

Phosphenium complexes 30. Supermesitylphosphenium complexes of molybdenum and tungsten: Synthesis and exchange reactions involving the P–H bond[☆]

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Abstract

Deprotonation of the complex salts $\{\text{Cp}(\text{OC})_3[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{M}\}\text{BF}_4$ ($\text{M} = \text{Mo}, \text{W}$) (**4a,b**), obtained from $[\text{Cp}(\text{OC})_3\text{M}]\text{BF}_4$ (**2a,b**) and $(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{PH}_2$ (**3**), yields the metallo-phosphanes $\text{Cp}(\text{OC})_3\text{M-P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**5a,b**). **5a,b** are thermally decarbonylated to the PH-functionalized phosphenium complexes $\text{Cp}(\text{OC})_2\text{M-P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**7a,b**), which can also be obtained by the base-assisted dehydrohalogenation of the bifunctional complexes $\text{Cp}(\text{OC})_2[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{M-Cl}$ (**9a,b**), prepared by a ligand exchange reaction from $\text{Cp}(\text{OC})_3\text{M-Cl}$ (**8a,b**) and **3**. The reaction of **7a,b** with CCl_4 affords the chloro-substituted phosphenium complex $\text{Cp}(\text{OC})_2\text{M-P}(\text{Cl})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**10a,b**) via H/Cl exchange at the sp^2 -phosphorus. Substitution of the P-bonded hydrogen by a methyl group is achieved by in situ deprotonation of **7b** and subsequent treatment with methyl iodide, yielding the diorgano-phosphenium complex $\text{Cp}(\text{OC})_2\text{M-P}(\text{Me})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**11**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metallo-phosphanes; Phosphenium–metal complexes; P–H bond; Exchange reaction

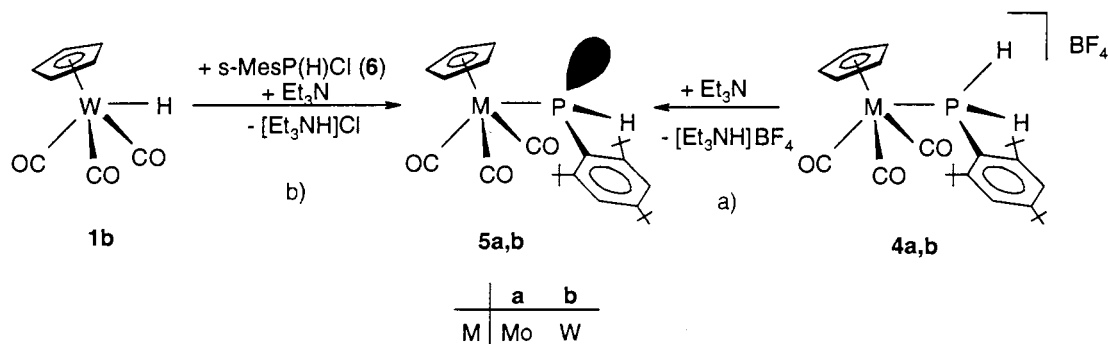
1. Introduction

The reactivity of diorgano-phosphenium metal complexes $\text{Cp}(\text{OC})_2\text{M=PR}_2$ [2–4] of molybdenum and tungsten is determined by the cyclo addition behaviour of the M=P bond towards a series of appropriate reagents like alcohols, diazoalkanes, organo-isocyanates, azides and phosphinidenes. In order to achieve consecutive coupling reactions involving the phosphorus atom, the functionalized systems $\text{Cp}(\text{OC})_2\text{M=P}(\text{H})\text{R}$ that offer a reactive P–H bond at the sp^2 -phosphorus were studied. The number of stable examples is rather limited, among which the struc-

turally characterized complexes $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{-Mo=P}(\text{H})\text{Ph}$, $(\text{Me}_3\text{CC}\equiv)(\text{Cl}_2)(\text{Et}_3\text{P})_2\text{W=P}(\text{H})\text{Ph}$ [5] and $\text{C}_5\text{Me}_5(\text{Me}_3\text{P})_2\text{Mo=P}(\text{H})\text{s-Mes}$ [6] are worth mentioning. Usually, the insufficient shielding of the M=P bond leads to serious problems concerning the isolation of these compounds, especially due to a pronounced tendency toward dimerization. Whereas the *tert*-butyl-substituted compounds $\text{C}_5\text{R}_5(\text{CO}_2)\text{W=P}(\text{H})\text{tBu}$ ($\text{R} = \text{Me}, \text{H}$) can only be spectroscopically identified in solution at low temperatures [7], the aryl-substituted species ($\text{R} = \text{Ph}, \text{Mes}$) have never been directly observed [8]. Therefore, we have attempted to stabilize these M=P(H)R bonds by introducing the extremely bulky *s*-mesityl substituent to the phosphorus with the purpose of performing, for the first time, controlled exchange reactions at the planar phosphorus. Preliminary accounts of this work have been published [7].

