g (78%). Selected IR (KBr,  $\text{cm}^{-1}$ ): 2065, 2002 vs,  $\nu(\text{C}=\text{O})$ . Anal. Calc. for  $\text{C}_{11}\text{H}_7\text{WCl}_3\text{O}_2$ : C, 28.64; H, 1.53. Found: C, 28.51; H, 1.33.  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$  300 MHz, r.t.,  $\delta$  ppm): 7.58–7.45 (m, 4H,  $\text{H}^{5-8}$ ); 5.90 (d, 2H,  $\text{H}^{1/3}$ ); 5.62 (t, 1H,  $\text{H}^2$ ).

#### 4.8. Preparation of $\text{IndW}(\eta^3\text{-Ind})(\text{CO})_2$ (**9**)

A mixture of KInd (0.25 g, 1.62 mmol) and  $\text{IndWCl}_3(\text{CO})_2$  (0.75 g, 1.62 mmol) was weighed in a Schlenk tube in the glovebox and placed in a cold bath at  $-80^\circ\text{C}$ . Precooled THF was added, and the temperature was slowly raised to room temperature. After 16 h, the mixture was taken to dryness and the residue was extracted with dichloromethane. The filtrate was taken to dryness. Yield: 0.65 g (85%). EA and IR (KBr) data are in agreement with Ref. [13].

#### 4.9. Preparation of $\text{CpW}(\eta^3\text{-Ind})(\text{CO})_2$ (**10**)

A mixture of NaCp (0.34 g, 2.16 mmol) and  $\text{IndWCl}_3(\text{CO})_2$  (1.0 g, 2.16 mmol) was weighed in a Schlenk tube in the glovebox and placed in a cold bath at  $-80^\circ\text{C}$ . Precooled THF was added, and the temperature was slowly raised to room temperature. After 16 h stirring, the mixture was taken to dryness and the residue was extracted with dichloromethane. The solution obtained was concentrated to dryness. Yield: 0.57 g (63%). EA and IR (KBr) data are in agreement with Ref. [2a].

#### 4.10. Preparation of $[\text{Ind}_2\text{W}(\text{CO})_2][\text{BF}_4]_2$ (**11**)

Solid  $\text{Ph}_3\text{CBF}_4$  (0.49 g, 1.50 mmol) was added to a solution of  $\text{IndW}(\eta^3\text{-Ind})(\text{CO})_2$  (0.35 g, 0.74 mmol) in dichloromethane at room temperature. The reaction mixture was stirred for 8 h and a white precipitate was formed. The solid was filtered off, washed with  $\text{Et}_2\text{O}$  and dried under vacuum. Yield: 0.38 g (80%). Found: C 37.40; H 2.20. Calc. for  $\text{C}_{20}\text{H}_{14}\text{B}_2\text{F}_8\text{O}_2\text{W}$ : C

37.31; H 2.19%. Selected IR (Nujol,  $\nu\text{ cm}^{-1}$ ) 2118, 2077 vs, ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 300 MHz, r.t.,  $\delta$  ppm): 7.74 (m, 4H,  $\text{H}^{5-8}$ ); 7.58 (m, 4H,  $\text{H}^{5-8}$ ); 6.88 (d, 4H,  $\text{H}^{1/3}$ ); 6.41 (t, 2H,  $\text{H}^2$ ).

#### 4.11. Preparation of $[\text{IndCpW}(\text{CO})_2][\text{BF}_4]_2$ (**12**)

Solid  $\text{Ph}_3\text{CBF}_4$  (0.89 g, 2.71 mmol) was added to a solution of  $\text{CpW}(\eta^3\text{-Ind})(\text{CO})_2$  (0.57 g, 1.35 mmol) in dichloromethane at room temperature. The reaction mixture was stirred for 8 h and a white precipitate was formed. The solid was filtered off, washed with  $\text{Et}_2\text{O}$  and dried under vacuum. Yield: 0.65 g (81%). EA and IR (KBr) data are in agreement with Ref. [2a].

