Reactivity of the *ansa*-Bridged Metallocene Dichlorides $[X(\eta^5\text{-}C_5H_4)_2]MCl_2$ (X = SiMe$_2$, CMe$_2$; M = Mo, W) toward Metallophosphide Anions $[PPh_2M'(CO)_x]^-$ (M′ = Cr, Mo, W, x = 5; M′ = Fe, x = 4). Formation of Heterobimetallic Complexes by Nucleophilic Substitution on a Cyclopentadienyl Ligand or on the Metal M

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Two kinds of *ansa* derivatives, $[SiMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ and $[CMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ (M = Mo, W), are reacted with metallophosphide anions $[PPh_2M'(CO)_x]^-$ (M′ = Cr, Mo, W, x = 5; M′ = Fe, x = 4). The silicon-bridged derivatives give the bimetallic systems $[SiMe_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3PPh_2M'(CO)_x)]M(H)(Cl)$, which result from a regioselective substitution at the 3-position on the cyclopentadienyl ligand. In contrast, with the CMe$_2$-bridged compounds, the substitution reaction occurs at the metallic center, giving μ-phosphido bimetallic complexes $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(Cl)(\mu\text{-}PPh_2)M'(CO)_x$. The solid-state structure of the bimetallic complex $[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Fe(CO)_4$ (**7d**) is reported.

Introduction

Electrophilic substitution reactions leading to functionalized cyclopentadienyl ligands are commonly encountered in electron-rich complexes such as ferrocene.[1] The d^6 electronic structure of the metal and the parallel Cp rings account for a rather high electron density on the rings. Metallocenes with early or middle transition metals do not exhibit this property, and the usual synthetic routes to Cp-functionalized derivatives involve complexation on prefunctionalized ligands, which limit the range of functional groups available on the complexes. In fact, the bending of cyclopentadienyl planes in early-metal metallocenes leads to a decrease of electron density retained on these rings.[2] However, there are some rare examples of the introduction of substituents on Cp ligands in group 6 metallocenes. Tungstenocene derivatives with exocyclic boron[3] or silyl[4] substituents have been recently reported but their formation results from a ligand transfer from metal to the Cp ring. On the other hand, substituted tungstenocene complexes have been prepared by reaction of heteroanionic nucleophiles with the cationic derivative $[Cp_2W(SMe_2)Br]^+$.[5a,b] In this last case the positive metallic charge draining some electron density from the aromatic ligands may be responsible for the activation of the Cp rings. However, as also mentioned by Cooper, the neutral dichloride Cp_2WCl_2 is able to undergo a ring substitution reaction when opposed to Grignard reagents;[5c,d] $MgCl_2$ is postulated to promote the reaction by Lewis acid complexation of a chloride in Cp_2WCl_2. We have recently shown that the dichlorides Cp_2MCl_2 (M = Mo, W) display similar reactivity with metallophosphide anions $[PPh_2M'(CO)_x]^-$. Bimetallic systems are easily built through a nucleophilic substitution of the cyclopentadienyl ligand by an anionic metallophosphide moiety.[6] The presence of methyl or *tert*-butyl groups on the rings does not affect the site of the substitution reaction.[7] Thus, one may anticipate that geometrical factors could be predominant in the orientation of the reaction between the two electrophilic zones of reactivity: the metal center or Cp ligands. On the basis of this belief, we undertook a study with *ansa* derivatives. Such structures are known to afford significant variations in the tilt of Cp rings and consequently in the π electron density distribution within the rings.[8] In this paper we wish to report the results obtained for SiMe$_2$ and CMe$_2$ *ansa*-bridged systems.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of purified argon. The solvents and eluents were dried by the appropriate procedure and distilled under argon from sodium and benzophenone immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Column chromatography was performed under argon with silica gel (70−230 mesh). Elemental analyses were carried out with a EA 1108 CHNS-O FISONS Instruments apparatus. Electron ionization mass spectra were run on a Kratos Concept 32S.

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[1] Deeming, A. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon: Oxford, U.K., **1982**; Vol. 4.

[2] Kubicki, M. M.; Kergoat, R.; Guerchais, J. E.; Bkouche-Waksman, I.; Bois, C.; L'Haridon, P. *J. Organomet. Chem.* **1981**, *219*, 329.

[3] (a) Braunschweig, H.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1613. (b) Hartwig, J. F.; He, X. *Organometallics* **1996**, *15*, 5350.

[4] Schubert, U.; Schenkel, A. *Chem. Ber.* **1988**, *121*, 939.

[5] (a) McNally, J. P.; Glueck, D.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 4838. (b) McNally, J. P.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 4500. (c) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420. (d) Forschner, T. C.; Corella, J. A., II Cooper, N. J. *Organometallics* **1990**, *9*, 2478.

[6] Rigny, S.; Leblanc, J. C.; Moïse, C. *New J. Chem.* **1995**, *19*, 145.

[7] (a) Rigny, S.; Bakhmutov, V. I.; Nuber, B.; Leblanc, J. C.; Moïse, C. *Inorg. Chem.* **1996**, *35*, 3202. (b) Comte, V.; Rigny, S.; Moïse, C. *Bull. Soc. Chim. Fr.* **1997**, *134*, 609.

[8] Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

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^1H and ^{31}P spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts are relative to internal TMS (^1H) or external H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet 205 IR-FT. PPh_2Cl (Strem) and $NaAlH_2(OCH_2CH_2OMe)_2$ (Aldrich) were used as received. $M'(CO)_5(THF)$ was prepared by the method indicated in the literature.[9] The lithium reagent, $Li[PPh_2M'(CO)_x]$ ($x = 5$, $M' = Cr$, Mo, W; $x = 4$, $M' = Fe$), was prepared according to the literature method[10] using low-chloride methyllithium (Janssen).

The *ansa* dichlorides (**4**, **5**) and dihydrides (**8**, **9**) were all prepared by adapting the procedure described by Green et *al.*[11]

$[SiMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ (M = Mo (1), M = W (2)). The procedure employed to prepare $Li_2[SiMe_2(\eta^5\text{-}C_5H_4)_2]$ has been described by Petersen et *al.* in the literature.[12] $[SiMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ was synthesized by the same procedure used for *ansa* CMe_2 complexes.[11] $[SiMe_2(\eta^5\text{-}C_5H_4)_2]MoCl_2$ (**1**) was obtained as a brown powder in 30% yield and $[SiMe_2(\eta^5\text{-}C_5H_4)_2]WCl_2$ (**2**) as a gray powder in 40% yield after recrystallization from chloroform.

$[SiMe_2(\eta^5\text{-}C_5H_4)_2]MoCl_2$ (1). ^1H NMR ($CDCl_3$): δ 0.06 (s, 6H, Me), 5.33 (m, 4H, C_5H_4), 6.54 (m, 4H, C_5H_4). Anal. Calcd for $C_{12}H_{14}Cl_2MoSi$: C, 40.81; H, 4.00. Found: C, 41.11; H, 3.86.

