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Synthesis of mixed-ring indenyl analogues of tungstenocene

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Abstract

A new stepwise preparation of tungstenocene derivatives $[Cp_2WL_2][BF_4]_2$ (L=CO or NCMe) from $[W(CO)_6]$ via $[CpW(\eta^3\text{-}C_3H_5)(CO)_2]$ and $[CpW(\eta^4\text{-}C_5H_6)(CO)_2]BF_4$ is described. Similar preparations, starting from $[(\eta^5\text{-}C_9H_7)W(\eta^3\text{-}C_3H_5)(CO)_2]$, lead to the first mixed-ring indenyl analogues of tungstenocene, $[IndCpWL_2][BF_4]_2$ (L = CO or NCMe) and $[CpW(\eta^3\text{-Ind})(CO)_2]$. Reversible ring slippage between $[(\eta^5\text{-}C_9H_7)W(CO)_2(NCMe)_2]BF_4$ and $[(\eta^3\text{-}C_9H_7)W(CO)_2(NCMe)_3]BF_4$ is observed.

Keywords: Tungstenocene; Molybdenocene; Indenyl compounds; Preparation; Metallocene; Cyclopentadienyl

1. Introduction

Recent years have witnessed an increasing effort towards the modification of steric, electronic, and other properties of well known organometallic ligands to achieve tunable reactivity control of their complexes. In this way, replacement of the cyclopentadienyl (Cp = η^5-C_5H_5) by other η^5 cyclic analogues (Cp′) has been a successful means of controlling the stability, reactivity and several other physicochemical properties of many organometallic complexes. Permethylated cyclopentadienyl, Cp*, (η^5-C_5Me_5) is the most common example of such a substitute, and has allowed the characterization of many complexes and reaction intermediates often inaccessible to chemical and/or spectroscopic studies in the case of the corresponding Cp species. Indenyl (Ind = η^5-C_9H_7) complexes represent another interesting type of Cp substitution, insofar as they display increased reactivity when compared with their Cp analogues [1a]. These substitutions have recently brought an extremely interesting series of developments in Group 4 metallocene chemistry since it was shown that chiral *ansa*-metallocenes bearing different η^5 rings, e.g. $[\{(\eta^5\text{-Ind})\text{-}CR_2\text{-}(\eta^5Cp)\}MX_2]$(M = Ti or Zr) led to stereochemical control of olefin polymerization [1b]. The electronic and stereochemical changes promoted by ring substitution on titanocene dichlorides have recently been studied [1c].

With regard to Group 6 metallocenes, the number of ring-substituted derivatives is much smaller due to the difficulty of preparing these complexes from simple starting materials [2a]. A simplified preparation of the parent dihalide $[Cp_2WCl_2]$ has been reported only very recently [2b]. Differentially-substituted metallocenes of type $[Cp(C_5H_4R)MX_2]$ have been reported by Cooper [2c,d] but the only similar indenyl derivatives known are $[(\eta^5\text{-}C_5H_4^iPr)Mo(\eta^3\text{-}C_9H_7)(N^tBu)]$ [2e] and the putative metallocene precursors $[(\eta^5\text{-Ind})W(\eta^3\text{-Ind})(CO)_2]$ [2f] and $[(\eta^5\text{-Ind})Mo(\eta^3\text{-Ind})(dppe)]$ [2g]. In a previous communication we reported a synthetic protocol for the preparation of molybdenocene and mixed ring molybdenocene derivatives, one of which $[IndCpMo(CO)(NCMe)][BF_4]_2$, was structurally characterized [3].

We now report the extension of this route to the preparation of tungstenocene derivatives as well as their indenyl-containing mixed-ring analogues.

2. Results and discussion

2.1. Preparation of tungstenocene complexes

The synthetic route used is based, as in the molybdenum case, on the transformations of the cationic diene complex $[CpW(\eta^4\text{-}C_5H_6)(CO)_2]BF_4$ (1). Three

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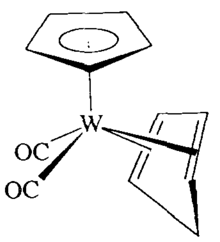
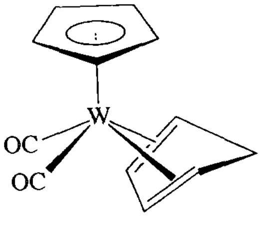
possibilities are depicted in Scheme 1 to transform this complex into a metallocene derivative, $[Cp_2W(CO)_2]^{n+}$: (i) abstraction of the exo-H of the methylene group with Ph_3CBF_4, leading to the dicationic tungstenocene derivative $[Cp_2W(CO)_2][BF_4]_2$ (**2**); (ii) CO loss followed by methylene endo-H migration to the metal to give $[Cp_2WH(CO)]^+$ (**3**); (iii) deprotonation to give the known $[CpW(\eta^3\text{-}Cp)(CO)_2]$ (**4**), a rare example of a ring-slipped η^3-Cp complex which leads to tungstenocene by CO loss [4].

