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# A New Type of Heterobimetallic Compound Containing Tungstenocene: Synthesis, Reactivity, NMR, and Stereochemical Studies

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Reaction of $[PPh_2M(CO)_5]Li$ salts (M = Cr or W) toward tungstenocene dichloride occurs via a cyclopentadienyl ring substitution and yields the corresponding binuclear compounds $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4PPh_2M(CO)_5]W(H)Cl$, **2**. They react with $LiAlH_4$ to give the corresponding dihydride complexes $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4PPh_2M(CO)_5]WH_2$, **3**. These species have been proven to be photosensitive leading to the cyclic heterobimetallic $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4\text{-}PPh_2\overline{M(CO)_4]W(\mu\text{-}H})H$ compounds, **4**; analytical data and spectroscopic measurements on complexes **4** indicate that a hydride group functions as a bridging ligand. Crystals of **4a** (M = Cr) were obtained as red needles, grown from toluene solution. An isotropic refinement of only 1243 data ($F > 5\sigma(F)$) from a low resolution data set (3707 data, $d_{\min} = 0.9$ Å) indicated significant systematic error. Thus it was possible only to ascertain that the connectivity of the non-hydrogen atoms is not inconsistent with the model proposed from solution NMR and that the Cr···W separation of 3.30 Å precludes a direct Cr−W bond. **4a** crystallizes in space group *Pbca* (No. 61), with $a = 19.693(8)$ Å, $b = 20.34(1)$ Å, $c = 11.695(5)$ Å, $V = 46823$ Å$^3$, and $Z = 8$. Further information on this preliminary structure determination is provided in the Supporting Information. These reactions have been investigated with stereochemical factors in mind using the ring substituted tungtenocene complex $(\eta^5\text{-}C_5H_4\text{-}Me)_2WCl_2$; the 1−3 regioselectivity of the ring disubstitution reaction is proposed on the basis of $^1H$ NMR experiments. The temperature dependent relaxation time measured between 295 and 213 K by the inversion recovery method makes it possible to determine a proton−proton distance between the two H ligands of 2.0 Å in **4′a**.

## Introduction

In stoichiometric or catalytic reactions, heterobinuclear organometallic complexes are currently of considerable interest because of their potential to exhibit various reactivities at the two different metal centers.[1] Several synthetic approaches to such systems have been explored, both with[2] or without[3] metal−metal bonds. However, the generally weak M−M′ bond of the former complexes appears to be unfavorable when investigating dinuclear reactivity.[4] The stability of the bimetallic framework of the latter complexes is enhanced by the presence of a bidentate ligand linking the two disparate metal sites.[5]

Over the past few years, our group has developed and explored the synthesis of metallocenic molecules (with group 5 or 6 metals) which contain an electron-donating site. Among the most successful classes of these ligands are compounds such as bis(cyclopentadienyl)−phosphido complexes $L_nM(PR_2)$ and some of their corresponding oxides or sulfides where M = Nb, Ta, Mo or W.[6]

Our examination of new routes to prepare bimetallic complexes concerns the preparation of systems with functionalized cyclopentadienyl ligands. Different methods have been re-

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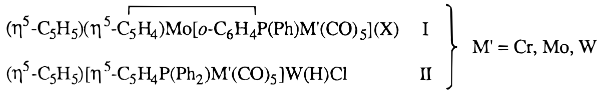
ported: (i) direct electrophilic substitutions, which are well documented for ferrocenic and cyclopentadienyl manganese tricarbonyl derivatives;[7] (ii) functionalization of the cyclopentadienyl ligand prior to its introduction to the metal center;[8] (iii) lithiation reactions of the metallocene complex;[5a,5b] (iv) direct cyclopentadienyl ligand substitution as reported with tungstenocene dihydride by reaction with alkyldichloroboranes.[9] We have recently observed that $Cp_2MCl_2$ (M = Mo,W) undergoes nucleophilic substitution at one Cp ring when exposed to a metalated phosphide, followed by an orthometalation reaction when M = Mo, leading to type I (M = Mo)[10] or II (M = W)[11] dinuclear complexes.



$$\left.\begin{array}{ll}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}\overline{C_5H_4)Mo[o\text{-}C_6H_4}P(Ph)M'(CO)_5](X) & \text{I} \\ (\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(Ph_2)M'(CO)_5]W(H)Cl & \text{II}\end{array}\right\} M' = Cr, Mo, W$$

In addition to stereochemical studies, our study will emphasize the properties of the type II bimetallic system inherent in the presence of a reactive tungsten site. In this regard we have investigated the reactivity of the dihydride complexes, and the results of this study are presented herein. The crystal structure and the full spectroscopic characterization of a new type of dinuclear species containing intramolecular bridging hydrido ligands are reported.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of purified argon. The solvents were dried by the appropriate procedure and distilled under argon prior to use. Standard Schlenk-line technique and conventional glass vessels were employed.

Elemental analyses were performed by the CNRS microanalytical laboratory. Field desorption and electron ionization mass spectra were run respectively on a Finnigan MAT 311 instrument and a Kratos Concept 32S. IR spectra were recorded on a Nicolet 205 instrument.

Dichloro complexes $Cp_2WCl_2$ and $(\eta^5\text{-}C_5H_4Me)_2WCl_2$ were prepared by published procedures.[12] The lithium reagent, $Li[M'(CO)_5PPh_2]$, was prepared according to the literature method[13] using low-chloride methyllithium (Janssen).

**NMR Procedures.** $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were collected on Bruker AC-200 and AC-80 spectrometers. The conventional inversion−recovery method (180−$\tau$−90) was used to determine $T_1$. The calculation of the relaxation times was carried out using the nonlinear three-parameter fitting routine of the spectrometers. Durations of the pulses were controlled in each experiment. In each $T_1$ experiment, the waiting period was 5 times the expected relaxation time and 10-11 variable delays were employed. Errors in such $T_1$ determinations were <5%. The symbols *o*, *m*, *p*, and *i* correspond to ortho, meta, para, and ipso carbons of the phenyl groups respectively.

**Preparation of Complexes 2 and 2′.** To 15 mL of a THF suspension of $Cp_2WCl_2$ (890 mg, 2.31 mmol) was added 5 mL of a THF solution of $Li[M'(CO)_5PPh_2]$ (2.33 mmol) (M′ = Cr, W) rapidly. The mixture was stirred at room temperature for 1 h. THF was removed in vacuo, and the residue was washed with 40 mL of pentane and chromatographed [eluent: toluene/THF, 1/1] to give **2** as a beige powder. **2′** was synthesized by the same procedure but using $(\eta^5\text{-}C_5H_4\text{-}Me)_2WCl_2$ instead of $Cp_2WCl_2$.