[☆] For part 29, see [1]

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Scheme 1.

2. Results

The complexes **7a,b** with a hydride substituted sp^2 -phosphorus can be generated via a decarbonylation as well as a dehydrochlorination reaction [2–4,7,8]. The first process requires the corresponding secondary metallo-phosphanes **5a,b**, which can be prepared from the hydrido-metal complexes $Cp(OC)_3M-H$ ($M = Mo, W$) (**1a,b**) in several steps. Hydride abstraction from **1a,b** by trityltetrafluoroborate at $-60^\circ C$ yields the cationic complexes $[Cp(OC)_3M]BF_4$ [9] (**2a,b**), which react with the primary phosphane (2,4,6-*t*Bu₃-C₆H₂)PH₂ (**3**) to form the yellow, light-sensitive complex salts **4a,b**. These can easily be deprotonated to give the secondary metallo-phosphanes **5a,b** when using triethylamine as a base at r.t. [10] (Scheme 1(a)).

An alternative synthetic route to the metallo-phosphane **5b** is offered by the direct reaction of the hydrido-tungsten species **1b** and the chloro-phosphane **6** in the presence of triethylamine (Scheme 1(b)). However, the tedious synthesis of **6** makes route (b) less attractive than route (a).

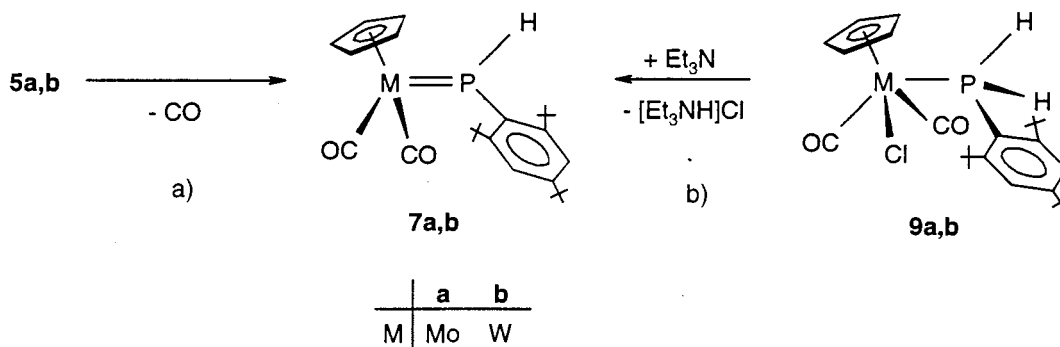
5a,b can be isolated in yields of at least 90% and are thermally stable at $60^\circ C$ (Mo) and $90^\circ C$ (W). Above $90^\circ C$, **5a** decomposes and turns blue. Using DTA and thermogravimetric techniques, the loss of one equivalent of CO in the melting process has been observed. When heated in methylcyclohexane, 1 mol of CO is eliminated from **5a** after 30 min at $75^\circ C$ and from **5b**

after 60 min at $120^\circ C$, respectively. In this process, the deep blue phosphonium complexes **7a,b** are generated that show a high thermal stability and good solubility in pentane (Scheme 2(a)).

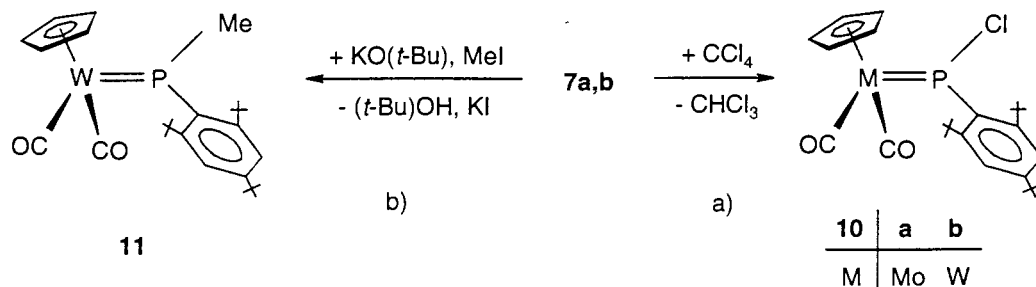
The synthesis of the phosphonium complexes **7a,b** via dehydrohalogenation starts with the *s*-mesityl-phosphane substituted chloro complexes **9a,b**, which can be obtained from the reaction of $Cp(OC)_3M-Cl$ (**8a,b**) with (2,4,6-*t*Bu₃-C₆H₂)PH₂ (**3**) performed in methylcyclohexane at 95 or $100^\circ C$, respectively.