$[SiMe_2(\eta^5\text{-}C_5H_4)_2]WCl_2$ (2). ^1H NMR ($CDCl_3$): δ 0.13 (s, 6H, Me), 5.78 (m, 4H, C_5H_4), 6.16 (m, 4H, C_5H_4). Anal. Calcd for $C_{12}H_{14}Cl_2WSi$: C, 32.68; H, 3.2. Found: C, 32.44; H, 3.3.

$[SiMe_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3PPh_2M'(CO)_x)]W(H)(Cl)$ (3). A 5 mL amount of a THF solution of $Li[PPh_2M'(CO)_x]$ (1 mmol) was rapidly added to 20 mL of a THF suspension of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]WCl_2$ (**2**; 440 mg, 1 mmol). The mixture was stirred at room temperature for 5 h. THF was removed *in vacuo*, and the residue was washed with pentane (2 × 20 mL) and chromatographed on silica gel (eluent toluene/THF (9/1)) to give an orange powder in 40% yield for **3a**, in 30% yield for **3b**, and in 30% yield for **3c**.

$[SiMe_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3PPh_2Cr(CO)_5)]W(H)(Cl)$ (3a). IR (ν_{CO}, THF): 2063 (m), 1940 (S + sh) cm^{-1}. ^1H NMR (CD_3COCD_3): δ −0.04 (s, 3H, Me), 0.47 (s, 3H, Me), 7.40−7.68 (m, 10H, C_6H_5). Anal. Calcd for $C_{29}H_{24}O_5ClWCrSi$: C, 44.49; H, 3.09. Found: C, 44.41; H, 3.2.

$[SiMe_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3PPh_2W(CO)_5)]W(H)(Cl)$ (3b). IR (ν_{CO}, THF): 2071 (m), 1938 (S + sh) cm^{-1}. ^1H NMR (CD_3COCD_3): δ −0.05 (s, 3H, Me), 0.48 (s, 3H, Me), 7.18−7.68 (m, 10H, C_6H_5). Anal. Calcd for $C_{29}H_{24}O_5ClW_2Si$: C, 38.08; H, 2.64. Found: C, 38.62; H, 2.94.

$[SiMe_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3PPh_2Fe(CO)_4)]W(H)(Cl)$ (3c). IR (ν_{CO}, THF): 2048 (m), 1970 (S), 1940 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ −0.01 (s, 3H, Me), 0.47 (s, 3H, Me), 7.41−7.60 (m, 6H, C_6H_5), 7.70−7.83 (m, 4H, C_6H_5). Anal. Calcd for $C_{28}H_{24}O_4ClWFeSi$: C, 44.33; H, 3.19. Found: C, 43.86; H, 3.02.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(Cl)(\mu\text{-}PPh_2)M'(CO)_5$ (6). To 15 mL of a THF suspension of $[CMe_2(\eta^5\text{-}C_5H_4)_2]MoCl_2$ (**4**; 340 mg, 1 mmol) was rapidly added 5 mL of a THF solution of $Li[PPh_2M'(CO)_x]$ (1 mmol; $x = 5$, $M' = Cr$, Mo, W). The mixture was stirred at room temperature for 5 h. THF was removed *in vacuo*; the residue was washed with pentane (2 × 20 mL) and chromatographed (eluent toluene/THF (9/1)) to give a red powder. All complexes were recrystallized from acetone as red crystals in 25% yield for **6a** (170 mg), in 15% yield for **6b** (60 mg), and in 35% yield for **6c** (240 mg). ^1H and ^{31}P NMR spectra were recorded at 50 °C in $CDCl_3$ and at 80 °C in DMSO-d_6 to obtain better resolution.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(Cl)(\mu\text{-}PPh_2)Cr(CO)_5$ (6a). IR (ν_{CO}, THF): 2064 (m), 1930 (S), 1915 (S), 1893 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.37 (s, 3H, Me), 1.07 (s, 3H, Me), 7.20−7.80 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.37 (s, 3H, Me), 1.07 (s, 3H, Me), 3.34 (m, 2H, C_5H_4), 5.70 (m, 2H, C_5H_4), 5.86 (m, 2H, C_5H_4), 6.02 (m, 2H, C_5H_4), 7.21−7.53 (m, 6H, C_6H_5), 7.75−7.82 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 3,61 (s). Anal. Calcd for $C_{30}H_{24}O_5ClPMoCr$: C, 52.94; H, 3.56. Found: C, 52.39; H, 4.1.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(Cl)(\mu\text{-}PPh_2)Mo(CO)_5$ (6b). IR (ν_{CO}, THF): 2060 (m), 1935 (S), 1920 (S), 1894 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.27 (s, 3H, Me), 1.01 (s, 3H, Me), 7.21−7.80 (m, 10H, C_6H_5). Unsatisfactory analysis was obtained for this compound, but the mass spectrum displays the M^+ fragment.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(Cl)(\mu\text{-}PPh_2)W(CO)_5$ (6c). IR (ν_{CO}, THF): 2062 (m), 1927 (S), 1916 (S), 1893 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.07 (s, 3H, Me), 0.41 (s, 3H, Me), 7.20−7.83 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.30 (s, 3H, Me), 1.08 (s, 3H, Me), 3.22 (m, 2H, C_5H_4), 5.71 (m, 2H, C_5H_4), 5.83 (m, 2H, C_5H_4), 6.0 (m, 2H, C_5H_4), 7.18−7.79 (m, 10H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −23.7 (s + d, $^1J_{WP}$ = 191 Hz). Anal. Calcd for $C_{30}H_{24}O_5ClPMoW$: C, 44.95; H, 2.98. Found: C, 45.39; H, 2.73.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)M'(CO)_x$ (7). A procedure similar to that for the molybdocene derivatives was followed using $[CMe_2(\eta^5\text{-}C_5H_4)_2]WCl_2$ (**5**; 430 mg, 1 mmol) and $Li[PPh_2M'(CO)_x]$ (1 mmol; $x = 5$, $M' = Cr$, Mo, W; $x = 4$, $M' = Fe$). All complexes were obtained as red crystals after recrystallization from acetone in 40% yield for **7a** (300 mg), in 20% yield for **7b** (160 mg), in 30% yield for **7c** (270 mg), and in 20% yield for **7d** (150 mg).