**$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4PPh_2Cr(CO)_5]W(H)Cl$, 2a.** Yield: 50%. IR (THF, $cm^{-1}$): 2062 w, 1938 s + sh ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$): $\delta$ −10.72 (s + d, $^1J(^{183}WH)$ = 58 Hz, 1H, WH), 4.12 (m, 1H, $C_5H_4$), 4.62 (s, 5H, $C_5H_5$), 4.63 (m, 1H, $C_5H_4$), 4.83 (m, 1H, $C_5H_4$), 5.82 (m, 1H, $C_5H_4$), 7.39−7.64 (m, 10H, $C_6H_5$). $^1H$ NMR ($C_6D_6$): $\delta$ −10.54 (s + d, $^1J(^{183}WH)$ = 58 Hz, 1H, WH), 3.50 (m, 1H, $C_5H_4$), 3.98 (m, 1H, $C_5H_4$), 4.14 (s, 5H, $C_5H_5$), 4.57 (m, 1H, $C_5H_4$), 5.03 (m, 1H, $C_5H_4$), 6.99−7.02 (m, 6H, $C_6H_5$), 7.44−7.53 (m, 2H, $C_6H_5$), 7.60−7.70 (m, 2H, $C_6H_5$). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): $\delta$ 48.9; $^{31}P\text{-}\{^1H\}$ NMR ($C_6D_6$): $\delta$ 48.2; $^{13}C\text{-}\{^1H\}$ NMR ($C_6D_6$): $\delta$ 79.69 (s, 1C, $C_5H_4$), 83.53 (s, 1C, $C_5H_4$), 85.49 (s, 5C, $C_5H_5$), 87.75 (d, J(CP) = 30 Hz, 1C, i-$C_5H_4$), 87.77 (d, J(CP) = 5 Hz, 1C, $C_5H_4$), 102.50 (d, J(CP) = 11.4 Hz, 1C, $C_5H_4$), 130.01 (s, 1C, *p*-$C_6H_5$), 130.48 (s, 1C, *p*-$C_6H_5$), 132.53 (d, J(CP) = 10.61 Hz, 2C, *o*-$C_6H_5$), 133.45 (d, J(CP) = 11.37 Hz, 2C, o-$C_6H_5$), 137.89 (d, J(CP) = 38.6 Hz, 1C, i-$C_6H_5$), 139.47 (d, J(CP) = 37.1 Hz, 1C, i-$C_6H_5$), (*m*-$C_6H_5$ masked by the solvent), 217.19 (d, J(CP) = 12.9 Hz, 4C, CO), 221.62 (d, J(CP) = 5.30 Hz, 1C, CO). Anal. Calcd for $C_{27}H_{20}PO_5WCrCl$: C, 44.62; H, 2.77. Found: C,44.3; H, 3.0.

**$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4PPh_2W(CO)_5]W(H)Cl$, 2b.** Yield: 50%. IR (THF, $cm^{-1}$): 2071 w, 1938 s + sh ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$): $\delta$ −10.72 (s + d, $^1J(^{183}WH)$ = 57 Hz, 1H, WH), 4.14 (m, 1H, $C_5H_4$), 4.53 (m, 1H, $C_5H_4$), 4.62 (s, 5H, $C_5H_5$), 4.87 (m, 1H, $C_5H_4$), 5.87 (m, 1H, $C_5H_4$), 7.43−7.64 (m, 10H, $C_6H_5$). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): $\delta$ 12.4 (s + d, $^1J(^{183}WH)$ = 255 Hz). MS (FD): 857.9 ($M^+$). Anal. Calcd for $C_{27}H_{20}PO_5W_2Cl$: C, 37.77; H, 2.35. Found: C, 38.0; H, 2.4.

**$(\eta^5\text{-}C_5H_4\text{-}Me)\{\eta^5\text{-}C_5H_3(1\text{-}Me)[3\text{-}PPh_2Cr(CO)_5]\}W(H)Cl$. 2′a:** Yield: 25%. IR (THF, $cm^{-1}$): 2062 w, 1937 s + sh ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$): $\delta$ −9.47 (s + d, $^1J(^{183}WH)$ = 74 Hz, 1H, WH), 2.00 (s, 6H, $CH_3$), 3.76 (m, 1H), 3.83 (m, 1H), 4.08 (m, 1H), 4.46 (m, 1H), 4.60 (m, 1H), 4.88 (m, 1H), 5.48 (m, 1H), $C_5H_3$ or $C_5H_4$, 7.42−7.62 (m, 10H, $C_6H_5$). $^1H$ NMR ($C_6D_6$): $\delta$ −9.04 (s + d, $^1J(^{183}WH)$ = 74 Hz, 1H, WH), 1.75 (s, 3H, $CH_3$), 1.86 (s, 3H, $CH_3$), 3.23 (m, 1H), 3.53 (m, 1H), 3.83 (m, 1H), 4.40 (m, 2H), 4.84 (m, 1H), 4.91 (m, 1H), $C_5H_3$ or $C_5H_4$, 6.91−7.04 (m, 6H, $C_6H_5$), 7.44−7.53 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 52.5. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 15.60 (s, 1C, $CH_3$), 16.58 (s, 1C, $CH_3$), 75.33 (s, 1C), 77.51 (s, 1C), 81.82 (d, J(CP) = 32 Hz, 1C, i-C), 84.61 (s, 1C), 85.43 (s, 1C), 86.03 (s, 1C), 86.41 (d, J(CP) = 6 Hz, 1C), 89.22 (s, 1C), 118.00 (s, 1C, i-C), (the third i-C masked), $C_5H_3$ or $C_5H_4$, 130.04 (s, 1C, *p*-$C_6H_5$), 130.33 (s, 1C, *p*-$C_6H_5$), 132.39 (d, J(CP) = 10.6 Hz, 2C, *o*-$C_6H_5$), 133.58 (d, J(CP) = 11.4 Hz, 2C, *o*-$C_6H_5$), 136.81 (d, J(CP) = 37.14 Hz, 1C, i-$C_6H_5$), 140.72 (d, J(CP) = 37.14 Hz, 1C, i-$C_6H_5$), (*m*-$C_6H_5$ masked by the solvent), 217.28 (d, J(CP) = 12.13 Hz, 4C, CO), 221.55 (d, J(CP) = 6.06 Hz, 1C, CO). MS (FD): 754.1 ($M^+$).

**$(\eta^5\text{-}C_5H_4Me)\{\eta^5\text{-}C_5H_3(1\text{-}Me)[3\text{-}PPh_2W(CO)_5]\}W(H)Cl$, 2′b.** Yield: 25%. IR (THF, $cm^{-1}$): 2071 w, 1936 s + sh ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$): $\delta$ −9.50 (s + d, $^1J(^{183}WH)$ = 72 Hz, 1H, WH), 1.99 (s, 6H, $CH_3$), 3.77 (m, 2H), 4.15 (m, 1H), 4.43 (m, 1H), 4.59 (m, 1H), 4.87 (m, 1H), 5.52 (m, 1H), $C_5H_3$ or $C_5H_4$, 7.42−7.56 (m, 10H, $C_6H_5$). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): $\delta$ 18.0 (s + d; $^1J(^{183}WP)$ = 251 Hz). MS (FD): 886.2 ($M^+$).