#### 4.12. Preparation of $\text{Ind}_2\text{WI}_2$ (**13**)

Solid (*n*-Bu) $_4\text{NI}$  (0.67 g, 1.82 mmol) was added to a solution of  $[\text{Ind}_2\text{W}(\text{CO})_2][\text{BF}_4]_2$  (0.39 g, 0.60 mmol) in dichloromethane (20 ml) at room temperature. After 6 h the solution was violet due to  $[\text{Ind}_2\text{WI}(\text{CO})][\text{BF}_4]$ . The solution was irradiated and refluxed for 28 h. A green precipitate formed slowly, and the solution became almost colourless. After being concentrated and cooled the precipitate was filtered, and washed with  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . Yield: 82%. Found: C 32.55; H 2.23. Calc. for  $\text{C}_{18}\text{H}_{14}\text{WI}_2$ : C 32.37; H 2.11%. Selected IR (KBr,  $\nu\text{ cm}^{-1}$ ) 3108 m, 3100 m, 1474 s, 1381 m, 1263 m, 976 vs, 802 vs, 737 m, 631 w.

#### 4.13. Preparation of $\text{IndCpWI}_2$ (**14**)

Solid (*n*-Bu) $_4\text{NI}$  (0.78 g, 2.13 mmol) was added to a solution of  $[\text{IndCpW}(\text{CO})_2][\text{BF}_4]_2$  (0.42 g, 0.71 mmol) in dichloromethane (20 ml) at room temperature. After 6 h the solution was violet due to  $[\text{IndCpWI}(\text{CO})][\text{BF}_4]$ . The solution was irradiated and refluxed for 48 h. A green precipitate formed slowly, and the solution became almost colourless. After being concentrated and cooled the precipitate was filtered, and washed with  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . Yield: 75%. Found: C 27.52; H 1.96. Calc. for  $\text{C}_{14}\text{H}_{12}\text{WI}_2$ : C 27.21; H 1.96%. Selected IR (KBr,  $\nu\text{ cm}^{-1}$ ) 3121 m, 3103 m, 1474 s, 1381 m, 972 m, 800 vs, 736 m, 544 m.

#### 4.14. Preparation of $\text{CpWCl}_3(\text{CO})_2$ (**15**)

Gaseous HCl was bubbled through a solution of  $\text{CpW}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2$  (1.30 g, 3.76 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) for 2 min, and the reaction mixture was stirred for a further 1 h to ensure completion of the reaction. After concentration to ca. 20 ml and addition of  $\text{Et}_2\text{O}$ , an orange precipitate was obtained. The

solid was filtered off, washed with Et<sub>2</sub>O, and dried under vacuum. Yield: 81%. <sup>1</sup>H-NMR and IR (solution) data are in agreement with Ref. [15a].

## 5. X-ray crystallography

### 5.1. General procedure

Suitable single crystals for the X-ray diffraction studies were grown by standard techniques from saturated solutions of **7a** in *n*-hexane/(CH<sub>3</sub>)<sub>2</sub>O/Et<sub>2</sub>O and **7b** in CH<sub>2</sub>Cl<sub>2</sub>/(CH<sub>3</sub>)<sub>2</sub>O/Et<sub>2</sub>O at room temperature. Both structures were solved by a combination of Patterson syntheses and difference-Fourier syntheses and refined by full-matrix least-squares calculations. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for X-ray Crystallography [18]. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V [19] system, including the programs PLATON-92 [20], PLUTON-92 [20], SHELXS-86 [21], and SHELXL-93 [22]. A summary of the crystal and experimental data is reported in Table 2.

### 5.2. Data collection, structure solution and refinement for complex **7a**

Preliminary examination and data collection were carried out on a Kappa CCD area detecting diffraction system (Nonius; Mach3) equipped with a rotating anode (Nonius FR591; 50 kV; 80 mA; 4.0 kW) and graphite monochromated Mo–K<sub>α</sub> radiation. Data collection was performed at 163 K within the Θ range of 3.59 < Θ < 30.01° with an exposure time of 10 s per frame (Θ offset = 10°, φ start = 0.0°, φ end = 360°, Δφ = 1°, dx = 40.0). A total number of 7500 reflections were collected. Raw data were reduced and scaled with the programs Denzo and HKL [23,24]. After merging a sum of 3480 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption effects were applied with the program DIFABS [20]. The unit cell parameters were obtained by full-matrix least-squares refinements of 10073 reflections. All ‘heavy atoms’ of the asymmetric unit were refined anisotropically. All hydrogen atoms were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with a SHELXL-93 weighting scheme and stopped at shift/err = 0.001.