Besides **9a,b**, the hydrido complex $Cp(OC)_3M-H$ (**1a,b**) is formed and finally converted into $[Cp(OC)_3M]_2$. This side reaction reduces the yield of **9a,b** to ca. 20%. Due to the high lability of **9a,b**, column chromatography could not be employed for purification. Dehydrochlorination of **9a,b** by triethylamine at r.t. leads to the double bonded systems **7a,b** in yields of 70 and 90%, respectively (Scheme 2(b)). The overall yield of **7a** could be improved from 19 to 38% when $Cp(OC)_3Mo-Cl$ (**8a**) and (2,4,6-*t*Bu₃-C₆H₂)PH₂ (**3**) directly reacted with triethylamine in methylcyclohexane at $55^\circ C$ in a one-step procedure. The lower reaction temperature suppresses some of the side reactions in the formation of **9a,b**.

Due to their high stability and ready accessibility, the phosphane–metal double bonded species **7a,b** appear to be well-suited for studying exchange reactions at the phosphorus involving the P–H moiety.



Scheme 2.



Scheme 3.

A chloro substituent can be introduced to the phosphorus using carbon tetrachloride as a reagent. The treatment of **7a,b** with one equivalent of carbon tetrachloride results in a complete H/Cl exchange within 3 days (**7a**) and 1 day (**7b**), respectively (Scheme 3(a)). The P–Cl functionalized double bonded complexes **10a,b** are obtained in quantitative yield as highly thermally stable purple crystals. This rare type of phosphonium complex has only been realized in the case of Cp(OC)₂Mo=P(Cl)(TMP) (TMP = 2,2,2',2'-tetramethylpiperidino) [11].

If a solution of **7b** in THF is combined at r.t. with an equimolar amount of KO(*t*Bu) followed by the addition of an excess of methyl iodide, the phosphonium complex **11** is formed, which is obtained as a light purple crystalline solid in 79% yield (Scheme 3(b)).

Compound **7b** displays the typical reactivity of M=P complexes towards HCl leading to the complete reformation of the phosphane-substituted chloro complex Cp(OC)₂[H₂(2,4,6-*t*Bu₃-C₆H₂)P]W–Cl (**9b**).

In summary, this paper shows that the *s*-mesityl ligand exerts a significant stabilizing effect on P–H functional phosphonium complexes, presumably due to an efficient steric shielding of the M=P bond. This effect should open the possibility of selective manipulations at the P–H function, which will be used for further exchange reactions at the sp²-phosphorus. The results of these investigations will be presented in forthcoming papers.

3. Experimental

All operations were performed in an atmosphere of purified and dried nitrogen. Solvents and glassware were prepared accordingly.

¹H-NMR: Varian T60, JEOL FX 90 Q and Bruker AC 200 (solvent used as reference). ³¹P-NMR: Bruker WH 90 and JEOL FX 90 Q. IR: Perkin-Elmer, Model 283 grating spectrometer. Melting points: differential thermo analysis (DTA); Thermal Analysis System Du Pont 9000. Starting materials: Cp(OC)₃M–H [M = Mo, W (**1a,b**)] [12], Cp(OC)₃M–Cl [M = Mo, W (**8a,b**)] [13], (2,4,6-*t*Bu₃-C₆H₂)P(H)Cl (**6**) [14] and (2,4,6-*t*Bu₃-

C₆H₂)PH₂ (**3**) [11] were prepared according to literature procedures. Triethylamine, trityltetrafluoroborate, potassium-*tert*-butanolate, methyl iodide and carbon tetrachloride were obtained commercially.