**Preparation of Complexes 3 and 3′.** To 20 mL of a THF solution of **2** (1.5 mmol), was added $LiAlH_4$ (excess 30%) slowly at 0 °C. The resulting mixture was stirred for 3 h at room temperature. Excess $LiAlH_4$ was filtered off. After hydrolysis of the filtrate, the solvent was removed in vacuo. **3** was then obtained as yellow needles after

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extraction with ether and purification by recrystallization from toluene. The same procedure was used for **3′** (using a THF solution of **2′**), but it was always obtained with **4′**. **3′** was never found pure.

**($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4PPh_2Cr(CO)_5$]$WH_2$, 3a.** Yield: 40%. IR (THF, $cm^{-1}$): 2061 w, 1936 s + sh ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −11.43 (s + d, $^1J(^{183}WH)$ = 73 Hz, 2H, WH), 3.92 (m, 2H, $C_5H_4$), 4.06 (s, 5H, $C_5H_5$), 4.43 (m, 2H, $C_5H_4$), 6.94−6.99 (m, 6H, $C_6H_5$), 7.46−7.55 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 48.9. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 74.60 (s, 5C, $C_5H_5$), 74.94 (s, 2C, $C_5H_4$), 78.66 (s, 2C, $C_5H_4$), (i-$C_5H_4$ not detected), 129.8 (s, 2C, *p*-$C_6H_5$), 132.96 (d, *J*(CP) = 11.9 Hz, 4C, *o*-$C_6H_5$), 139.16 (d, *J*(CP) = 37.4 Hz, 2C, i-$C_6H_5$), (*m*-$C_6H_5$masked by the solvent), 217.59 (d, *J*(CP) = 13.8 Hz, 4C, CO), 221.82 (d, *J*(CP) = 6.2 Hz, 1C, CO). MS (FD): 692.1 ($M^+$ ). Anal. Calcd for $C_{27}H_{21}WPCrO_5$: C, 46.85; H, 3.06. Found: C, 47.1; H, 3.0.

**($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4PPh_2W(CO)_5$]$WH_2$, 3b.** Yield: 40%. IR (THF, $cm^{-1}$): 2072 w, 1937 s + sh ($\nu_{CO}$); $^1H$ NMR ($C_6D_6$): $\delta$ −11.44 (s + d, $^1J(^{183}WH)$ = 72 Hz, 2H, WH), 3.88 (m, 2H, $C_5H_4$), 4.04 (s, 5H, $C_5H_5$), 4.46 (m, 2H, $C_5H_4$), 6.93−6.97 (m, 6H, $C_6H_5$), 7.44−7.54 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 15.1 (s + d, $^1J(^{183}WP)$ = 255 Hz). MS (EI): 824 ($M^+$ ). Anal. Calcd for $C_{27}H_{21}W_2PO_5$: C, 39.35; H, 2.57. Found: C, 39.0; H, 2.6 .

**($\eta^5$-$C_5H_4Me$)\{$\eta^5$-$C_5H_3$(1-Me)[3-$PPh_2Cr(CO)_5$]\}$WH_2$, 3′a.** Yield: 30%. IR (THF, $cm^{-1}$): 2060 w, 1938 s + sh ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −10.85 (dd, $^2J(HH)$ = 8.9 Hz, $^1J(^{183}WH)$ = 76 Hz, 1H, WH), −10.24 (dd, $^2J(HH)$ = 8.9 Hz, $^1J(^{183}WH)$ = 77 Hz, 1H, WH), 1.78 (s, 3H, $CH_3$), 1.97 (s, 3H, $CH_3$), 3.52 (m, 1H), 3.79 (m, 1H), 3.88 (m, 1H), 4.19 (m, 1H), 4.29 (m, 1H), 4.39 (m, 1H), 4.46 (m, 1H), $C_5H_3$ or $C_5H_4$, 6.96−6.99 (m, 6H, $C_6H_5$), 7.50−7.58 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 48.9. These characteristics are obtained from the spectrum of the crude material.

**($\eta^5$-$C_5H_4Me$)\{$\eta^5$-$C_5H_3$(1-Me)[3-$PPh_2W(CO)_5$]\}$WH_2$, 3′b:** The characteristics of this product cannot be obtained.

**Preparation of Complexes 4 and 4′.** A solution of **3** (1.5 mmol) in THF (100 mL) was irradiated with a HANAU TQ 150 lamp for 3 h at room temperature. The solvent was evaporated to give a red powder. The crude product was chromatographed (eluent: toluene). **4** was recrystallized from toluene as red needles. **4′** was prepared by the same procedure, using a solution of **3′**.

**($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4PPh_2\overline{Cr(CO)_4]W(\mu\text{-}H}$)H 4a.** Yield: 60%. IR (THF, $cm^{-1}$): 1999 w, 1893 s, 1848 s ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −17.08 (s + d, $^1J(^{183}WH)$ = 67 Hz, 2H, WH), 3.56 (m, 2H, $C_5H_4$), 4.17 (s, 5H, $C_5H_5$), 4.46 (m, 2H, $C_5H_4$), 6.96−7.02 (m, 6H, $C_6H_5$), 7.91−8.00 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 47.7. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 76.71 (d, *J*(CP) = 4.5 Hz, 2C, $C_5H_4$), 77.01 (s, 5C, $C_5H_5$), 77.35 (d, *J*(CP) = 6.8 Hz, 2C, $C_5H_4$), (i-$C_5H_4$ not detected), 128.81 (d, *J*(CP) = 9.85 Hz, 4C, *m*-$C_6H_5$), 130.35 (s, 2C, *p*-$C_6H_5$), 132.71 (d, *J*(CP) = 13.64 Hz, 4C, *o*-$C_6H_5$), 136.92 (d, *J*(CP) = 31.08 Hz, 2C, i-$C_6H_5$), 221.44 (d, *J*(CP) = 14.5 Hz, 1C, CO), 221.61 (d, *J*(CP) = 14.5 Hz, 1C, CO), 230.00 (d, *J*(CP) = 1.7 Hz, 1C, CO), 230.71 (d, *J*(CP) = 13.7 Hz, 1C, CO). MS (FD): 664.2 ($M^+$). Anal. Calcd for $C_{26}H_{21}PCrWO_4$: C, 47.01; H, 3.19. Found: C, 47.9; H, 3.3.