The preparation of (**1**) was accomplished in a simple sequence of reactions. In a first step, $[W(CO)_3(NCEt)_3]$ (**5**) reacts with allyl chloride in NCMe to give $[W(\eta^3\text{-}C_3H_5)Cl(CO)_2(NCMe)_2]$ (**6**). [5] We found this procedure preparatively more convenient than the reaction of (**5**) with allyl chloride in NCEt, since (**6**) is considerably easier to purify than $[W(\eta^3\text{-}C_3H_5)Cl(CO)_2(NCEt)_2]$ (**7**) which we characterized only partially. Treatment of **6** with LiCp affords the known $[CpW(\eta^3\text{-}C_3H_5)(CO)_2]$ (**8**) in 80% yield [6]. However, we found out that treatment of a mixture of **6** and cyclopentadiene with NEt_3 is a much simpler and convenient method of preparing **8**, avoiding LiCp and low-temperature procedures. Treatment of **8** with HBF_4Et_2O in CH_2Cl_2 gives a deep red solution which is further treated with an excess of cyclopentadiene. An orange solution is formed which, after concentration and addition of Et_2O, gives a good yield of yellow **1**. The IR spectrum shows the two expected CO stretching vibrations (2046 and 1985 cm^{-1}) as well as the typical ν ($C\text{-}H_{exo}$) vibration at 2822 cm^{-1}. The ^1H NMR spectrum at room temperature shows only one Cp singlet and four multiplets for the diene protons. No change in this spectrum is observed when the temperature is lowered to −60°C, showing that only one of the two possible isomers prone (**a**) or supine (**b**), is present. Given the difference in the chemical shifts of the two methylene protons of the C_5H_6 ligand, we assign the spectrum to the supine isomer (**b**) [7].



(**a**) *prone*

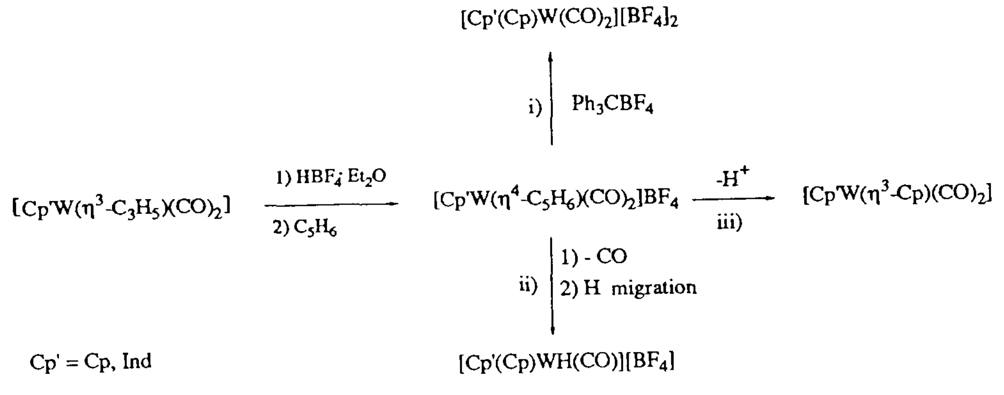


(**b**) *supine*

This situation is different from the one found for the Mo analogue, for which a mixture of the prone and supine isomers at −65°C which interconvert rapidly at room temperature is observed [8]. The higher stability of the W complex compared with the Mo analogue made it impossible to prepare the carbonyl hydride derivative **3** by overnight irradiation of a solution of **1** in CH_2Cl_2 with W lamp irradiation according to step (ii) of Scheme 1. Analogous irradiation of the Mo complex $[CpMo(\eta^4\text{-}C_5H_6)(CO)_2]^+$ readily gives $[Cp_2MoH(CO)]^+$ [3].

Treatment of **1** with Ph_3CBF_4, forms the off-white dication salt $[Cp_2W(CO)_2][BF_4]_2$ (**2**) according to path (i) in Scheme 1. The ^1H NMR spectrum of **2** can be measured in NCMe-d_3 without signs of CO substitution by NCMe solvent, again in contrast with the Mo analogue where such substitution is facile and gives $[Cp_2Mo(NCMe)(CO)]^{2+}$ [8]. As expected for this type of dication, the Cp protons are rather deshielded, giving rise to a singlet at δ 6.46 ppm in the ^1H NMR spectrum. CO substitution is observed under prolonged irradiation of **2** in NCMe. The product recovered after 14 h irradiation with a 60 Watt W lamp showed IR stretches and ^1H NMR signals assignable to a mixture of **2** and the known $[Cp_2W(NCMe)_2]^{2+}$ (ν(N≡C) 2328, 2299 cm^{-1}; δ 5.97 ppm, Cp; δ 2.73 ppm, $NCCH_3$) [9].