^1H and ^{31}P NMR spectra were recorded at 50 °C in $CDCl_3$ and at 80 °C in DMSO-d_6 to obtain better resolution.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Cr(CO)_5$ (7a). IR (ν_{CO}, THF): 2051 (m), 1930 (S), 1916 (S), 1894 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (s, 3H, Me), 0.30 (s, 3H, Me), 7.20−7.78 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.27 (s, 3H, Me), 1.03 (s, 3H, Me), 3.50 (m, 2H, C_5H_4), 5.76 (m, 2H, C_5H_4), 5.85 (m, 2H, C_5H_4), 5.96 (m, 2H, C_5H_4), 7.22−7.44 (m, 6H, C_6H_5), 7.70−7.82 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −32.75 (s + d, $^1J_{WP}$ = 185 Hz). Anal. Calcd for $C_{30}H_{24}O_5ClPWCr$: C, 46.99; H, 3.15. Found: C, 46.41; H, 3.37.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Mo(CO)_5$ (7b). IR (ν_{CO}, THF): 2060 (m), 1927 (S), 1915 (S), 1894 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.31 (s, 3H, Me), 0.96 (s, 3H, Me), 7.18−7.74 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.29 (s, 3H, Me), 1.04 (s, 3H, Me), 3.54 (m, 2H, C_5H_4), 5.67 (m, 2H, C_5H_4), 5.82 (m, 2H, C_5H_4), 5.96 (m, 2H, C_5H_4), 7.18−7.45 (m, 6H, C_6H_5), 7.68−7.76 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −57.7 (s + d, $^1J_{WP}$ = 190 Hz). Anal. Calcd for $C_{30}H_{24}O_5ClPWMo$: C, 44.45; H, 2.98. Found: C, 44.69; H, 3.04.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)W(CO)_4$ (7c). IR (ν_{CO}, THF): 2060 (m), 1927 (S), 1915 (S), 1893 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.30 (s, 3H, Me), 0.96 (s, 3H, Me), 7.20−7.74 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.29 (s, 3H, Me), 1.04 (s, 3H, Me), 3.55 (m, 2H, C_5H_4), 5.73 (m, 2H, C_5H_4), 5.84 (m, 2H, C_5H_4), 5.97 (m, 2H, C_5H_4), 7.17−7.45 (m, 6H, C_6H_5), 7.68−7.76 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −55.35 (s + d, $^1J_{WP}$ = 193 Hz). Anal. Calcd for $C_{30}H_{24}O_5ClPW_2$: C, 40.10; H, 2.69. Found: C, 40.08; H, 3.07.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Fe(CO)_4$ (7d). IR (ν_{CO}, THF): 2028 (m), 1950 (S), 1926 (S), 1901 (S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.65 (s, 3H, Me), 1.10 (s, 3H, Me), 7.20−7.83 (m, 10H, C_6H_5). ^1H NMR (DMSO-d_6): δ 0.61 (s, 3H, Me), 0.98 (s, 3H, Me), 4.10 (m, 2H, C_5H_4), 5.46 (m, 2H, C_5H_4), 5.54 (m, 2H, C_5H_4), 5.78 (m, 2H, C_5H_4), 7.14−7.40 (m, 6H, C_6H_5), 7.68−7.77 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −16.33 (s + d, $^1J_{WP}$ = 190 Hz). Anal. Calcd for $C_{29}H_{24}O_4ClPWFe$: C, 46.9; H, 3.26. Found: C, 46.9; H, 3.13.

$[CMe_2(\eta^5\text{-}C_5H_4)_2M(H)(PPh_2H)]Cl$ (M = Mo (10), M = W (11)) and $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(H)(PPh_2)$ (M = Mo (12), M

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[9] Werner, H.; Leonhard, K.; Burschka, C. *J. Organomet. Chem.* **1978**, *160*, 291.

[10] Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.

[11] Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395.

[12] Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

= W (13)). Syntheses of the salts **10** and **11**[13] and the complexes **12** and **13**[14] were adapted from the procedures described in the literature. Treatment of **8** or **9** with PPh_2Cl in toluene leads to the phosphine salt $[CMe_2(\eta^5\text{-}C_5H_4)_2M(H)(PPh_2H)]Cl$, which is deprotonated in aqueous KOH. **12** is obtained as a gray powder in 50% yield and **13** as a brown powder in 80% yield.

$[CMe_2(\eta^5\text{-}C_5H_4)_2Mo(H)(PPh_2H)]Cl$ (10). ^1H NMR (CD_3COCD_3): δ −6.19 (d, $^2J_{PH}$ = 42 Hz, 1H, Mo−H), 1.15 (s, 3H, Me), 1.38 (s, 3H, Me), 5.18 (m, 2H, C_5H_4), 5.23 (m, 2H, C_5H_4), 5.32 (m, 2H, C_5H_4), 5.85 (m, 2H, C_5H_4), 7.18−7.81 (m, 10H, C_6H_5), 7.76 (d, $^2J_{PH}$ = 395 Hz, 1H, P−H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 33.22 (s). Anal. Calcd for $C_{25}H_{26}ClPMo$: C, 61.43; H, 5.36. Found: C, 60.44; H, 6.02.

$[CMe_2(\eta^5\text{-}C_5H_4)_2W(H)(PPh_2H)]Cl$ (11). ^1H NMR (CD_3COCD_3): δ −8.6 (d + dd, $^2J_{PH}$ = 37.5 Hz, $^1J_{WH}$ = 118 Hz, 1H, W−H), 1.09 (s, 3H, Me), 1.24 (s, 3H, Me), 5.13 (m, 2H, C_5H_4), 5.16 (m, 2H, C_5H_4), 5.27 (m, 2H, C_5H_4), 5.67 (m, 2H, C_5H_4), 7.36−7.62 (m, 10H, C_6H_5), 7.91 (d, $^2J_{PH}$ = 398 Hz, 1H, P−H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ −13.85 (s + d, $^1J_{WP}$ = 229 Hz). Anal. Calcd for $C_{25}H_{26}ClPW$: C, 52.06; H, 4.54. Found: C, 53.0; H, 4.93.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(H)(PPh_2)$ (12). ^1H NMR (CD_3COCD_3): δ −5.23 (d, $^2J_{PH}$ = 36 Hz, 1H, Mo−H), 1.11 (s, 3H, Me), 1.14 (s, 3H, Me), 3.82 (m, 2H, C_5H_4), 4.71 (m, 2H, C_5H_4), 4.8 (m, 2H, C_5H_4), 5.24 (m, 2H, C_5H_4), 7.18−8.10 (m, 10H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ −22.79 (s). Anal. Calcd for $C_{25}H_{25}PMo$: C, 66.38; H, 5.57. Found: C, 67.14; H, 6.33.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(H)(PPh_2)$ (13). ^1H NMR (CD_3COCD_3): δ −7.14 (d + dd, $^2J_{PH}$ = 32 Hz, $^1J_{WH}$, 1H, W−H), 0.87 (s, 3H, Me), 0.98 (s, 3H, Me), 4.62 (m, 4H, C_5H_4), 4.82 (m, 1H, C_5H_4), 4.89 (m, 1H, C_5H_4), 5.09 (m, 2H, C_5H_4), 6.93−7.84 (m, 10H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ −50.36 (s + d, $^1J_{WP}$). Anal. Calcd for $C_{25}H_{25}PW$: C, 55.58; H, 4.66. Found: C, 54.27; H, 4.90.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]M(H)(\mu\text{-}PPh_2)M'(CO)_5$ (M = Mo (14), M = W (15)) and $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(\mu\text{-}PPh_2,H)M'(CO)_4$ (M = Mo (14′), M = W (15′)). The complexes **14** + **14′** and **15** + **15′** were prepared by adapting a procedure described for the parent Cp complexes in the literature.[15] To a THF solution (20 mL) of $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(H)(PPh_2)$ (1 mmol) was added an excess (30%) of $M'(CO)_5(THF)$. The mixture was stirred for 1 h at room temperature. During this time, the solution turned from yellow to orange. The solvent was removed under vacuum, and the crude product was washed with pentane and purified by chromatography.