**($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4PPh_2\overline{W(CO)_4]W(\mu\text{-}H}$)H, 4b.** Yield: 60%. IR (THF, $cm^{-1}$): 2006 w, 1890 s, 1845 s ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −14.33 (ddd, $^2J(PH)$ = 3 Hz, $^1J(^{183}WH)$ = 67.6 Hz, $^1J(^{183}WH)$ = 14.8 Hz, 2H, WH), 3.59 (m, 2H, $C_5H_4$), 4.15 (s, 5H, $C_5H_5$), 4.58 (m, 2H, $C_5H_4$), 6.91−7.04 (m, 6H, $C_6H_5$), 7.83−7.93 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 3.6 (s + d, $^1J(^{183}WP)$ = 236 Hz). MS (FD): 796.4 ($M^+$). Anal. Calcd for $C_{26}$ $H_{21}PW_2O_4$: C, 39.23; H, 2.66. Found: C, 39.1; H, 2.6.

**($\eta^5$-$C_5H_4Me$)\{$\eta^5$-$C_5H_3$(1-Me)[3-$PPh_2\overline{Cr(CO)_4]\}W(\mu\text{-}H}$)H, 4′a.** Yield: 50%. IR (THF, $cm^{-1}$): 1998 w, 1888 s, 1846 s ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −18.2 (dd, $^2J(HH)$ = 8 Hz, $^1J(^{183}WH)$ = 71 Hz, 1H, WH), −13.9 (dd, $^2J(HH)$ = 8 Hz, $^1J(^{183}WH)$ = 67 Hz, 1H, WH), 1.15 (s, 3H, $CH_3$), 1.95 (s, 3H, $CH_3$), 3.48 (m, 1H), 3.94 (m, 1H), 3.98 (m, 1H), 4.04 (m, 1H), 4.17 (m, 1H), 4.33 (m, 1H), 4.51 (m, 1H), $C_5H_3$ or $C_5H_4$, 7.00−7.10 (m, 6H, $C_6H_5$), 7.91−8.06 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 48.3. MS (FD): 692.4 ($M^+$). Anal. Calcd for $C_{28}H_{25}PCrWO_4$: C, 48.58; H, 3.64. Found: C, 49.3; H, 4.5.

**($\eta^5$-$C_5H_4$-Me)\{$\eta^5$-$C_5H_3$(1-Me)[3-$PPh_2\overline{W(CO)_4]\}W(\mu\text{-}H}$)H. 4′b.** Yield: 50%. IR (THF, $cm^{-1}$): 2004 w, 1889 s, 1843 s ($\nu_{CO}$). $^1H$ NMR ($C_6D_6$): $\delta$ −14.6 (ddd, $^2J(HH)$ = 8 Hz, $^1J(^{183}WH)$ = 66 Hz, $^2J(PH)$ = 2.5 Hz, 1H, WH), −12.5 (ddd, $^2J(HH)$ = 8 Hz, $^1J(^{183}WH)$ = 72 Hz, $^2J(PH)$ = 4 Hz, $^1J(^{183}WH)$ masked, 1H, WH), 1.08 (s, 3H, $CH_3$), 1.98 (s, 3H, $CH_3$), 3.53 (m, 1H), 3.90 (m, 2H), 4.08 (m, 1H), 4.18 (m, 1H), 4.45 (m, 1H), 4.58 (m, 1H), $C_5H_3$ or $C_5H_4$, 6.91−7.04 (m, 6H, $C_6H_5$), 7.86−7.98 (m, 4H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 4.0 (s + d, $^1J(^{183}WP)$ = 236 Hz). MS (FD): 824.4 ($M^+$).

**Scheme 1**

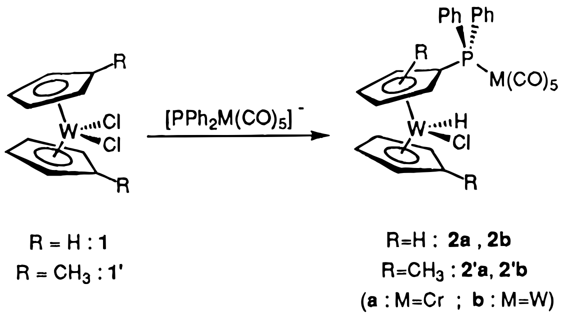
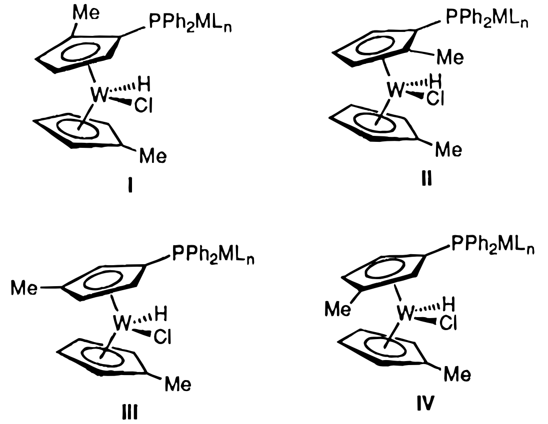


**Chart 1**[a]



[a] Only one enantiomeric form is represented.

## Results and Discussion

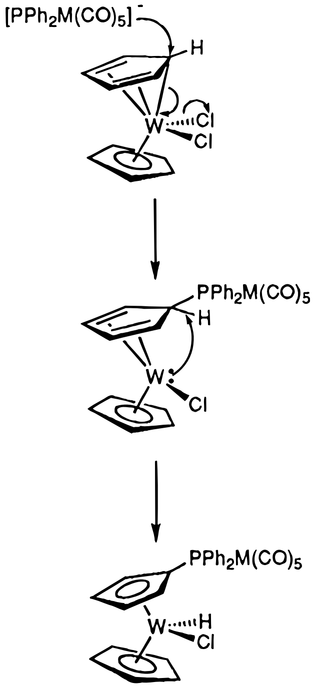
**Complexes 2 and 2′.** The bimetallic complexes **2a** (M = Cr) and **2b** (M = W) are synthesized via the rapid addition of the freshly prepared [$PPh_2M(CO)_5$]Li salt to $Cp_2WCl_2$ suspended in THF, under an inert atmosphere at room temperature (Scheme 1). Compounds **2** are separated from reactants by chromatography; they are fully characterized by field desorption mass spectrometry, IR, and $^1H$ and $^{31}P$ NMR.

The typical patterns of the [$M(CO)_5$] fragments are present in the infrared spectra. The $^1H$ NMR spectra of **2** are consistent with a ring substitution reaction; the newly generated chiral tungsten is responsible for the four signals of the substituted cyclopentadienyl protons, and the hydride signal is located at −10.54 ppm (**2a**) and −10.72 ppm (**2b**) with the expected $^{183}W$−H coupling (*ca.* 57 Hz).