These results uncover an alternative route to deriva-



Scheme 1.

tives of the tungstenocene fragment through the simple preparation of $[Cp_2W(CO)_2][BF_4]_2$. However, the method may be less attractive than the corresponding synthesis of molybdenocenes due to the more difficult preparation of the allylic complex **8** and to the recently reported high yield preparation of $[Cp_2WCl_2]$ [2b].

The facile deprotonation of coordinated dienes in the complexes $[CpMo(\eta^4\text{-diene})(CO)_2]^+$ to give $[CpMo(\eta^3\text{-enyl})(CO)_2]$ derivatives is well known [10]. As indicated in path (iii) of Scheme 1, we thought that the deprotonation of **1** could provide an alternative preparation of $[CpW(\eta^3\text{-Cp})(CO)_2]$ (**4**) just as we have found for the similar $[CpMo(\eta^3\text{-indenyl})(CO)_2]$ [3,8]. However, attempted deprotonation with NaH both in THF and toluene and with LiN^iPr_2, in THF at −30°C gave no identifiable product. The initial yellow suspension darkened very slowly but the blue colour of **4** could not be clearly detected and the reaction finally gave an orange solution which contained a mixture of yet uncharacterized products. A similar behaviour was observed using the weaker base NEt_3 in CH_2Cl_2 at −30°C. This prompted us to try the alternative way of producing **4**, described in Eq. (1), which parallels the reported preparation of $[CpMo(\eta^3\text{-Ind})(CO)_2]$ [3].

As in the Mo case, the crystalline intermediate (**9**), possibly $[\{CpW(CO)_2I\}_2]$, was not positively identified. However, it reacts instantaneously with TlCp to give the expected deep blue colour of **4**. Unfortunately, we still have not been able to isolate **4** from this reaction mixture because steady decomposition to give a dark red solution was unavoidable. The instability of **4** under reducing conditions was noted by Brintzinger and coworkers [4].

$$\underset{(\mathbf{8})}{[CpW(\eta^3\text{-}C_3H_5)(CO)_2]} \xrightarrow[\text{2) } NBu_4I]{\text{1) } HBF_4\cdot Et_2O} \underset{(\mathbf{9})}{\text{red crystals}}$$

$$\xrightarrow{TlCp} \underset{(\mathbf{4})}{[CpW(\eta^3\text{-}Cp)(CO)_2]} + TlI \qquad (1)$$

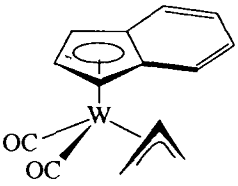
2.2. *Preparation of the mixed-ring tungstenocene analogues*

The synthetic strategy aiming at the preparation of the mixed-ring analogues of tungstenocene is depicted in Scheme 1 for the case where Cp′ = Ind and closely follows the one already developed for molybdenocene complexes [3]. By reaction of LiInd with **6**, the novel allyl complex $[IndW(\eta^3\text{-}C_3H_5)(CO)_2]$ (**10**) is readily obtained. The IR spectrum shows the expected two, very strong and somewhat broadened CO stretching vibrations (see Table 1). This broadening arises from the presence of two isomers with the prone (*exo*) and supine (*endo*) allyl conformations, (**c**) and (**d**) and this hypothesis is supported by the ^1H NMR spectrum since at room temperature two sets of signals are assignable to these isomers.

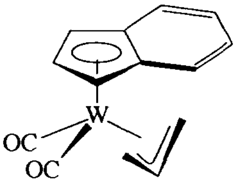
Table 1
Values for CO stretching vibrations of selected complexes (KBr pellets)

	Compound	$\nu(CO)\ cm^{-1}$
1	$[CpW(\eta^4\text{-}C_5H_6)(CO)_2]BF_4$	2046; 1984
2	$[Cp_2W(CO)_2][BF_4]_2$	2133; 2087
4	$[CpW(\eta^3\text{-}Cp)(CO)_2]$	1955; 1872 [a]
8	$[CpW(\eta^3\text{-}C_3H_5)(CO)_2]$	1935; 1846 [b]
10	$[IndW(\eta^3\text{-}C_3H_5)(CO)_2]$	1941; 1852 [b]
12	$[IndW(\eta^4\text{-}C_5H_6)(CO)_2]BF_4$	2046; 1973
13	$[IndCpW(CO)_2][BF_4]_2$	2116; 2071
15	$[CpW(\eta^3\text{-Ind})(CO)_2]$	1955; 1880
16	$[IndW(\eta^3\text{-Ind})(CO)_2]$	1949; 1871 [c]

[a] Nujol mull see Ref. [4a]; [b] CH_2Cl_2 solution; [c] $CHCl_3$ solution, see Ref. [2f].