3.1. {Tricarbonyl(η⁵-cyclopentadienyl)[2,4,6-tri(*tert*-butyl)-phenylphosphane]molybdenum(II)}tetrafluoroborate (**4a**)

A solution of [Cp(OC)₃Mo]BF₄ [9] (**2a**) in 6 ml of dichloromethane, prepared from 233 mg (0.95 mmol) of Cp(OC)₃Mo–H (**1a**) and 313 mg (0.95 mmol) of trityltetrafluoroborate, is combined with 264 mg (0.95 mmol) of (2,4,6-*t*Bu₃-C₆H₂)PH₂ (**3**) at –78°C in the dark and warmed up to r.t. After stirring for 2 h, the light red solution is reduced in vacuo to 3 ml and **4a** is precipitated by dropwise addition of 10 ml of ether. **4a** is separated, washed with 3 ml of ether and pentane and dried in vacuo. Yield 445 mg (77%), light yellow powder, m.p. 186°C (decomp.). Molar conductivity [S cm² mol^{–1}] in acetonitrile (25°C): 136.6 (*c* = 4.5 × 10^{–4} mol l^{–1}). ¹H-NMR (200.1 MHz, [D₃]-acetonitrile): δ (ppm) 7.80 [d, ⁴J(PCCCH) = 4.0 Hz, 2H, *m*-H], 6.78 [¹J(PH) = 405.0 Hz, 2H, H₂P], 5.95 [d, ³J(PMoCH) = 0.7 Hz, 5H, H₅C₅], 1.57 [d, ⁵J(PCCCH) = 0.8 Hz, 18H, *o*-(H₃C)C], 1.32 (s, 9H, *p*-(H₃C)C). ³¹P{¹H}-NMR (36.4 MHz, [D₃]-acetonitrile): δ (ppm) –80.5 (s). IR (dichloromethane): ν(PH) = 2420 (w); ν(CO) = 2063 (s), 1990 (vs, br) cm^{–1}. Calc. for C₂₆H₃₆BF₄MoO₃P (610.30): C, 51.17; H, 5.95; found: C, 49.79; H, 5.46.

3.2. {Tricarbonyl(η⁵-cyclopentadienyl)[2,4,6-tri(*tert*-butyl)-phenylphosphane]tungsten(II)}tetrafluoroborate (**4b**)

Prepared as described for **4a** from 324 mg (0.97 mmol) of Cp(OC)₃W–H (**1b**), 320 mg (0.97 mmol) of trityltetrafluoroborate and 270 mg (0.97 mmol) of (2,4,6-*t*Bu₃-C₆H₂)PH₂ (**3**) in 7 ml of dichloromethane after stirring for 3 h at r.t. Yield 557 mg (82%), light yellow powder, m.p. 201°C (decomp.). Molar conductivity [S cm² mol^{–1}] in acetonitrile (25°C): 127.1 (*c* =

$4.8 \cdot 10^{-4} \text{ mol l}^{-1}$). $^1\text{H-NMR}$ (60 MHz, $[\text{D}_3]$ -acetonitrile): δ (ppm) 7.78 [d, $^4J(\text{PCCCH}) = 4.0 \text{ Hz}$, 2H, *m*-H], 7.05 [d, $^1J(\text{PH}) = 414.0 \text{ Hz}$, 2H, H_2P], 6.00 [d, $^3J(\text{PWCH}) = 0.8 \text{ Hz}$, 5H, H_5C_5], 1.52 [d, $^5J(\text{PCCCCH}) = 0.8 \text{ Hz}$, 18H, *o*-(H_3C)C], 1.29 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_3]$ -acetonitrile): δ (ppm) -112.8 [s, $^1J(\text{WP}) = 187.0 \text{ Hz}$]. IR (dichloromethane): $\nu(\text{PH}) = 2420$ (w); $\nu(\text{CO}) = 2062$ (s), 1975 (vs br) cm^{-1} . Calc. for $\text{C}_{26}\text{H}_{36}\text{BF}_4\text{O}_3\text{PW}$ (698.22): C, 44.73; H, 5.20; found: C, 44.20; H, 5.06.

3.3. [Tricarbonyl(η^5 -cyclopentadienyl)molybdenum(II)] [2,4,6-*tri*(*tert*-butyl)-phenyl]phosphane (**5a**)