The basic synthetic methodology was used to prepare complexes **2′** from the corresponding tungstenocene dichloride $Cp'_2WCl_2$ ($Cp'$ = $\eta^5$-$C_5H_4Me$). In this case, the ring substitution reaction occurs at a prostereogenic cyclopentadienyl ligand. Two sets of planar prochiral $\alpha$ and $\beta$ (to the methyl group) hydrogen atoms can be substituted leading to four (**I**−**IV**) racemic isomers (Chart 1).

However, a careful examination of the $^1H$ NMR spectra of the crude material reveals the formation of only one bimetallic complex **2′** and shows the presence of seven inequivalent types of cyclopentadienyl hydrogens, at room temperature. These observations suggest that the substitution reaction occurs via a

**Scheme 2**



completely *regioselective* pathway, leading to a 1−2 *or* a 1−3 disubstituted cyclopentadienyl ligand, or a *diastereoselective* reaction, excluding the possibility of a ready inversion of the chiral tungsten center or at planar chiral ring.

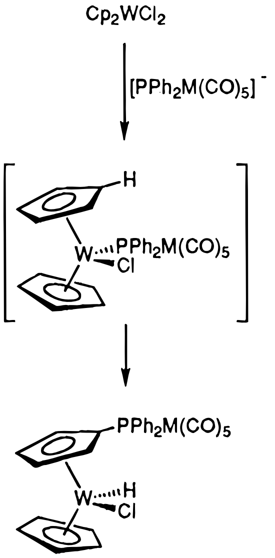
The 1,3-regioselectivity (structure of this ring substitution reaction is proposed on the basis of NMR decoupling experiments (*vide infra*): however, the exact structure (**III** or **IV**) of complexes **2′a** or **2′b** is not elucidated.

Two mechanistic pathways can account for the substitution at the Cp ring: first, in a $S_N2'$ type reaction, a direct attack of the metallophosphide anion on the cyclopentadienyl ligand with a concomitant displacement of a chloride ion can occur. The final step involves insertion of the tungsten carbenic moiety into a Cp C−H bond (Scheme 2); such a mechanism has been proposed by Green for the reaction of $Cp_2WCl_2$ with $C_6F_5Li$[14] and more recently by Cooper[15] for nucleophilic substitution reactions on the cationic tungstenocene derivative $[Cp_2W(Br)(SMe_2)]^+$.

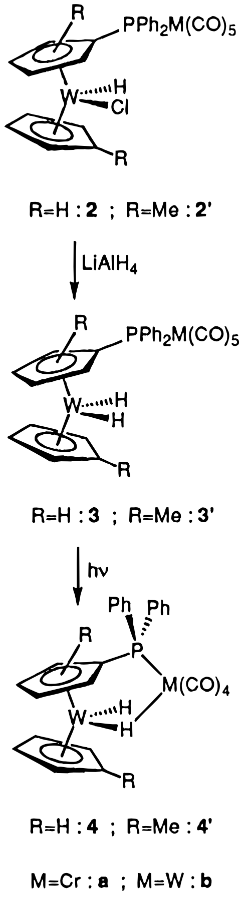
In the second possibility (Scheme 3), postulated by Schubert for the formation of ring silylated tungstenocene[16 a] or molybdenocene[16b] complexes, the products result from an intramolecular migration of the silyl group, primarily bound to the metal center. With molybdenum, the rearrangement can be induced by a basic agent (Li$^n$Bu or LDA) which is supposed to achieve a deprotonation at the Cp ligand. The opposite electronic character of a phosphorus group compared with a silyl group prompts us to preclude this molecular rearrangement hypothesis, but no direct evidence allows us to reach this conclusion unambiguously.

**Complexes 3, 3′, 4 and 4′.** A pale orange-colored solution of complexes **2** in THF reacts rapidly with $LiAlH_4$ at 0 °C to produce a yellow species. After hydrolysis, solvent elimination and extraction with ether, the crude product affords pure yellow crystals of complexes **3** on recrystallization from toluene.

**Scheme 3**



**Scheme 4**



The infrared spectrum of **3a** shows the CO absorptions, at 2061 and 1936 cm$^{-1}$ (large with a shoulder), characteristic of the $[Cr(CO)_5]$ group without notable shift compared to those of precursor **2a**. However, $^1H$ NMR data for **3** clearly demonstrate the $C_s$ symmetry of these dihydride complexes since only two resonance signals are observed for the Cp ring protons.

Carbon monoxide is evolved by photochemical exposure of complexes **3** in THF solution. After chromatographic work up, analytically pure complexes **4** are obtained as red crystals by recrystalization from toluene (Scheme 4). These new cyclic $\mu$-hydrido bimetallic complexes result from a donor (W−H bonds) − acceptor (Lewis acid Cr center) interaction. Their structure is well established according to their spectroscopic data. More specifically, the proton NMR spectrum of **4** exhibits a

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(14) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1969**, 2215.

(15) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420.

(16) (a) Schubert, U.; Schenkel, A. *Chem. Ber.* **1988**, *121*, 939. (b) Seebald, S.; Mayer, B.; Schubert, U. *J. Organomet. Chem.* **1993**, *462*, 225.