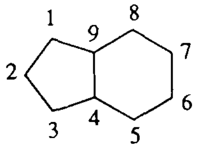
(**c**)



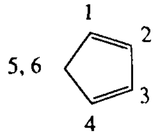
(**d**)

We assign the prone conformation (**c**) to the more abundant isomer (83%) on the basis of the abnormally high field shift of the resonance of its *meso* allylic proton (δ − 0.52 ppm) compared with the normal value of δ 3.51 ppm found for the other isomer. The ring currents of the indenyl ligand are held responsible for this shift and will more obviously affect the prone isomer (**c**). A careful study of the NMR spectra of the fluxional analogue $[IndMo(\eta^3\text{-}C_3H_5)(CO)_2]$ has reached the same conclusions [7]. Treatment of **10** with HBF_4Et_2O in CH_2Cl_2 followed by addition of an excess of NCMe led to the isolation of a brick-red microcrystalline complex **11** which, after recrystallization from $NCMe/Et_2O$, analyses for $C_{17}H_{16}BF_4N_3O_2W$. On the basis of well established chemistry, one of the formulations $[\eta^3\text{-}IndW(CO)_2(NCMe)_3]BF_4$ (**11a**) and

$[\eta^5\text{-IndW(CO)}_2(\text{NCMe})_2]\text{BF}_4\text{NCMe}$ (**11b**) can be assigned. The ^{1}H NMR spectrum of **11** in CD_2Cl_2 seemed to support the second since it is very similar to the spectrum of the well known $[\text{IndMo(CO)}_2(\text{NCMe})_2]\text{BF}_4$ in the same solvent [12]. The three indenyl signals have the chemical shifts and relative areas expected for the $H_{5\text{-}8}$ protons, $H_{1/3}$ and H_2 protons, as in (**e**).

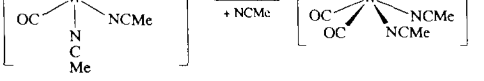


(**e**)



(**f**)

Besides the expected single resonance of the two NCMe ligands, another signal due to one free NCMe molecule is observed, which we assigned to solvent of crystallization as in **11b**. However, during the preparation of the NMR sample the colour changed from brick-red to yellow, suggesting that some modification takes place. Accordingly, recrystallization of **11** from CH_2Cl_2/Et_2O gives a yellow compound analyzing for $[\text{IndW(CO)}_2(\text{NCMe})_2]\text{BF}_4$ (**11c**). Furthermore, the ^{1}H NMR spectrum of **11** in $NCMe_3$ differs considerably from that in CD_2Cl_2. Instead of the relatively sharp resonance at δ 7.52 ppm, multiplets corresponding to the $H_{5\text{-}8}$ protons appear at higher field, δ 6.55–6.48 ppm. Simultaneously, the $H_{1/3}$ and H_2 resonances also move to higher fields and the single NCMe resonance observed integrates for three molecules. These chemical shifts are similar to the ones observed for other *trihapto* indenyl ligands as in $[\text{CpMo}(\eta^3\text{-Ind})(\text{CO})_2]$ [3] and its W analogue **15** (see below) and are consistent with a structure **11a** when dissolved in, or recrystallized from, NCMe. The equilibrium described in Eq. (2) explains these observations. The initial brick-red complex recrystallized from NCMe has structure **11a** with a *trihapto* indenyl ligand. Upon dissolution in dichloromethane, one NCMe dissociates and the indenyl regains the pentahapto coordination as in **11c**. Recrystallization of **11c** from NCMe reforms the brick-red **11a**, showing the reversibility of these transformations. Classical examples of similar hapticity changes have been reported for the isoelectronic $[\text{IndRe(CO)}_3]$ upon reaction with PMe_3 [1a].



(2)

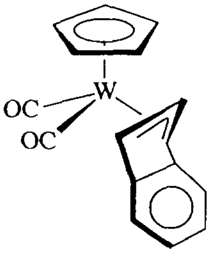
(**11a**) (**11c**)

Reaction of **11** with an excess of cyclopentadiene in dichloromethane affords the cation $[\text{IndW}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})_2]\text{BF}_4$ (**12**) as a yellow crystalline complex. The IR spectrum (KBr) immediately shows the higher lability of this species when compared to its cyclopentadienyl analogue **1**. The number of bands observed in the stretching CO region increases from two to four within ca. 5 min. The relative intensities of these peaks also change with time and the colour of the pellet turns from yellow to dark brown. This behaviour has been observed for the Mo analogue and we believe it is related to substitution of CO by Br from the KBr pellet [3]. The ^{1}H NMR spectrum of **12** at room temperature only shows one set of signals for the indenyl and the diene protons. By the argument used for **1** above, the supine conformation is assigned to **12**.