Tungsten Complexes. The complexes **15** and **15′** were separated by chromatography with toluene as eluent. The monobridged compound was obtained in 35% yield for **15a**, 20% yield for **15b**, and 40% yield for **15c** (based on the complex $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(H)(PPh_2)$) from the first yellow band, and the dibridged complex was recovered (20% yield for **15′a**, 15% yield for **15′b**, and 30% yield for **15′c**) from the second orange band.

Molybdenum Complexes. An analogous reaction leads to tetracarbonyl product together with a small amount of pentacarbonyl product, and for M′ = Mo, only the dibridged complex **14′b** is obtained. Monobridged complexes are light- and temperature-sensitive and spontaneously give in solution the dibridged compounds. All recrystallizations of monobridged complexes were unsuccessful. Red or orange crystals were obtained by recrystallization from acetone for the dibridged complexes (20% yield for **14′a**, 10% yield for **14′b**, and 25% yield for **14′c**).

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(H)(\mu\text{-}PPh_2)Cr(CO)_5$ (14a). IR (ν_{CO}, THF): 2046 (m), 1966 (S), 1929 (S), 1895 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 0.93 (s, 3H, Me), 0.98 (s, 3H, Me), 7.18−7.35 (m, 6H, C_6H_5), 7.50−7.65 (m, 4H, C_6H_5).

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(H)(\mu\text{-}PPh_2)Mo(CO)_5$ (14b). not isolated.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(H)(\mu\text{-}PPh_2)W(CO)_5$ (14c). IR (ν_{CO}, THF): 2075 (m), 1948 (S), 1928 (S), 1881 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.03 (s, 3H, Me), 1.2 (s, 3H, Me), 7.22−7.68 (m, 10H, C_6H_5).

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(\mu\text{-}PPh_2,H)Cr(CO)_4$ (14′a). IR (ν_{CO}, THF): 1987 (m), 1892 (S), 1872 (S), 1855 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.35 (s, 3H, Me), 1.41 (s, 3H, Me), 7.28−7.40 (m, 6H, C_6H_5), 8.1−8.12 (m, 4H, C_6H_5). Anal. Calcd for $C_{29}H_{25}O_4PMoCr$: C, 56.51; H, 4.09. Found: C, 56.82; H, 4.13.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(\mu\text{-}PPh_2,H)Mo(CO)_4$ (14′b). IR (ν_{CO}, THF): 2001 (m), 1896 (S), 1882 (S), 1857 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.34 (s, 3H, Me), 1.37 (s, 3H, Me), 7.24−7.35 (m, 6H, C_6H_5), 8.04−8.12 (m, 4H, C_6H_5). Unsatisfactory analysis was obtained for this compound, but the mass spectrum displays the M^+ fragment.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(\mu\text{-}PPh_2,H)W(CO)_4$ (14′c). IR (ν_{CO}, THF): 1995 (m), 1890 (S), 1874 (S), 1852 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.34 (s, 3H, Me), 1.39 (s, 3H, Me), 7.25−7.51 (m, 6H, C_6H_5), 8.04−8.12 (m, 6H, C_6H_5). Anal. Calcd for $C_{29}H_{25}O_4PMoW$: C, 46.55; H, 3.37. Found: C, 46.25; H, 3.65.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(H)(\mu\text{-}PPh_2)Cr(CO)_5$ (15a). IR (ν_{CO}, THF): 2048 (m), 1930 (S), 1915 (S), 1898 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 0.85 (s, 3H, Me), 0.88 (s, 3H, Me), 7.17−7.4 (m, 6H, C_6H_5), 7.59−7.67 (m, 4H, C_6H_5). Anal. Calcd for $C_{30}H_{25}O_5PWCr$: C, 49.20; H, 3.44. Found: C, 49.91; H, 3.81.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(H)(\mu\text{-}PPh_2)Mo(CO)_5$ (15b). IR (ν_{CO}, THF): 2060 (m), 1934 (S), 1921 (S), 1898 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 0.85 (s, 3H, Me), 0.93 (s, 3H, Me), 7.15−7.34 (m, 6H, C_6H_5), 7.64−7.7 (m, 4H, C_6H_5). Anal. Calcd for $C_{30}H_{25}O_5PWMo$: C, 46.42; H, 3.25. Found: C, 45.91; H, 3.42.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(H)(\mu\text{-}PPh_2)W(CO)_5$ (15c). IR (ν_{CO}, THF): 2059 (m), 1927 (S), 1916 (S), 1894 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 0.86 (s, 3H, Me), 0.94 (s, 3H, Me), 7.14−7.32 (m, 6H, C_6H_5), 7.50−7.66 (m, 4H, C_6H_5). Anal. Calcd for $C_{30}H_{25}O_5PW_2$: C, 41.7; H, 2.92. Found: C, 39.7; H, 2.6.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(\mu\text{-}PPh_2,H)Cr(CO)_4$ (15′a). IR (ν_{CO}, THF): 1987 (m), 1890 (S), 1870 (S), 1852 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.27 (s, 3H, Me), 1.32 (s, 3H, Me), 7.12−7.36 (m, 6H, C_6H_5), 8.07−8.15 (m, 4H, C_6H_5). Anal. Calcd for $C_{29}H_{25}O_4PWCr$: C, 49.45; H, 3.58. Found: C, 49.07; H, 3.47.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(\mu\text{-}PPh_2,H)Mo(CO)_4$ (15′b). IR (ν_{CO}, THF): 2002 (m), 1880 (S), 1861 (S), 1804 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.26 (s, 3H, Me), 1.29 (s, 3H, Me), 7.24−7.36 (m, 6H, C_6H_5), 8.05−8.14 (m, 4H, C_6H_5). Anal. Calcd for $C_{29}H_{25}O_4PWMo$: C, 46.55; H, 3.37. Found: C, 47.12; H, 3. 82.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(\mu\text{-}PPh_2,H)W(CO)_4$ (15′c). IR (ν_{CO}, THF): 1996 (m), 1888 (S), 1874 (S), 1851 (S) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 1.25 (s, 3H, Me), 1.30 (s, 3H, Me), 7.30−7.36 (m, 6H, C_6H_5), 8.10−8.14 (m, 4H, C_6H_5). Anal. Calcd for $C_{29}H_{25}O_4PW_2$: C, 41.66; H, 3.01. Found: C, 42.01; H, 3.42.