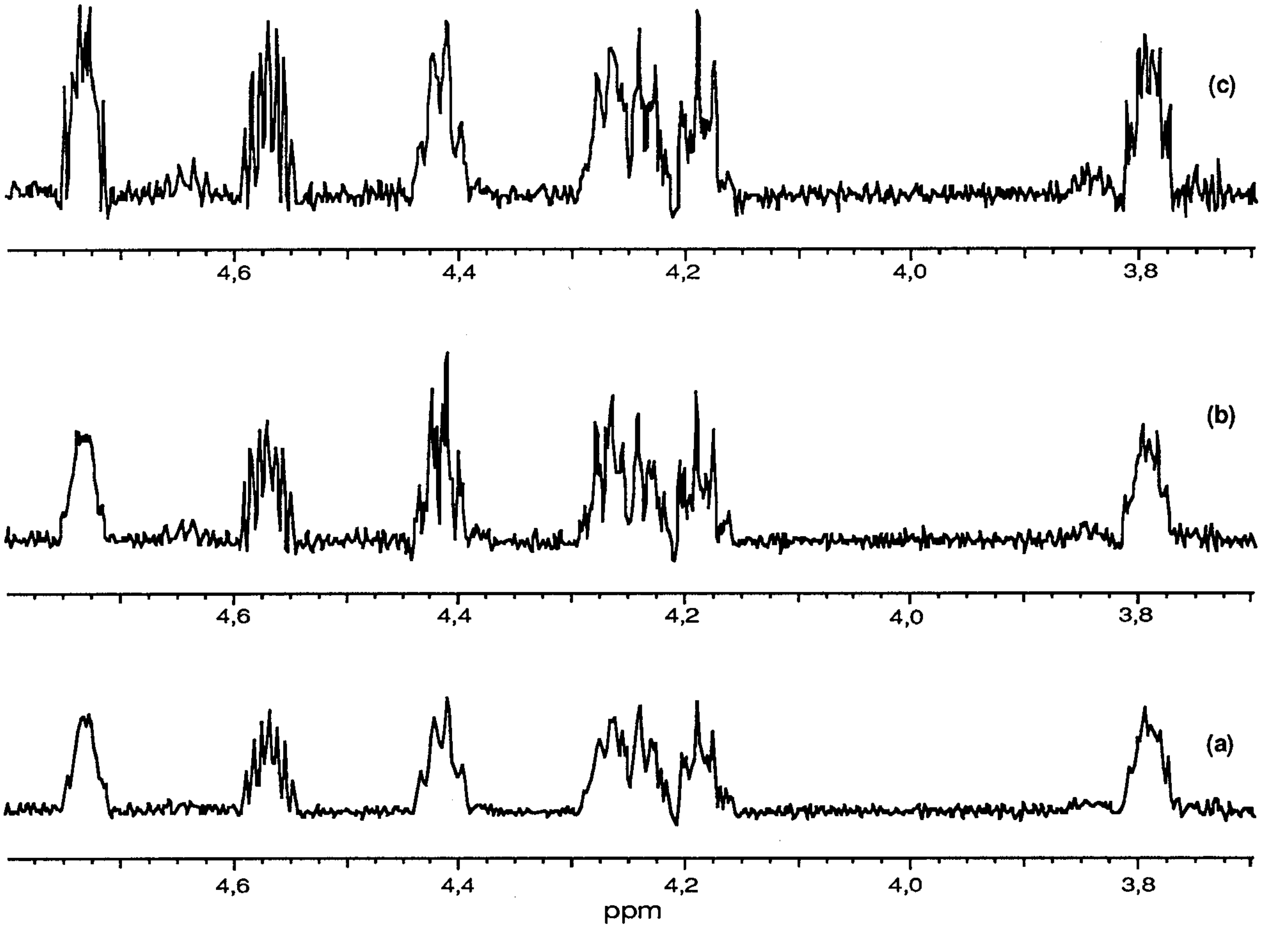


**Figure 1.** Cp region of the $^1H$ NMR spectrum of **4′a** in toluene-$d_8$ at 295 K (200 MHz) (a) when the $CH_3C^1$ (b) and $CH_3C^8$ (c) protons are irradiated.

highly shielded hydride resonance compared with precursor **3** that appears near −11.4 ppm; however, the high field shift is clearly dependent on the nature of the metal M (M = Cr, $\Delta\delta$ = 5.65 ppm; M = W, $\Delta\delta$ = 2.8 ppm). The $^1H$ NMR and $^{13}C$ NMR spectra of **4** accord with the $C_s$ symmetry of these molecules.

These procedures have also been successfully used for preparing the methylated complexes **3′** and **4′**; but after reduction of the monohydride complexes **2′**, the crude material consists of a **3′** + **4′** mixture. Unfortunately, complexes **3′** do not survive silica gel chromatography and can not be further purified. However, corresponding pure **4′** complexes are obtained by complete photochemical irradiation of the preceding mixture as microcrystalline red solids . The $^1H$ NMR spectra show at high field an AMX (A, M = H; X = W) pattern assignable to the diastereotopic $WH_2$ hydrides and a set of seven signals for the cyclopentadienyl protons: these observations are consistent with the presence of the chiral plane due to the homoannular heterodisubstitution.

In order to determine the regioselectivity of the ring-substitution reaction and to ascertain the $\mu$-hydrido structure, further detailed NMR studies of complex **4′a** are reported below.

**$^1H$ and $^{13}C$ NMR and $^1H$ NMR Relaxation Studies of Complexes 3a, 3a′, 4a, and 4′a.** Structural features of the bimetallic dihydride complexes obtained in this work and relative arrangements of the $CH_3$ and phosphorus groups in the twice substituted Cp rings of complexes **3′** and **4′** have been mainly established by the detailed NMR study of compound **4′a**.

The $^1H$ NMR spectrum of this complex in toluene-d$_8$ at 295 K shows a remarkably broadened resonance at 2.210 ppm and a quite narrow singlet at 1.460 ppm assigned (see below) to the $CH_3$ groups at $C^1$ and $C^8$ atoms, respectively (Table 1, Chart 2).

**Table 1.** $^1H$ NMR Chemical Shifts and Coupling Constants for Complex **4′a** in Toluene-$d_8$ at 295 K

| proton | $\delta$ ppm) | $J$ (Hz) | $T_1$ (s) at 295 K, 200 MHz | $T_1$min (s) (T (K)), at 200 Mhz |
|---|---|---|---|---|
| $CH_3-C^1$ | 2.210 | $J(CH_3-WH^{11}) = 1.0$ | 1.35 | 0.222 (233) |
| $CH_3-C^8$ | 1.460 | | 0.890 | 0.259 (233) |
| $H^2$, $H^5$ | 4.419 | $J(H^{2,5}-H^{3,4}) = 2.7$ | 2.233 | 0.725 (233)[a] |
| | 4.280 | $J(H^{2,5}-H^{4,3}) = 2.0$<br>$J(H^{2,5}-WH^{12}) = 0.5$ | 2.285 | 0.672 (233)[a] |
| $H^3$ | 4.194 | $J(H^3-H^4) = 3.1$<br>$J(H^3-WH^{11}) = 1.0$ | 2.042 | 0.525 (233)[a] |
| $H^4$ | 4.245 | | 2.210 | 0.672 (233)[a] |
| $H^9$ | 3.795 | $J(H^9-H^{10}) = 2.9$<br>$J(H^7-H^9) = 1.5$<br>$J(H^9-WH^{11}) = 1.0$<br>$J(H^9-P) = 1.5$ | 1.633 | 0.447 (223) |
| $H^{10}$ | 4.574 | $J(H^{10}-P) = 2.7$<br>$J(H^{10}-H^9) = 2.9$<br>$J(H^{10}-H^7) = 1.5$<br>$J(H^{10}-WH^{12}) = 1.4$ | 1.895 | 0.725 (233)[a] |
| $H^7$ | 4.737 | $J(H^7-WH^{11}) = 1.0$<br>$J(H^7-P) = 2.0$ | 1.869 | 0.545 (223) |
| $H^{11}$ | −13.91 | $J(H^{12}-H^{11}) = 7.9$<br>$J(H^{11}-W) = 67.0$ | 1.541 | 0.347 (223) |
| $H^{12}$ | −18.27 | $J(H^{12}-W) = 72.0$ | 1.614 | 0.344 (223) |

[a] Near to a minimum.