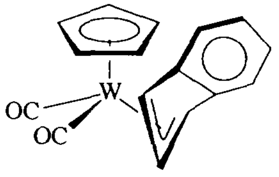
In the same fashion as **1** and still following Scheme 1, **12** reacts with Ph_3CBF_4 to give the mixed-ring dication $[\text{IndCpW(CO)}_2][\text{BF}_4]_2$ (**13**) as an off-white powder. The CO stretching vibrations in the IR spectrum (KBr) occur at slightly lower wavenumbers than the ones found for **2** (2116, 2071 cm^{-1} vs. 2133, 2087 cm^{-1}) suggesting that η^5-Ind is a better overall electron donor than η^5-Cp, at least to the fragment CpW(CO)_2^{2+} (see discussion below).

13 may be recrystallized from NCMe without CO replacement in contrast with its Mo congener $[\text{IndCpMo(CO)}_2]^{2+}$. However, prolonged irradiation (ca. 24 h, 60 Watt W lamp) of a solution of **13** in NCMe induced practically complete CO substitution. The final product, although analysing correctly for $[\text{IndCpW(NCMe)}_2][\text{BF}_4]_2$ (**14**), and showing the expected IR (ν (N≡C) 2328, 2299 cm^{-1}) and ^{1}*H* NMR signals (δ 2.71 ppm, $NCCH_3$; cf 2.80 for $[\text{Cp}_2\text{W(NCMe)}_2][\text{BF}_4]_2$ [9]) still contains minor impurities, probably $[\text{IndCpW(CO)(NCMe)}][\text{BF}_4]_2$ as suggested by a minor CO band and small resonances in the regions of Ind, Cp and NCMe (δ 2.78 ppm). To the best of our knowledge, **13** and **14** represent the first examples of actual tungstenocene analogues containing one indenyl.

Deprotonation of **12** by means of NEt_3 in CH_2Cl_2 solution or NaH in THF suspension gives the hexane soluble, sublimable, $[\text{CpW}(\eta^3\text{-Ind})(\text{CO})_2]$ (**15**). This complex has the two CO stretching vibrations at 1955 and 1880 cm^{-1} (KBr), values almost identical to three measured for **4** (Table 1). The ^{1}H NMR spectrum at −20°C is very well defined and shows two conformers corresponding to the prone and supine orientations of the η^3-indenyl ring as shown in **15a** and **15b**. We assign the structure **15a** to the most abundant isomer present (86%) since it is favoured on steric grounds and corresponds to the preferred conformation of the η^3-allyl when coordinated to the CpM(CO)_2 fragment, as verified spectroscopically for many allylic ligands [11] and also in the structure of the isoelectronic $[\text{IndW}(\eta^3\text{-Ind})(\text{CO})_2]$ (**16**) [1e]. At room temperature only a slight broadening of the signals is observed, indicating that the rotation of the η^3-indenyl ring is not very facile. This hindered rotation is associated with and increases with a "slip-fold" distortion of the indenyl ring because of η^3 coordination [13a]. This type of distortion has been shown to correlate with the chemical shifts of the quaternary C atoms of the indenyl C4 and C9 [13b]. The measured value of δ 152.0 ppm for these C atoms points to a high degree of distortion with a fold angle possibly larger than 25°. The isoelectronic **16** and [CpMo(η^3-Ind)(CO)$_2$] (**17**) have fold angles of 26° and 21°, respectively [2e,8].



(15a)



(15b)

The chemical shifts of the indenyl protons are consistent with the η^3-coordination and the spectrum is almost identical to the spectrum of **17** at −65°C, pointing to higher flexibility in the latter. An interesting feature of these NMR spectra is the downfield shift observed for the H_2 proton of the *trihapto* indenyl (*meso* allylic) at ca. δ 7 ppm. This is a much higher value than the values found for the equivalent proton in [(η^5-Ind)W(η^3-Ind)(CO)$_2$] (δ 4.78 ppm) [2e] and [(η^5-Ind)Mo(η^3-Ind)dppe] (δ 5.84ppm) [2f] and other η^3-indenyls [13b]. However, chemical shifts of ca. δ 7ppm have been reported for this type of proton [1a].