Reduction of 7c. **7c** was reduced by $NaAlH_2(OCH_2CH_2OMe)_2$ (2 M in toluene) in toluene. After 4 h of stirring, the solution was hydrolyzed slowly by degassed water. The orange organic layer was decanted and extracted. Evaporation of the solvent afforded **15c**.

Chlorination of 15c. To a solution of **15c** (2 mmol) in 10 mL of chloroform was added 5 mL of CCl_4. Then, the mixture was stirred at room temperature overnight. **7c** was then isolated as a red powder.

Irradiation of $[CMe_2(\eta^5\text{-}C_5H_4)_2]M(Cl)(\mu\text{-}PPh_2)W(CO)_5$. A solution of **6c** (M = Mo) or **7c** (M = W) (1.5 mmol) in THF was irradiated with a HANAU TQ 150 lamp for 2 h at room temperature. The solvent was evaporated off to give a red powder. The crude product was chromatographed (eluent toluene) and was recrystallized from toluene as red crystals.

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[13] Kubicki, M. M.; Kergoat, R.; Cariou, M.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1987**, *322*, 357.

[14] Barré, C.; Kubicki, M. M.; Leblanc, J. C.; Moïse, C. *Inorg. Chem.* **1990**, *29*, 5244.

[15] Barré, C.; Boudot, P.; Kubicki, M. M.; Moïse, C. *Inorg. Chem.* **1995**, *34*, 284.

Table 1. Crystallographic Data for $[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Fe(CO)_4$ (7d)

mol formula	$WFeClPO_5C_{32}H_{30}$
fw	800.72
color, dimens, mm	red; 0.35 × 0.20 × 0.10
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
cell dimens	
a, Å	10.095(2)
b, Å	10.846(3)
c, Å	14.526(2)
α, deg	87.47(2)
β, deg	81.09(1)
γ, deg	83.14(2)
V, Å^3	1559.4(6)
Z	2
d_{calcd}, g cm^{-3}	1.705
F(000)	788
radiation, Å	*λ*(Mo Kα), 0.710 73
scan type	*ω*
scan speed, deg min^{-1}	2.30−9.23
scan width, deg	$\Delta\omega = 0.88 + 0.347 \tan\theta$
θ range, deg	2−25
linear abs, *μ*, cm^{-1}	44.045
no. of rflns measd	6683
temp, K	296(1)
decay, %	−26.5, corrected
cutoff for obsd data	$I \geq 3.3\sigma(I)$
no. of unique obsd data (NO)	4396
no. of variables (NV)	440
R(*F*)	0.035
$R_w(F)$	0.046
wght, $w^{-1} = [\sigma^2(I) + (pF_o{}^2)^2]^{1/2}$, *p*	0.04
GOF	3.090
ρ_{max}/ρ_{min} (DF)	1.76^a/−0.18

[a] Close to the tungsten atom.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]Mo(\mu\text{-}PPh_2,Cl)W(CO)_4$ (16). IR (ν_{CO}, THF): 2036 (m), 1910 (S), 1884 (S) cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 1.08 (s, 3H, Me), 1.14 (s, 3H, Me), 7.26−8.15 (m, 10H, C_6H_5). Unsatisfactory analysis was obtained for this compound, but the mass spectrum displays the M$^+$ fragment.

$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(\mu\text{-}PPh_2,Cl)W(CO)_4$ (17). IR (ν_{CO}, THF): 2037 (m), 1910 (S), 1890 (S) cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 1.08 (s, 3H, Me), 1.32 (s, 3H, Me), 7.26−7.39 (m, 6H, C_6H_5), 8.12−8.22 (m, 4H, C_6H_5). Anal. Calcd for $C_{28}H_{25}O_4ClPW_2$: C, 40.01; H, 2.78. Found: C, 40.00; H, 2.99.

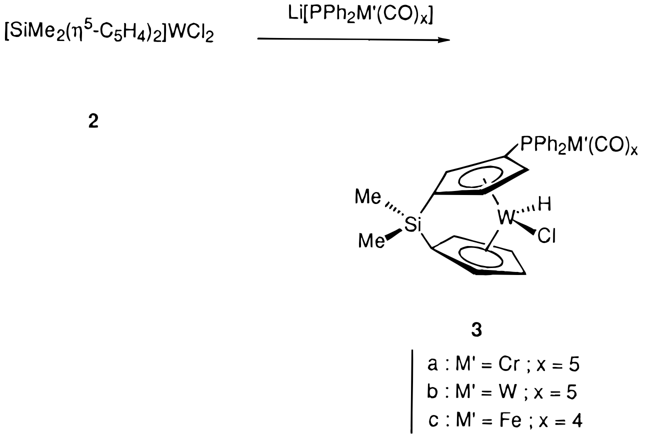
X-ray Structure Analysis of 7d. A red crystal having the approximate dimensions 0.35 × 0.2 × 0.1 mm was used for unit cell measurements and intensity data collection, carried out at 296 K on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (*λ* = 0.710 73 Å). The pertinent crystallographic data are given in Table 1. All calculations have been carried out by use of the MOLEN package with neutral-atom scattering factors taken from the usual source.

Intensities were corrected for Lorentz and polarization effects as well as for rather large linear decay. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. There is one solvent (acetone) molecule per organometallic molecule. All non-hydrogen atoms of the organometallic molecule were refined with anisotropic thermal parameters, and the hydrogen atoms were placed in calculated positions. The solvent molecule was refined in an isotropic model. The hydrogen atoms for both the organometallic and the acetone molecules were ridden on the atoms bearing them and included in the final calculations with B_{iso} fixed at values equal to $1.3B_{eq}$ for the corresponding carbon atoms.

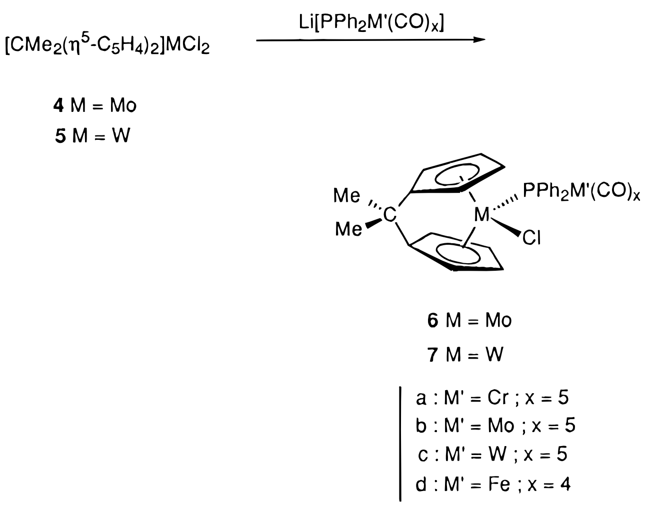
Results and Discussion

SiMe$_2$-Bridged Complexes. The *ansa* dimethylsilyl dichlorides $[SiMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ (M = Mo (**1**), W (**2**)) were prepared from MCl_4L (M = Mo, L = $(OEt_2)_2$; M = W, L = dme) and the corresponding dilithium salt $Li_2[SiMe_2(\eta^5\text{-}C_5H_4)_2]$ according to the recent work of Green *et al.*[11] These complexes are isolated as maroon powders sparingly soluble in dichloromethane and chloroform. Surprisingly, no characterizable material can be isolated from molybdenum dichloride **1** and the metallophosphide anions. In contrast, reactions performed with the tungstenocene derivative **2** proceed cleanly, affording the Cp substituted products **3** (Scheme 1).