The Cp protons of **4′a** are manifested as seven multiplets (Figure 1a) in full accord with the planar chiral complex. We have found that irradiation of the signal at 2.210 ppm leads to

**Chart 2**

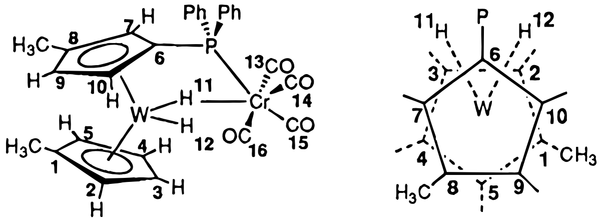


**Table 2.** $^{13}C\{^1H\}$ NMR Chemical Shifts and Coupling Constants for Complex **4′a** in $C_6D_6$ at 295 K

| C | $\delta$ (ppm) | $J$ (Hz) |
|---|---|---|
| $CH_3$ | 15.05 and 14.72 | |
| $C^1$ | 99.257 | |
| $C^2$, $C^5$ | 83.26, 82.44 | |
| $C^3$, $C^4$ | 75.44, 73.12 | |
| $C^6$ | 63.80 | $J(C^6{-}P) = 40.1$ |
| $C^7$, $C^9$, $C^{10}$ | 84.13, 82.14, 71.92 | |
| $C^8$ | 98.14 | $J(C^8{-}P) = 4.5$ |
| $P{-}C_6H_5$ | | |
| $C_\alpha$ | 136.97, 137.99 | $J(C_\alpha{-}P) = 36.7$ |
| $C_{ortho}$ | 132.88, 132.45 | $J(C_{ortho}{-}P) = 12.9$ |
| $C_{meta}$ | 128[a] | |
| $C_{para}$ | 130.35, 130.21 | |
| $C^{15}O$ | 230.59 | |
| $C^{14}O$ | 231.04 | $J(CO{-}P) = 14.5$ |
| $C^{13}O$, $C^{16}O$ | 221.73, 221.44 | $J(CO{-}P) = 14.4$ and 15.2 |

[a] Masked by the solvent.

transformations of only two multiplets of the Cp protons centered at 4.419 and 4.280 ppm in Figure 1b. A similar result is observed on irradiation of the signal at 1.460 ppm: the two broadened multiplets at 3.795 and 4.737 ppm (Figure 1a) transform to the well-resolved resonances in Figure 1c. Both these effects are interpreted by H−H decoupling of the $CH_3$ and Cp protons separated by four chemical bonds[17] and thus, the 1−3 arrangement of the $CH_3$ and phosphorus groups (Chart 2) can be accurately deduced from the double resonance experiments.

Selective H−H decoupling experiments have allowed determination of the proton−proton, proton−phosphorus and proton−$^{183}W$ coupling constants in **4′a**; from these, it is possible to carry out the spectral assignments in Table 1.

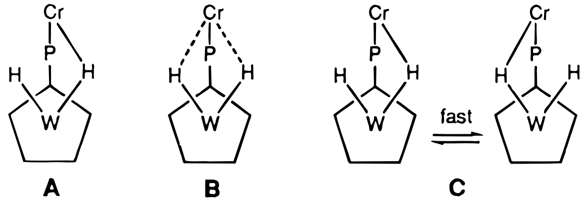
It has been reported earlier that the $J$(HP) splittings of 2−2.4 Hz are easily resolved in the $^1H$ NMR spectra of 1,1′-bis(diphenylphosphino)ferrocene and its Pt derivatives when the **$^1$H**(Cp) and **$^{31}$P** nuclei are coupled through three chemical bonds. At the same time, the corresponding $^4J$(HP) constants were unresolved for these compounds.[18] In full agreement with these data, resonances of $H^7$ and $H^{10}$ show the $^3J$(HP) values of 2.0 and 2.7 Hz providing satisfactory additional evidence for the 1−3-substituted Cp ring in **4′a**. In turn, the observation of the $H^7$ and $H^9$ resonances in the $CH_3$ decoupling experiments allows the correct assignments for both $CH_3$ groups in Table 1.

The $^{13}C\{^1H\}$ and proton-coupled $^{13}C$ NMR data collected for a $C_6D_6$ solution of **4′a** at 295 K provide the spectral assignments in Table 2, which correspond correctly to $^{13}C$ NMR data reported earlier for Cr−carbonyl complexes.[19]

**Table 3.** Carbonyl Chemical Shifts for Complexes **4′a**, **4a** and **3a** in $C_6D_6$ at 295 K

| complex | $\delta$ (ppm) (assignments) | $2J$(CO−P) (Hz) |
|---|---|---|
| **4′a** | 221.73, 221.44 (cis to P and $WH_2$) | 14.4, 15.2 |
| | 230.59 (trans to P) | <3 |
| | 231.04 (trans to $WH_2$) | 14.5 |
| **4a** | 221.61 (cis to P and $WH_2$) | 14.5 |
| | 230.00 (trans to P) | 1.7 |
| | 230.71 (trans to $WH_2$) | 13.7 |
| **3a** | 217.59 (cis to P) | 13.8 |
| | 221.82 (trans to P) | 6.2 |

**Scheme 5**



**Scheme 6**

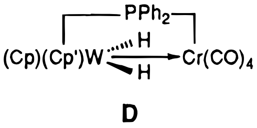


Table 2 shows the four CO groups to be nonequivalent in **4′a**. The resonances at 231.04, 221.73, and 221.44 ppm can be attributed to the CO ligands located cis to the $PPh_2Cp$ moiety on the basis of the well-resolved $^2J$(CP) constants of 14−15 Hz.[19b] No C−P coupling was resolved for the signal at 230.59 ppm assigned therefore to the trans-located CO ligand.

This approach based on the $^2J$(CP) constants was used to attribute the signals in the carbonyl region of the $^{13}C\ \{^1H\}$ NMR spectrum of compound **4a** (Table 3). In this case, doublet resonances at 230.71 and 230.00 ppm with the $J$(CP) values of 13.7 and 1.7 Hz correspond to the CO ligands located cis and trans to the phosphorus group, respectively. Another two CO groups (located cis to the $PPh_2Cp$ moiety) are equivalent and observed as a doublet resonance at 221.61 ppm with $J(CP) = 14.5$ Hz.

Comparison of the spectral behaviors of compounds **4a** and **4′a** containing the $PCr(CO)_4$ moieties and complex **3** with the octahedral $PCr(CO)_5$ fragment shows that Cr centers in **4a** and **4′a** are rigid on the NMR time scale. Therefore formation of W−H−Cr bridges[20] in **4a** and **4′a** (structures **A**, **B** and **C** in Scheme 5) can be suggested in order to explain this structural rigidity.