The complexes **4**, **8**, **10**, **15**, and **16** are members of a larger class of compound, namely [(η^5-Cp′)W(η^3-allyl)(CO)$_2$] and, with the exception of **4** and **16**, all have Mo analogues. Given the similarity of structural and electronic features of these complexes, the comparison of the values of the ν(CO) (see Table 1), should be indicative, even in a crude first approximation, of the relative electron-richness of the metal which, in turn, reflects the relative donor capabilities of the ligands. As noted above, comparison of the ν(CO) values of **2** and **13** (see Table 1) suggest a higher donor ability of η^5-Ind compared to η^5-Cp towards the fragment CpW(CO)$_2^{2+}$) in keeping with its higher basicity. Another interesting and less obvious conclusion is reached on comparing ν(CO) for **4**, **8** and **15**, which suggest the following decreasing order of donor ability: η^3-C_3H_5 > η^3-Ind ≈ η^3-Cp. Comparison of **10** and **16** seems to confirm the donor order η^3-C_3H_5 > η^3-Ind. However, these comparisons must be made with the utmost caution in the absence of further complementary experimental and theoretical data. Indeed, the ν(CO) values of **8** and **10** suggest that η^5-Cp is a better overall donor than η^5-Ind towards W(η^3-C_3H_5)(CO)$_2$, in apparent contradiction with the first conclusion drawn above. Therefore, these qualitative conclusions are being more thoroughly tested in a further study including ^{13}C NMR, cyclic voltammetry, accurate IR data and MO calculations of both the Mo and W complexes.

3. Experimental details

All preparations and manipulations were done with standard Schlenk techniques under argon. Solvents were dried by standard procedures (THF and Et_2O over Na/benzophenone ketyl; CH_2Cl_2, NCMe, and NCEt over CaH_2), distilled under argon, and kept over 4 molecular sieves (3A for NCMe).

Microanalyses were performed by Mr. M. Barth of the Anorganisch-chemisches Institut of the Technical University of Munich, Germany. NMR spectra were measured on Bruker CXP 300 and IR spectra measured on a Unicam Mattson Mod 7000 FTIR spectrometers. [W(CO)$_3$(NCEt)$_3$] [14] and Ph_3CBF_4 [15] were prepared as published. Modified preparations of [W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] [5] and a new preparation of [CpW(η^3-C_3H_5)(CO)$_2$] [6] are given below.

3.1. Preparation of [CpW(η^4-C_5H_6)(CO)$_2$]BF_4 1

A solution of [CpW(η^3-C_3H_5)(CO)$_2$] (0.50 g, 1.45 mmol) in CH_2Cl_2 (20 ml) was treated with 1 equiv. of HBF_4 Et_2O. After 15 min the excess of C_5H_6 (3 ml) was added to the solution and the reaction left for 2 h. The resulting mixture was concentrated to 10 ml and THF added. The light-yellow precipitate formed was filtered, washed with Et_2O, and recrystallized from CH_2Cl_2/Et_2O at −30°C. Yield 86%. Found: C, 31.20; H, 2.47. Calc. for $C_{12}H_{11}BF_4O_2W$: C, 31.48; H, 2.42%. Selected IP (KBr, cm^{-1}): 2822, m, ν(C-H_{exo}); 2046, 1984, vs, ν(CO). ^{1}H NMR (d^{6}Me$_2$CO, 300 MHz, r.t.): 6,23 (s, 2H, $H_{2/3}$); 6.06 (s, 5H, cp); 5.68 (d, 1H, H_5); 4.11 (d, 1H, H_6); 3.84 (s, 2H, $H_{1/4}$) (see (**f**) for proton numbering.

3.2. Preparation of [Cp_2W(CO)$_2$][BF_4]$_2$ 2

A solution of [CpW(η^4-C_5H_6)(CO)$_2$]BF_4 (0.25 g, 0.55 mmol) in CH_2Cl_2 was treated with a solution of Ph_3CBF_4 (0.18 g, 0.55 mmol) in the same solvent. After 8 h of stirring at room temperature, the off-white precipitate was filtered, and washed with Et_2O (3 × 10 ml). Yield 81%. Found: C, 26.36; H, 1.92; W, 33.32.

Calc. for $C_{12}H_{10}B_2F_8O_2W$: C, 26.51; H, 1.85; W, 33.82%. Selected IR (KBr, cm^{-1}): 2133, 2087, vs, ν(CO), ^{1}H NMR (d^{3}NCMe; 300 MHz) δ 6.46 ppm (s, Cp).

3.3. Preparation of [W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] 6

A solution of [W(CO)$_3$(NCEt)$_3$] (2 g, 4.62 mmol) in NCMe (20 ml) was treated with an excess of allyl chloride (5 ml). After 0.5 h a fine microcrystalline yellow precipitate started to separate. After 2 h, the solution was concentrated and upon addition of a little Et_2O, full precipitation was achieved. After filtration and washing with Et_2O, the yield was 96%.

3.4. Preparation of [W(η^3-C_3H_5)Cl(CO)$_2$(NCEt)$_2$] 7

A solution of [W(CO)$_3$(NCEt)$_3$] (2 g 4.62 mmol) in NCEt (20 ml) was treated with an excess of allyl chloride (5 ml). After 2 h, the reaction mixture was concentrated. Upon addition of Et_2O an oily residue separated which, was solidified to a yellow microcrystalline powder after repeated washings and scratching with Et_2O/hexane mixtures. Yield 60%. Selected IR (KBr, cm^{-1}): 2286, m, ν(C≡N); 1938, 1838, vs, ν(CO).