A suspension of 271 mg (0.40 mmol) of $\{\text{Cp}(\text{OC})_3[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{Mo}\}\text{BF}_4$ (**4a**) in 12 ml of methylcyclohexane is combined at 0°C with a solution of 45 mg (0.40 mmol) of triethylamine in 2 ml of methylcyclohexane and the mixture is stirred for 1 h at r.t., resulting in a yellow colour. Insoluble $[\text{Et}_3\text{NH}]\text{BH}_4$ is separated by filtration, volatiles are removed in vacuo and the remaining **5a** is washed with 4 ml of pentane and dried in vacuo. Yield 207 mg (89%), yellow powder, m.p. 85°C (decomp.). $^1\text{H-NMR}$ (90 MHz), $[\text{D}_6]$ -benzene): δ (ppm) 7.72 [d, $^4J(\text{PCCCH}) = 2.0 \text{ Hz}$, 2H, *m*-H], 5.13 [d, $^1J(\text{PH}) = 213.0 \text{ Hz}$, 1H, HP], 4.80 [d, $^3J(\text{PMoCH}) = 1.6 \text{ Hz}$, 5H, H_5C_5], 1.68 [s, 18H, *o*-(H_3C)C], 1.25 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) -120.3 (s). IR (methylcyclohexane): $\nu(\text{PH}) = 2409$ (w); $\nu(\text{CO}) = 2005$ (s), 1946 (vs), 1930 (vs) cm^{-1} . Thermogravimetry ($10^\circ\text{C min}^{-1}$; $[\text{M}]\text{-CO}$ 85– 113°C , melt): CO calc. 5.36; found, 4.80. Calc. for $\text{C}_{26}\text{H}_{35}\text{MoO}_3\text{P}$ (522.51): C, 59.77; H, 6.75; found: C, 58.81; H 6.53.

3.4. [Tricarbonyl(η^5 -cyclopentadienyl)tungsten(II)] [2,4,6-*tri*(*tert*-butyl)-phenyl]phosphane (**5b**)

(a) Prepared as described for **5a** from 269 mg (0.42 mmol) of $\{\text{Cp}(\text{OC})_3[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{W}\}\text{BF}_4$ (**4b**) and 43 mg (0.42 mmol) of triethylamine in 10 ml of methylcyclohexane after stirring for 1.5 h. Yield 241 mg (94%).

(b) A mixture of 257 mg (0.77 mmol) of $\text{Cp}(\text{OC})_3\text{W-H}$ (**1b**), 242 mg (0.77 mmol) of $(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P(H)Cl}$ (**6**) and 105 mg (1.04 mmol) of triethylamine in 10 ml of benzene is stirred for 1 h at r.t. The solution changes from pink to brown and insoluble $[\text{Et}_3\text{NH}]\text{Cl}$ is formed. Insolubles are separated by filtration and the filtrate is evaporated in vacuo to yield **5b**, which is washed with 8 ml of cold pentane and dried in vacuo. Yield 253 mg (54%), yellow powder, m.p. 117°C . $^1\text{H-NMR}$ (200.1 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 7.67 [d, $^4J(\text{PCCCH}) = 2.0 \text{ Hz}$, 2H, *m*-H], 5.30 [d, $^1J(\text{PH}) = 221.0 \text{ Hz}$, 1H, HP], 4.82 [d, $^3J(\text{PWCH}) = 1.6 \text{ Hz}$, 5H, H_5C_5], 1.69 [s, 18H,

o-(H_3C)C], 1.29 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) -141.0 [s, $^1J(\text{WP}) = 50.6 \text{ Hz}$]. IR (methylcyclohexane): $\nu(\text{PH}) = 2410$ (w); $\nu(\text{CO}) = 2003$ (s), 1938 (vs), 1922 (vs) cm^{-1} . Calc. for $\text{C}_{26}\text{H}_{35}\text{O}_3\text{PW}$ (610.40): C, 51.16; H, 5.78; found: C, 50.73; H, 5.90.

3.5. *Cis*-dicarbonyl(chloro)(η^5 -cyclopentadienyl) [2,4,6-*tri*(*tert*-butyl)-phenyl]phosphane]molybdenum(II) (**9a**)

A mixture of 210 mg (0.75 mmol) of $\text{Cp}(\text{OC})_3\text{Mo-Cl}$ (**8a**) and 289 mg (1.04 mmol) of $(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{PH}_2$ (**3**) in 15 ml of methylcyclohexane is stirred for 2 days at 95°C . After cooling to r.t., the solution is reduced in vacuo to 5 ml. Impure **9a** is crystallized by cooling to -78°C , separated by filtration and recrystallized from 3 ml of boiling methylcyclohexane. Yield 80 mg (20%), red powder, m.p. 158°C (decomp.). $^1\text{H-NMR}$ (200.1 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 7.56 [d, $^4J(\text{PCCCH}) = 2.9 \text{ Hz}$, 1H, *m*-H], 7.54 [d, $^4J(\text{PCCCH}) = 2.9 \text{ Hz}$, 1H, *m*-H], 6.49 [dd, $^1J(\text{PH}) = 329.0 \text{ Hz}$, $^2J(\text{HHP}) = 8.5 \text{ Hz}$, 1H, HP], 6.15 [dd, $^1J(\text{PH}) = 389.0 \text{ Hz}$, $^2J(\text{HHP}) = 8.5 \text{ Hz}$, 1H, HP], 4.88 (s, 5H, H_5C_5), 1.40 [s, 18H, *o*-(H_3C)C], 1.20 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) -46.5 (s). IR (benzene): $\nu(\text{PH}) = 2388$ (w); $\nu(\text{CO}) = 1974$ (vs), 1898 (vs) cm^{-1} . Calc. for $\text{C}_{25}\text{H}_{36}\text{ClMoO}_2\text{P}$ (530.91): C, 56.56; H, 6.83; found: C, 56.19; H, 6.48.