Scheme 1



Scheme 2



Substitution on the Cp ring occurs with total regioselectivity at the 3 position as evidenced by COSY and selective decoupling experiments. Furthermore, it must be pointed out that the reaction leads to a unique diastereoisomer (racemic), although two stereogenic units—plane and center—are formed simultaneously. The same stereochemical trend was previously observed with the methyl and *tert*-butyl tungstenocene derivatives.[7]

CMe$_2$-Bridged Complexes. We have also synthesized the *ansa* precursors $[CMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ (M = Mo (**4**), W (**5**)) according to the Green's procedure.[11]

Treatment of dichlorides **4** and **5** with anions $[PPh_2M'(CO)_x]^-$ in THF for 5 h at room temperature results in the formation of bimetallic complexes **6** and **7** (Scheme 2). These compounds are isolated in moderate yields (20−40%) after chromatographic purification as red solids insoluble in hydrocarbon or aromatic solvents and sparingly soluble in chloroform or acetone. Their ^{1}H NMR data are consistent with a substitution

Table 2. NMR Data for the Complexes 3,[b] 6,[a] 7,[a] 14,[b] 14′,[b] 15,[b] 15′,[b] 16,[a] and 17[a]

	^1H NMR (ppm)		
compd	C_5H_4	M−*H*	^{31}P NMR (ppm) *P*Ph_2
3a	4.21, 4.47, 4.84, 5.06, 5.70, 5.80, 6.06	−9.6 (d + dd, $^1J_{WH} = 60$ Hz, $J_{PH} = 9$ Hz)	49.67 (s)
3b	4.28, 4.51, 4.90, 5.07, 5.74, 5.91, 6.02	−9.5 (d + dd, $^1J_{WH} = 60$ Hz, $J_{PH} = 10$ Hz)	15.46 (s + d, $^1J_{WP} = 253$ Hz)
3c	4.38, 4.48, 4.92, 5.07, 5.71, 5.88 (2H)	−9.8 (d + dd, $^1J_{WH} = 57$ Hz, $J_{PH} = 7$ Hz)	62.03 (s)
6a	2.97, 3.10, 5.2 (2H), 5.68, 5.82, 6.19 (2H)		1.02 (s)
6b	3.09, 5.00, 5.21, 5.26, 5.47, 5.67, 5.89, 6.29		−11.5 (s)
6c	3.11 (2H), 5.22 (2H), 5.97 (4H)		−29.43 (s + d, $^1J_{WP} = 193$ Hz)
7a	3.30, 5.28, 5.47 (2H), 5.60 (2H), 5.96, 6.18		−35.29 (s + d, $^1J_{WP} = 185$ Hz)
7b	4.88 (2H), 5.50 (2H), 5.68 (2H), 5.96 (2H)		−62.98 (s + d, $^1J_{WP} = 189$ Hz)
7c	3.31 (2H), 5.45 (2H), 5.66 (2H), 5.87 (2H)		−62.97 (s + d, $^1J_{WP} = 189$ Hz)
7d	4.19 (2H), 5.54 (2H), 5.80 (2H), 5.85 (2H)		−13.6 (s + d, $^1J_{WP} = 202$ Hz)
14a	4.58 (2H), 4.78 (2H), 4.87 (2H), 5.33 (2H)	−4.85 (d, $^2J_{PH} = 44$ Hz)	3.02 (s)
14c	4.71 (2H), 4.91 (2H), 5.01 (2H), 5.41 (2H)	−5.55 (d, $^2J_{PH} = 43$ Hz)	−1.02 (s + d,$^1J_{WP} = 190$ Hz)
14′a	3.35 (2H), 5.19 (2H), 5.51 (2H), 5.61 (2H)	−13.65 (d, $^2J_{PH} = 22$ Hz)	132.33 (s)
14′b	3.44 (2H), 5.34 (4H), 5.60 (2H)	−12.32 (d, $^2J_{PH} = 18$ Hz)	103.01 (s)
14′c	3.35 (2H), 5.19 (2H), 5.51 (2H), 5.61 (2H)	−12.08 (d + dd, $^1J_{WH} = 31$ Hz, $^2J_{PH} = 14$ Hz)	91.6 (s + d, $^1J_{WP} = 190$ Hz)
15a	4.5 (2H), 4.93 (4H), 5.25 (2H)	−7.25 (d + dd, $^1J_{WH} = 96$ Hz, $^2J_{PH} = 37$ Hz)	−37.15 (s + d, $^1J_{WP} = 180$ Hz)
15b	4.69 (2H), 4.84 (2H), 4.93 (2H), 5.10 (2H)	−7.25 (d + dd, $^1J_{WH} = 89$ Hz, $^2J_{PH} = 37$ Hz)	−48.61 (s + d, $^1J_{WP} = 173$ Hz)
15c	4.70 (2H), 4.85 (2H), 4.95 (2H), 5.12 (2H)	−7.15 (d + dd, $^1J_{WH} = 82$ Hz, $^2J_{PH} = 37$ Hz)	−65.6 (s + d, $^1J_{WP} = 185$ Hz)
15′a	3.35 (2H), 4.48 (2H), 5.25 (2H), 5.66 (2H)	−15.35 (d + dd, $^1J_{WH} = 70$ Hz, $^2J_{PH} = 15$ Hz)	91.9 (s + d, $^1J_{WP} = 205$ Hz)
15′b	3.40 (2H), 5.37 (4H), 5.65 (2H)	−14.4 (d + dd, $^1J_{WH} = 77$ Hz, $^2J_{PH} = 10$ Hz)	62.7 (s + d, $^1J_{WP} = 193$ Hz)
15′c	3.44 (2H), 5.41 (2H), 5.47 (2H), 5.73 (2H)	−15.2 (d + ddd, $^1J_{WH} = 76$ Hz, $^1J_{WH} = 32$ Hz, $^2J_{PH} = 6$ Hz)	47.72 (s + dd, $^1J_{WP} = 193$ Hz, $^1J_{WP} = 229$ Hz)
16	3.69 (2H), 5.01 (2H), 5.16, 5.44, 6.3 (2H)		87.14 (s + d, $^1J_{WP} = 256$ Hz)
17	3.63 (2H), 5.12 (2H), 5.35 (2H), 5.46 (2H)		47.2 (s + d, $^1J_{WP} = 248$ Hz)