Table 2

Crystallographic data for [IndW(η<sup>4</sup>-C<sub>5</sub>H<sub>6</sub>)(CO)<sub>2</sub>]<sub>2</sub>BF<sub>4</sub> (**7a**) and [IndCpWH(CO)]BF<sub>4</sub> (**7b**)

	<b>7a</b>	<b>7b</b>
Chemical formula	C <sub>16</sub> H <sub>13</sub> BF <sub>4</sub> O <sub>2</sub> W	C <sub>15</sub> H <sub>13</sub> BF <sub>4</sub> OW
Formula weight	507.92	479.92
Colour/shape	Yellow-brown/fragment	Yellow/fragment
Crystal size (mm)	0.64 × 0.30 × 0.10	0.21 × 0.19 × 0.06
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (pm)	729.98(3)	715.0(3)
<i>b</i> (pm)	783.06(3)	1484.0(6)
<i>c</i> (pm)	1419.20(4)	1389.2(6)
α (°)	100.210(2)	90
β (°)	104.557(2)	99.18(3)
γ (°)	93.441(2)	90
<i>V</i> (10 <sup>6</sup> pm <sup>3</sup> )	768.09(5)	1455(1)
<i>Z</i>	2	4
<i>T</i> (K)	163	300
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	2.196	2.191
μ (mm <sup>-1</sup> )	7.57	7.98
<i>F</i> <sub>000</sub>	480	904
λ (pm)	71.073	71.073
Device/scan method	CCD/φ-rotation	MACH3/Θ – 2Θ
Θ range (°)	3.59–30.01	2.75–26.37
Data collected ( <i>h, k, l</i> )	±10, ±11, ±18	±8, –18, –17
No. of reflections collected	7500	2797
No. of independent reflections	3480	2686
No. of observed reflections	3480 (all data)	2686 (all data)
No. of parameters refined	269	199
<i>R</i> <sub>int</sub>	0.0231	0.0317
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0236	0.0680
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.0581	0.1378
Goodness-of-fit (GoF) <sup>c</sup>	1.057	1.185
Weights <i>a/b</i> <sup>d</sup>	0.0283/1.7454	0.0358/38.5034
Δρ <sub>max/min</sub> (e Å <sup>-3</sup> )	+0.85/–1.04	+4.23/–1.11 <sup>e</sup>

$$^a R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

$$^c \text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$$

$$^d w \equiv 1/[\sigma^2(F_o^2) + (a * P)^2 + b * P] \text{ with } P: [\max(0 \text{ or } F_o^2) + 2F_o^2]/3$$

<sup>e</sup> The remarkable high values are due to an unsatisfied correction for absorption effects and to an unresolved twin problem.

### 5.3. Data collection, structure solution and refinement for complex **7b**

Preliminary examination and data collection were carried out on an automatic four-circle (Nonius; Cad4) equipped with a rotating anode (Nonius FR591; 40 kV; 30 mA; 1.2 kW) and graphite monochromated Mo–K<sub>α</sub> radiation. Data collection was performed at 300 K within the Θ range of 2.75 < Θ < 26.37° (scan modulus = Θ – 2Θ; scan time = 60 s, scan width = (1.05 + 0.50 tan Θ)). A total number of 3227 reflections were collected. 126 systematic absent reflections together with 304 negative intensities were rejected from the original data set. After merging a sum of 2686 independent reflections remained and were used for all calculations. Data were corrected for Lorentz



and polarization effects. Corrections for absorption effects were applied with the program DIFABS [20]. The unit cell parameters were obtained by full-matrix least-squares refinements of 18 high angle data with the programs SET4 and CELLDIM [25]. All 'heavy atoms' of the asymmetric unit were anisotropically refined. All hydrogen atoms were calculated in ideal positions (riding model), included in the structure factor calculations, but not refined except the hydride hydrogen atom which was neither found in the difference Fourier map nor calculated. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with a SHELXL-93 weighting scheme and stopped at shift/err = 0.001.

## 6. Supplementary material available

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-7a, and CCDC-7b. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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