3.6. *Cis*-dicarbonyl(chloro)(η^5 -cyclopentadienyl) [2,4,6-*tri*(*tert*-butyl)-phenyl]phosphane]tungsten(II) (**9b**)

Prepared as described for **9a** from 183 mg (0.52 mmol) of $\text{Cp}(\text{OC})_3\text{W-Cl}$ (**8b**) and 236 mg (0.85 mmol) of $(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{PH}_2$ (**3**) in 15 ml of methylcyclohexane after 2 days at 100°C . Yield 72 mg (23%), red powder, m.p. 161°C (decomp.). $^1\text{H-NMR}$ (60 MHz, benzene): δ (ppm) 7.50 [d, $^4J(\text{PCCCH}) = 2.7 \text{ Hz}$, 1H, *m*-H], 7.46 [d, $^4J(\text{PCCCH}) = 2.7 \text{ Hz}$, 1H, *m*-H], 7.20 [d, $^1J(\text{PH}) = 365.0 \text{ Hz}$, 1H, HP], 7.05 [d, $^1J(\text{PH}) = 347.0 \text{ Hz}$, 1H, HP], 5.00 (s, 5H, H_5C_5), 1.40 [s, 18H, *o*-(H_3C)C], 1.20 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) -71.4 [s, $^1J(\text{WP}) = 272.4 \text{ Hz}$]. IR (benzene): $\nu(\text{PH}) = 2380$ (w); $\nu(\text{CO}) = 1956$ (vs), 1882 (vs) cm^{-1} . Calc. for $\text{C}_{25}\text{H}_{36}\text{ClO}_2\text{PW}$ (618.79): C, 48.52; H, 5.86; found: C, 49.19; H, 5.80.

3.7. Dicarbonyl(η^5 -cyclopentadienyl)[2,4,6-*tri*(*tert*-butyl)-phenyl- λ^4 -phosphandiyl]molybdenum(II) (**7a**)

(a) A solution of 122 mg (0.23 mmol) of $\text{Cp}(\text{OC})_3\text{Mo-P(H)}(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**5a**) in 10 ml of methylcyclohexane is heated to 75°C for 30 min, where upon the colour changes from yellow to deep blue.

Volatiles are removed in vacuo and the remaining **7a** is washed with 3 ml of pentane and dried in vacuo. Yield 108 mg (93%).

(b) A solution of 187 mg (0.35 mmol) of $\text{Cp}(\text{OC})_2[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{Mo}-\text{Cl}$ (**9a**) is treated with 36 mg (0.35 mmol) of triethylamine and stirred for 20 min at r.t., whereupon the solution turns blue. Insoluble $[\text{Et}_3\text{NH}]\text{Cl}$ is separated and volatiles are removed in vacuo. The remaining **7a** is washed with 3 ml of pentane and dried in vacuo. Yield 162 mg (94%).

(c) A solution of 72 mg (0.70 mmol) of Et_3N in 2 ml of methylcyclohexane is added dropwise at r.t. to a mixture of 198 mg (0.70 mmol) of $\text{Cp}(\text{OC})_3\text{Mo}-\text{Cl}$ (**8a**) and 197 mg (0.70 mmol) of $(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{PH}_2$ (**3**) in 10 ml of methylcyclohexane. The solution is stirred for 90 min at 55°C, whereupon it turns blue. $[\text{Et}_3\text{NH}]\text{Cl}$ is separated, the filtrate is evaporated in vacuo and the remaining blue residue is purified by column chromatography (column 10×1.5 cm; Al_2O_3 , activity IV, neutral; pentane). **7a** is obtained by evaporation of the first blue fraction in vacuo. Yield 121 mg (35%), blue microcrystalline powder, m.p. 102°C (decomp.). $^1\text{H-NMR}$ (200.1 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 9.95 [d, $^1J(\text{PH}) = 408.0$ Hz, 1H, HP], 7.44 [d, $^4J(\text{PCCCH}) = 2.0$ Hz, 2H, *m*-H], 5.08 (s, 5H, H_5C_5), 1.35 [d, $^5J(\text{PCCCCCH}) = 0.9$ Hz, 18H, *o*-(H_3C)C], 1.12 [s, 9 H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz $[\text{D}_6]$ -benzene): δ (ppm) 266.2 ppm (s). IR (pentane): $\nu(\text{PH}) = 2294$ (w); $\nu(\text{CO}) = 1960$ (vs), 1890 (vs) cm^{-1} . Calc. for $\text{C}_{25}\text{H}_{35}\text{MoO}_2\text{P}$ (494.51): C, 60.73; H, 7.13; found: C, 60.77; H, 7.17.