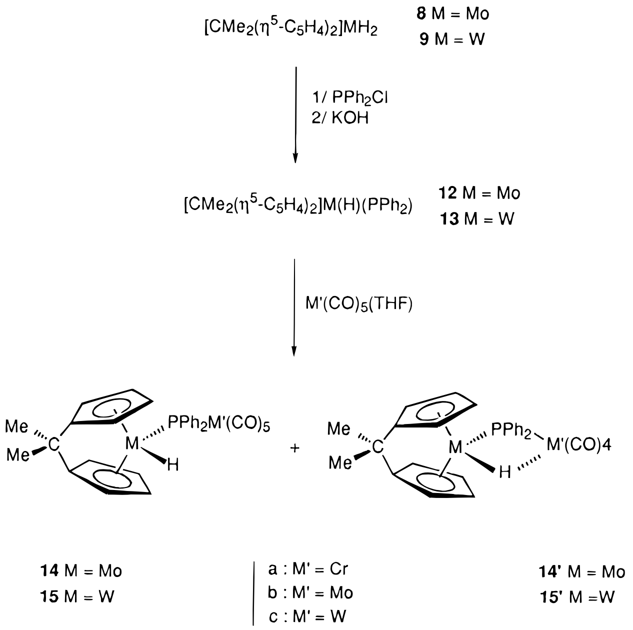
[a] NMR spectra recorded in $CDCl_3$. [b] NMR spectra recorded in CD_3COCD_3.

occurring on the metal center by displacement of a chloride ion. The eight Cp protons resonate in two well-separated ranges: a set of three or four signals located between 6 and 5 ppm and a set of one (2H) or two (1H) signals shifted to high field near 3.5 ppm (Table 2). All these signals appear as broad multiplets at room temperature. They become sharp at higher temperature, indicating severe molecular steric strains. ^{31}P NMR data agree with the coordination of the phosphido group to the metal center. The shielding of ^{31}P resonances displayed by complexes **6** and **7** is typical of μ-phosphido structures.[15−18] The chemical shifts are, as expected, dependent on the nature of M and M′, and the resonances in **7** are accompanied by a pair of ^{183}W satellites. Only one pair of satellites is observed for ditungsten complex **7c**, suggesting the same value (190 Hz) of $^1J_{PW}$ coupling constant for both metals.

The complexes **6** and **7** may also be formed by starting from *ansa* hydrides. This approach is based on our general strategy of terminal phosphido complex formation followed by metal carbonyl unit complexation[15] (Scheme 3).

Dihydrides **8** and **9**[11] react instantaneously with PPh_2Cl, affording after treatment with base the metallophosphines **12** and **13**. These terminal phosphido complexes react at room temperature with $[M'(CO)_5]$ fragments (M′ = Cr, Mo, W), leading to a mixture of mono- and dibridged complexes **14** + **14′** and **15** + **15′**, respectively. Separation of the complexes is achieved by chromatography. Hydrido bridging in **14′** or **15′** is clearly evidenced by the high-field resonances of M-H protons and the deshielding (by some 100 ppm) of ^{31}P resonances with respect to the monobridged complexes **14** or **15**. Such a downfield shift is indicative of a large decrease of the M−P−M′ angle in the cyclic dibridged structures.

Scheme 3



Treatment of complex **15c** by CCl_4 results in the formation of **7c**. In reverse, chloro compound **7c** can be transformed to the hydride **15c** by reaction with $NaAlH_2(OCH_2CH_2OMe)_2$ (Scheme 4).

Upon photochemical irradiation, the chloro complexes **6c** and **7c** give, as shown in Scheme 5, the μ-phosphido μ-chloro compounds **16** and **17**, respectively. The ^1H NMR spectra exhibit for the Cp proton resonances a set of three multiplets between 5 and 5.5 ppm and a more shielded one at 3.8 ppm. The ^{31}P NMR resonances of **16** and **17** are shifted downfield ($\Delta\delta$ +100 ppm) relative to **6c** and **7c**. As for the hydrido-bridged analogs, such a deshielding is due to the ring closure upon the formation of the chloro bridge.

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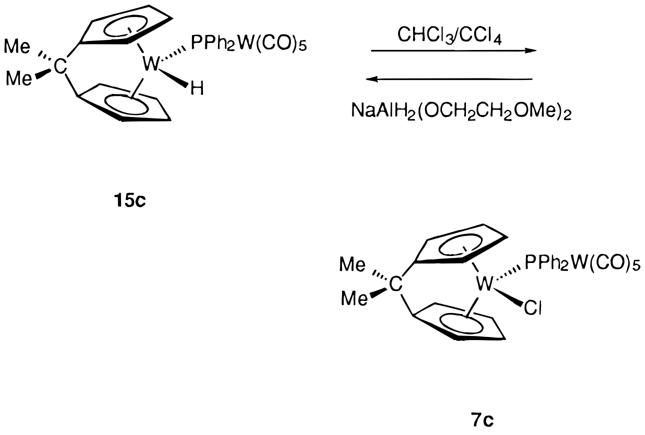
(16) (a) Boni, G.; Sauvageot, P.; Moïse, C. *J. Organomet. Chem.* **1995**, *489*, C32. (b) Boni, G.; Sauvageot, P.; Marpeaux, E.; Moïse, C. *Organometallics* **1995**, *14*, 5652.

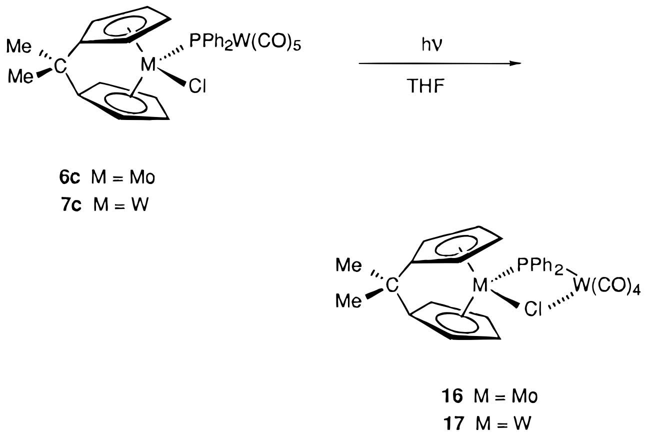
(17) Oudet, P.; Perrey, D.; Bonnet, G.; Moïse, C.; Kubicki, M. M. *Inorg. Chim. Acta* **1995**, *237*, 79.

(18) Sauvageot, P.; Blacque, O.; Kubicki, M. M.; Jugé, S.; Moïse, C. *Organometallics* **1996**, *15*, 2399.