3.5. Preparation of [CpW(η^3-C_3H_5)(CO)$_2$] 8

Method (a) Cold (−80°C) THF (30 mL) was slowly transferred via a stainless steel transfer needle into a Schlenk tube which contained a mixture of [W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] (2.49 g, 6.25 mmol) and LiCp (0.45 g 6.25 mmol) at −80°C. After slow warming to room temperature with stirring, the reaction mixture was kept for 18 h. The orange-brown solution was evaporated to dryness and the residue extracted with hexane at 40°C for some hours. Upon filtration and concentration of the resulting yellow solution, [CpW(η^3–C_3H_5)(CO)$_2$] precipitates as a yellow powder which may be further recrystallized from Et_2O/hexane. Yield 81%.

Method (b). A solution of [W(η^3–C_3H_5)Cl(CO)$_2$(NCMe)$_2$] (1 g 2.51 mmol) in CH_2Cl_2 (20 ml) was treated with freshly distilled C_5H_6 (0.5 ml) and in excess of NEt_3 (1 ml). After 15 h with stirring at room temperature the reaction mixture was evaporated to dryness and the residue extracted with hexane to give the product in 80% yield after concentration and cooling.

3.6. Preparation of [IndW(η^3–C_3H_5)(CO)$_2$] 10

Prepared as **8** from LiInd (0.60 g, 4.90 mmol) and [W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] (1.95 g, 4.90 mmol). The yellow product was recrystallized from Et_2O/hexane in 86% yield. Found: C, 42.79; H, 3.13. Calc. for $C_{14}H_{12}O_2W$: C, 42.45; H, 3.05% Selected IR (KBr, cm^{-1}): 1921, 1859, vs, ν (CO). ^{1}H NMR (CD_2Cl_2, 300 MHz) Prone 7.10–6.99 (m, 4H, H_{5-8} of C_9H_7); 6.10 (d, 2H, $H_{1/3}$ of C_9H_7); 5.63 (t, 1H, H_2 of C_9H_7); 2.25 (d, 2H, *syn* C_3H_5); 1.15 (d, 2H, *anti* C_3H_5); −0.52 (m, 1H, *meso* C_3H_5). Supine 7.10–6.99 (m, 4H, H_{5-8} of C_9H_7); 5.89 (d, 2H, $H_{1/3}$ of C_9H_7); 5.66 (t, 1H, H_2 of C_9H_7); 3.50 (m, 1H, *meso* C_3H_5); 3.29 (d, 2H, *syn* C_3H_5); 0.75 (d, 2H, *anti* C_1H_5). (see (**e**) for numbering.)

3.7. Preparation of [IndW(CO)$_2$(NCMe)$_3$]BF$_4$ **11a**

A solution of [IndW(η^3–C_3H_5)(CO)$_2$] (0.25 g, 0.63 mmol) in CH_2Cl_2 (20 ml) was treated with 1 equiv. of $HBF_4 \cdot Et_2O$. After 15 min the mixture was treated with NCMe (5 ml), stirred for 1 h and taken to dryness. The residue was recrystallized from NCMe/Et_2O as brick-red microcrystals. Yield 96%. Found: C, 36.08; H, 2.99; N, 7.38. Calc. for $C_{17}H_{16}N_3BF_4O_2W$: C, 36.14; H, 2.85; N, 7.44 Selected IR (KBr, cm^{-1}): 2318, 2289, w, ν (N≡C); 1955, 1878, vs, ν(CO). ^{1}H NMR (NCMe, 300 MHz) δ 6.55–6.48 (m, 4H, H_{5-8}); 5.46 (s, 1H, H_2); 5.02 (d, 2H, $H_{1/3}$); 2.03 (s, 9H, $NCCH_3$).

3.8. Preparation of [IndW(CO)$_2$(NCMe)$_2$]BF$_4$ **11c**

After recrystallization of **11a** from CH_2Cl_2/Et_2O, yellow crystals of (**11c**) are obtained. Found: C, 34.44; H, 2.45; N, 5.34;. Calc. for $C_{15}H_{13}BF_4N_2O_2W$: C, 34.39; H, 2.50; N, 5.34% ^{1}H NMR (CD_2Cl_2, 300 MHz), 7.52 (s, 4H, H_{5-8}); 6.16 (d, 2H, $H_{1/3}$), 5.24 (t, 1H, H_2), 2.49 (s, 6H, $NCCH_3$).