3.8. Dicarboxyl(η^5 -cyclopentadienyl)[2,4,6-tri(*tert*-butyl)-phenyl]- λ^4 -phosphanediyl]tungsten(II) (**7b**)

(a) A solution of 241 mg (0.39 mmol) of $\text{Cp}(\text{OC})_3\text{W}-\text{P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**5b**) in 12 ml of methylcyclohexane is stirred for 1 h at 120°C. After removal of volatiles in vacuo the purple residue is extracted with 10 ml of pentane. Evaporation of the extract in vacuo yields pure **7b**. Yield 216 mg (95%).

(b) A solution of 80 mg (0.13 mmol) of $\text{Cp}(\text{OC})_2[\text{H}_2(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)\text{P}]\text{W}-\text{Cl}$ (**9b**) in 0.5 ml of benzene is combined with 79 mg (0.78 mmol) of triethylamine at r.t., whereupon the solution turns violet immediately. After 10 min, insoluble $[\text{Et}_3\text{NH}]\text{Cl}$ is separated and the solvent is removed in vacuo. The remaining residue is extracted with 2 ml of pentane and the extract is evaporated in vacuo to yield **7b**. Yield 52 mg (69%), violet powder, m.p. 108°C. $^1\text{H-NMR}$ (60 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 12.8 [d, $^1J(\text{PH}) = 379.0$ Hz, 1H, HP], 7.44 [d, $^4J(\text{PCCCH}) = 2.0$ Hz, 2H, *m*-H], 5.08 [d, $^3J(\text{PWCH}) = 0.3$ Hz, 5H, H_5C_5], 1.37 [d, $^5J(\text{PCCCCCH}) = 0.7$ Hz, 18H, *o*-(H_3C)C], 1.15 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 211.8 [s, $^1J(\text{PW}) = 604.0$ Hz]. IR (pentane):

$\nu(\text{PH}) = 2299$ (w); $\nu(\text{CO}) = 1953$ (vs), 1881 (vs) cm^{-1} . Calc. for $\text{C}_{25}\text{H}_{35}\text{O}_2\text{PW}$ (582.43): C, 51.56; H, 6.06; found: C, 51.89; H, 5.69.

3.9. Dicarboxyl(η^5 -cyclopentadienyl){[2,4,6-tri(*tert*-butyl)-phenyl](chloro)- λ^4 -phosphanediyl}molybdenum(II) (**10a**)

A solution of 84 mg (0.17 mmol) of $\text{Cp}(\text{OC})_2\text{Mo}=\text{P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**7a**) in 5 ml of pentane is treated with 26 mg (0.17 mmol) of CCl_4 at r.t. After 3 days, a change of colour from blue to violet is observed. Volatiles are removed in vacuo and the remaining **10a** is washed with 3 ml of pentane and dried in vacuo. Yield 89 mg (99%), red-violet powder, m.p. 116°C (decomp.). $^1\text{H-NMR}$ (90 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 7.63 [d, $^4J(\text{PCCCH}) = 4$ Hz, 2H, *m*-H], 5.07 (s, 5H, C_5H_5), 1.65 [d, $^5J(\text{PCCCCCH}) = 1.1$ Hz, 18H, *o*-(H_3C)C], 1.12 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 259.1 (s). IR (pentane): $\nu(\text{CO}) = 1972$ (vs), 1909 (vs) cm^{-1} . UV (cyclohexane): $\lambda_{\text{max}} = 193.6, 240.0, 303.4$ nm ($\epsilon = 57956, 17057, 15261$) ($c = 2.3 \times 10^{-4}$ mol·l $^{-1}$), 507.6 nm ($\epsilon = 208.7$) ($c = 2.3 \times 10^{-3}$ mol·l $^{-1}$). Calc. for $\text{C}_{25}\text{H}_{34}\text{ClMoO}_2\text{P}$ (528.89): C, 56.77; H, 6.48; Cl, 6.70; found: C, 56.46; H, 6.82; Cl, 6.68.