Scheme 4



Scheme 5



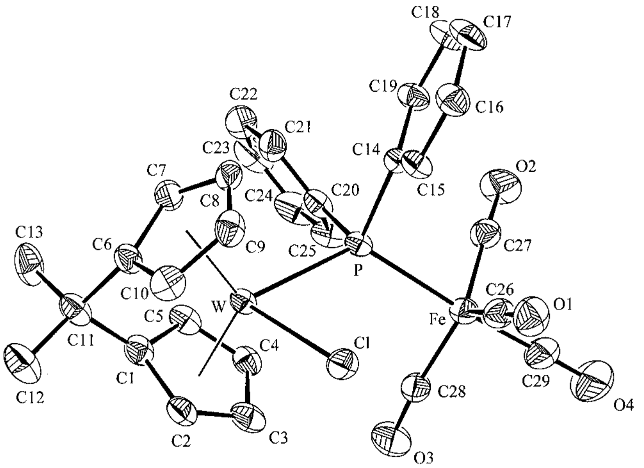


Figure 1. Molecular structure of $[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Fe(CO)_4$ (**7d**) (30% probability level).

Table 3. Selected Bond Distances (Å) and Angles (deg) for$[CMe_2(\eta^5\text{-}C_5H_4)_2]W(Cl)(\mu\text{-}PPh_2)Fe(CO)_4$ (7d)

W−Fe	4.412(1)	W−C6	2.23(1)
W−CP1	1.94	W−C7	2.280(9)
W−CP2	1.96	W−C8	2.371(9)
W−Cl	2.430(2)	W−C9	2.36(1)
W−P	2.626(2)	W−C10	2.23(1)
W−C1	2.239(9)	Fe−P	2.371(3)
W−C2	2.244(9)	Fe−C26	1.786(9)
W−C3	2.35(1)	Fe−C27	1.79(1)
W−C4	1.36(1)	Fe−C28	1.78(1)
W−C5	2.244(8)	Fe−C29	1.75(1)
CP1−W−CP2	125.5	P−Fe−C29	175.5(4)
Cl−W−P	82.17(7)	W−P−Fe	123.95(9)
P−Fe−C26	90.9(3)	C14−P−C20	102.6(4)
P−Fe−C27	85.7(3)	C1−C11−C6	94.0(7)
P−Fe−C28	95.4(3)	$C_5(1)-C_5(2)^b$	115.9

[a] CP1 and CP2 are the geometrical centers of C1−C5 and C6−C10 rings, respectively. [b] Dihedral angle between C_5 (C1−C5) and C_5 (C6−C10) planes.

The molecular geometry of **7d** has been etablished by X-ray analysis. The crystal structure is built from organometallic and solvent acetone molecules. The dinuclear organometallic molecule (Figure 1) consists of *ansa*-tungstenocene monochloride and tetracarbonyl iron fragments singly bridged by a diphenylphosphide group.

Selected bond lengths and angles are gathered in Table 3. **7d** exhibits a largely opened W−P−Fe angle and rather long W−P and Fe−P bonds resulting from steric requirements of the metallic units (Table 3).

The W···Fe separation of 4.412(1) Å is nonbonding. These overall features agree with the parameters generally observed in monobridged μ-PR_2 complexes containing a metallocene and metal carbonyl fragments.[15,17,18]

The Fe−P bond length of 2.371(3) Å is longer than the usual range observed for $PR_3Fe(CO)_4$ molecules[19] (2.25−2.30 Å). It is even longer than that reported for the tetracarbonyliron complex with P^tBu_3[20] (2.364(1)Å). Thus, our chloro *ansa*-tungstenocene phosphine seems to be slightly bulkier than the *tert*-butyl one.

The Cl−W−P angle of 82.17(7)° is essentially the same as the Cl−M−Cl angles found for *ansa* or non-*ansa* group 6 metallocenes.[11,21] However, an examination of the structural parameters associated with the cyclopentadienyl rings indicates that the presence of the methylene bridge between these rings leads to some geometrical modifications with respect to the usual non-*ansa* bis(cyclopentadienides). The CP1−W−CP2 angle (125.5°) as well as the bending (dihedral) angle between the best planes of the cyclopentadienyl rings (115.9°) correspond very well to the parameters reported for other *ansa*-metallocenes.[11,12] The pairs of C3/C4 and C8/C9 atoms deviate by 0.1 and 0.08 Å from the planes defined by C1/C2/C5 and C6/C7/C10 atoms, respectively, away from the tungsten atom. The W−C distances involving the atoms of these pairs (mean 2.36 Å) are longer than for the other six carbons (mean 2.24 Å). This shows that the substitution of a bulky $PPh_2Fe(CO)_4$ ligand by one chloride in the coordination polyhedron of the tungsten atom has little or no steric effect, confirming a considerable opening of the metal coordination sphere in the vicinity of the metallocene frontier orbitals[22] in *ansa* complexes.

The striking difference in reactivity observed between the two *ansa* structures can be rationalized by considering the Cp ring tilting effect introduced by the single atom bridging. Comparison of Cp−M−Cp angles between *ansa* CMe_2 bridged and non-*ansa* derivatives for M = Mo, W[11] and for M = Ti, Zr[23] shows that the tie

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[19] (a) Howell, J. A. S.; Palin, M. G.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *Inorg. Chem.* **1993**, *32*, 3493 and references cited therein. (b) Kilbourn, B. T.; Raeburn, U. A.; Thompson, D. T. *J. Chem. Soc. A* **1969**, 1906.

[20] Pickard, J.; Rösch, L.; Schumann, H. *J. Organomet. Chem.* **1976**, *107*, 241.

[21] Labella, L.; Chernega, A.; Green, M. L. H. *J. Organomet. Chem.* **1995**, *485*, C18.

[22] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, 1729.

causes a decrease in the bending angle of 15−20°. Consequently, such decreases open the metal environment and render possible the approach of the sterically demanding metallophosphide anion to the metallic center. In contrast, the crystallographic data available for the *ansa* complexes $[SiMe_2(\eta^5\text{-}C_5H_4)_2]MCl_2$ (M = Ti, Zr,Hf[23] or M = Nb[24]) indicate no significant modification in the Cp tilting (small decrease of about 2°) with respect to the unsubstituted parent compounds. This is not surprising, since the covalent radius of silicon is about 1.5 times that of carbon. Therefore, it becomes understandable why the same substitution site is observed both in the *ansa* $SiMe_2$ and in Cp_2MCl_2 complexes.

Supporting Information Available: For **7d**, tables of X-ray crystallographic data, including atomic coordinates, anisotropic thermal parameters, interatomic distances and angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

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[23] Shaltout, R. M.; Corey, J. Y. *Tetrahedron* **1995**, *51*, 4309.

[24] Antinolo, A.; Martinez-Ripoll, M.; Mugnier, Y.; Otero, A.; Prashar, S.; Rodriguez, A. M. *Organometallics* **1996**, *15*, 3241.