3.9. Preparation of [IndW(η^4–C_5H_6)(CO)$_2$]BF$_4$ 12

A solution of [IndW(η^3–C_3H_5)(CO)$_2$] (0.25 g, 0.63 mmol) in CH_2Cl_2 (20 ml) was treated with 1 equiv. of $HBF_4 \cdot Et_2O$. After 15 min the mixture was treated with NCMe (5 ml), stirred for 1 h, and taken to dryness. The residue was taken up in CH_2Cl_2 (20 ml) and treated with an excess of C_5H_6 (3 ml). After 2 h, the mixture was concentrated to ca. 5 ml and THF added. The yellow precipitate was filtered, washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O at −30°C to give pale yellow microcrystals. Yield 87%. Found: C, 37.59; H, 2.41; Calc. for $C_{16}H_{13}BF_4O_2W$: C, 37.84; H, 2.58%. Selected IR (KBr, cm^{-1}): 2837, m, ν(C–H_{exo}); 2046, 1973, vs, ν (CO). ^{1}H NMR (Me_2CO, 300 MHz, r.t.): δ 7.85–7.57 (m, 4H, H_{5-8}); 6.43 (d, 2H, $H_{1/3}$); 6.33 (t, 1H, H_2) 5.71 (d, 1H, H_6 of C_5H_6); 5.42 (s, 2H, $H_{2/3}$ of C_5H_6); 3.82 (d, 1H, H_5 of C_5H_6); 3.73 (s, 2H, $H_{1/4}$ of C_5H_6) (see (**e**) and (**f**) for numbering).

3.10. Preparation of [IndCpW(CO)$_2$][BF$_4$]$_2$ 13

A solution of [IndW(η^4–C_5H_6)(CO)$_2$]BF$_4$ (0.25 g, 0.49 mmol) in CH_2Cl_2 was treated with a solution of

Ph_3CBF_4 (0.16 g, 0.49 mmol) in the same solvent. After 8 h of stirring at room temperature, the off-white precipitate was filtered, and washed with Et_2O (3 × 10 ml). Yield 88%. Found: C, 32.40; H, 2.04. Calc. for $C_{16}H_{12}B_2F_8O_2W$: C, 32.37; H, 2.04%. Selected IR (KBr, cm^{-1}): 2116, 2071, vs, ν (CO). ^1H NMR (NCMe-d_3 300 MHz); 7.91 (s, 4H, H_{5-8}); 6.85 (d, 2H, $H_{1/3}$); 6.62 (s, 1H, H_2); 6.24 (s, 5H, cp).

3.11. Preparation of [CpW(η^3-Ind)CO)$_2$] 15

Method (a). A solution of [IndW(η^3-C_3H_5)$(CO)_2$] (0.50 g, 1.26 mmol) in CH_2Cl_2 (20 ml) was treated with 1 equiv. of HBF_4 Et_2O. After 15 min $^nBu_4NI$ (0.46 g, 1.26 mmol) was added to the solution. After stirring for 3 h at room temperature, the mixture was taken to dryness and the residue suspended in THF (20 ml). An excess of TlCp (0.40 g, 1.48 mmol) was added to the suspension and the mixture vigorously stirred for 2 h. After filtration to separate TlI, the solution was evaporated to dryness and the residue extracted with hexane. The resulting solution was concentrated and cooled to −30°C to give a microcrystalline ruby-red product. This was further recrystallized from a concentrated hexane/Et_2O mixture cooled to −30°C for several days. Yield 85%.

Method (b). A suspension of [IndW(η^4-C_5H_6)-$(CO)_2$]BF_4 (0.50 g; 1.26 mmol) in THF (20 ml) was treated with an excess NaH for 4 h with vigorous stirring. The resulting ruby-red solution was filtered and evaporated to dryness. The product was recrystallized as described above. Alternatively it may be sublimed directly from this residue but with lower yield. Yield 62%.

Method (c). A solution of [IndW(η^4-C_5H_6)$(CO)_2$]-BF_4 (0.50 g, 1.26 mmol) in CH_2Cl_2 (25 ml) was treated with an excess of NEt_3 for 1 h with stirring. The reaction mixture was evaporated to dryness and the product extracted with a mixture of Et_2O/hexane from which it was recrystallized by concentration and cooling. Yield 86%. Found: C, 45.71; H, 2.79; Calc. for $C_{16}H_{12}O_2W$: C, 45.74; H, 2.88%. Selected IR (KBr, cm^{-1}): 1955, 1880, vs, ν (CO). ^1H NMR (Me$_2$CO-d$_6$, 300 MHz, −20°C): δ ppm 7.07 (t, 1H, H_2 of C_9H_7); 6.66–6.47 (m, 4H, H_{5-8} of C_9H_7); 5.07 (s, 5H, cp); 4.95 (d, 2H, $H_{1/3}$ of C_9H_7). ^{13}C NMR ($CDCl_3$, 75 MHz, r.t.; δ ppm): 227.63, CO; 152.03, $C_{4/9}$; 121.94, $C_{5/8}$; 115.95 $C_{6/7}$; 100.16, C_2; 95.58, cp; 49.06, $C_{1/3}$ (see (**e**) for numbering).

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