3.10. Dicarboxyl(η^5 -cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl](chloro)- λ^4 -phosphanediyl}tungsten(II) (**10b**)

A solution of 85 mg (0.15 mmol) of $\text{Cp}(\text{OC})_2\text{W}=\text{P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**7b**) in 5 ml of benzene is treated with 22 mg (0.15 mmol) of CCl_4 and stirred for 22 h at r.t. Volatiles are removed in vacuo, the remaining **10b** is washed with 3 ml of pentane and dried in vacuo. Yield 86 mg (96%), violet microcrystalline solid, m.p. 120°C. $^1\text{H-NMR}$ (200.1 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 7.65 [d, $^4J(\text{PCCCH}) = 4.0$ Hz, 2H, *m*-H], 5.07 (s, 5H, H_5C_5), 1.60 [d, $^5J(\text{PCCCCCH}) = 1.0$ Hz, 18H, *o*-(H_3C)C], 1.08 [s, 9H, *p*-(H_3C)C]. ^{31}P -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 201.8 [s, $^1J(\text{WP}) = 711.6$ Hz]. IR (pentane): $\nu(\text{CO}) = 1969$ (vs), 1904 (vs) cm^{-1} . UV (cyclohexane): $\lambda_{\text{max}} = 193.7, 243.2, 303.8$ nm ($\epsilon = 65638, 24628, 21383$) ($c = 1.9 \times 10^{-4}$ mol·l $^{-1}$), 490.3 nm ($\epsilon = 340$) ($c = 1.9 \times 10^{-3}$ mol·l $^{-1}$). Calc. $\text{C}_{25}\text{H}_{34}\text{ClO}_2\text{P}_2\text{W}$ (616.80): C, 48.68; H, 5.56; Cl, 5.75; found: C, 48.72; H, 5.74; Cl, 5.82.

3.11. Dicarboxyl(η^5 -cyclopentadienyl){[2,4,6-tri(*tert*-butyl)-phenyl](methyl)- λ^4 -phosphanediyl}tungsten(II) (**11**)

To a solution of 85 mg (0.15 mmol) of $\text{Cp}(\text{OC})_2\text{W}=\text{PH}(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**7b**) in 10 ml of THF 19 mg (0.15 mmol) of $\text{KO}(t\text{Bu})$ is added at 0°C where-

upon the colour of the solution turns from violet to dark green immediately. Addition of 114 mg (0.80 mmol) of methyl iodide results in a change of colour back to violet. After removal of volatiles in vacuo, the remaining solid is dissolved in 2 ml of pentane and purified by column chromatography (column 10×1.5 cm; Al_2O_3 , activity IV, neutral; pentane). **11** is isolated by evaporation of the violet fraction in vacuo. Yield 69 mg (79%), violet microcrystalline solid, m.p. 135°C (decomp.). $^1\text{H-NMR}$ (200.1 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 7.47 [d, $^4J(\text{PCCCH}) = 2.3$ Hz, 2H, *m*-H], 5.12 (s, 5H, H_5C_5), 1.58 [d, $^2J(\text{PCH}) = 15.1$ Hz, 3H, (H_3C)P], 1.52 [d, $^5J(\text{PCCCCH}) = 1.0$ Hz, 18H, *o*-(H_3C)C], 1.24 [s, 9H, *p*-(H_3C)C]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (36.4 MHz, $[\text{D}_6]$ -benzene): δ (ppm) 262.8 [s, $^1J(\text{WP}) = 617.8$ Hz]. IR (pentane): $\nu(\text{CO}) = 1940$ (vs), 1868 (vs); (benzene): 1928 (vs), 1850 (vs) cm^{-1} . Calc. for $\text{C}_{26}\text{H}_{37}\text{O}_2\text{PW}$ (596.40): C, 52.36; H, 6.25; found: C, 51.68; H, 6.44.

3.12. Reaction of **7b** with etherial HCl

A solution of 87 mg (0.15 mmol) of $\text{Cp}(\text{OC})_2\text{W}=\text{P}(\text{H})(2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2)$ (**7b**) in 5 ml of diethyl ether is combined at r.t. with an etherial solution of 6 mg (0.16 mmol) of hydrogen chloride. The colour of the solution turns from blue to red. After removal of volatiles in vacuo, the remaining **9b** is washed with 3 ml pentane, dried in vacuo and spectroscopically identified by comparison with an authentic sample. Yield 88 mg (92%).

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