It should be noted that metal−metal bonding (structure **D**, Scheme 6) interactions, as proposed for $Cp_2WH_2{\cdot}Cr(CO)_5$,[4b] can be deduced neither from $^1H$, $^{13}C$ NMR data nor from an X-ray structure study of **4a** (ORTEP, Figure 4), that indicates a large separation (3.30 Å) between the two metallic atoms; therefore, they are not considered in this section of the work.

In addition structures **A**, **B** and **C** have already been discussed for different bimetallic complexes, for example, $(Cp_2W(\mu\text{-}H)_2Rh(PPh_3)_2)PF_6$,[20a] and $[CrWH(CO)_{10}]^-$.[20e]

The neutron diffraction study of $Cp_2MoH_2$ has shown the pseudotetrahedral coordination around the Mo center and the

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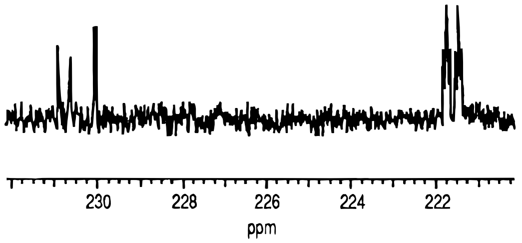

**Figure 2.** Carbonyl region of the $^{13}C$ NMR spectrum of complex **4a** in $C_6D_6$ (295 K) with selective decoupling of the $PPh_2$ protons.

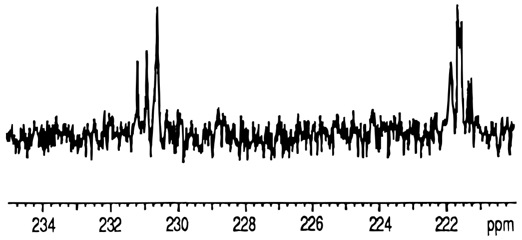

**Figure 3.** Carbonyl region of the $^{13}C$ NMR spectrum of complex **4′a** in $C_6D_6$ (295 K) with selective decoupling of the $PPh_2$ protons.

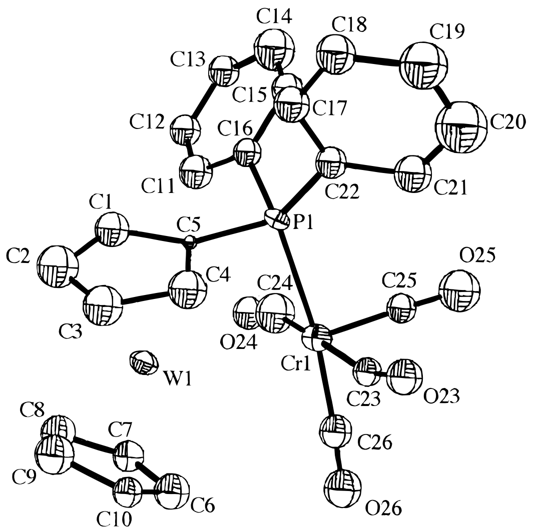

**Figure 4.** ORTEP drawing of the ($\eta^5$-$C_5H_5$)[$\eta^5$-$C_5H_4PPh_2$-Cr(CO)$_4$]W($\mu$-H)(H), **4a**. Selected bond lengths (Å): Cr1−P1 = 2.36(2), W1−C5 = 2.28(3), P1−C5 = 1.83(4), P1−C16 = 1.82(3), P1−C22 = 1.81(4). Selected bond angles (deg): Cr1−P1−C5 = 102(1), P1−Cr1−C23 = 95(2), P1−Cr1−C24 = 88(2), P1−Cr1−C25 = 96(2), P1−Cr1−C26 = 173(2).

location of the hydride ligands with a H−Mo−H angle of 75.5°.[21a] It has also been found that geometries of the $Cp_2$-$WH_2$ moieties in some heterobimetallic complexes remain pseudotetrahedral despite the formation of the W−H−metal bridges.[20b, 21b] Therefore the arrangement of the hydride ligands shown in Chart 2 seems to be quite reasonable for complexes **4a** and **4′a**. It should be noted that this location is shown for a conformation of **4′a** in which steric interactions between the bulky groups are minimal. We believe that the $^4J(C^1CH_3-W-H^{11})$ coupling constant of 1.0 Hz through four chemical bonds is resolved in the $^1H$ NMR spectrum of **4′a** due to the trans-locations of the above nuclei in such a conformation.

To support the hydride arrangement in Scheme 4, $^1H$ $T_1$ relaxation time measurements[22] have been performed in a toluene-$d_8$ solution of **4′a** between 295 and 213 K and we have found that the $T_1$ times reach a minimum at 223−233 K for all observed protons. Table 1 lists the data obtained.

Intramolecular proton−proton and metal−proton dipole−dipole interactions are known to dominate the $T_1$ relaxation of hydride ligands in transition metal hydride systems.[22a,c,23] The $T_{1\min}$ values were found to be very similar for the WH resonances and for the $^{183}$WH satellites of **4′a** showing metal−proton interactions to be insignificant. The contribution caused by the influence of the Cp, $CH_3$ and $PPh_2$ protons can be also ignored because of their remoteness from the WH ligands. Thus, the proton−proton distance between the H ligands of **4′a** is calculated as 2.0 Å from eq 1. Equation 1 is valid for classical hydrides in the case of an isotropic molecular motion.[24]

$$r_{H\cdots H}\,(\text{Å}) = 2.405(200T_{1\min}/\nu)^{1/6} \qquad (1)$$

However, it has recently been shown that this isotropic motion approach, even though not strictly correct, provides quite reliable structural information.[23c] The W−H bond lengths in different hydride complexes (including the bridging hydride systems) lie between values of 1.718[25a] and 1.86 Å.[20d,25b] Then, the H−W−H angle can be calculated for **4′a** as 72 or 66°, respectively. Thus, the relaxation data correctly support the above suggested H location.

The proton−proton distance of 2.0 Å seems to be quite realistic because practically the same value can be calculated from $T_1$ relaxation data collected for the $CH_3$ protons of **4′a** at room temperature. Molecular reorientations of the $CH_3$ groups are known to be anisotropic due to very fast rotation around the C−$CH_3$ bond.[26a] In the fast motion regime this rotation leads to the maximum anisotropy effect described in eq 2.[23c,26a]

$$T_1^{(\text{aniso})} = 4T_1^{(\text{iso})} \qquad (2)$$

Table 1 shows that the room temperature $T_1^{(\text{aniso})}$ value amounts to 1.35 and 0.890 s for the $CH_3$ groups at $C^1$ and $C^8$, respectively. It is clear that a contribution caused by dipole−dipole interactions between the $CH_3$ protons and the neighboring protons of the bulky $PPh_2$ group should be minimal in the first case. Each proton in the $CH_3$ group interacts with two neighboring protons of this group and therefore the experimental $T_1$ value of 1.35 s is 2 times smaller than that in the case of the interaction of only two protons: 2.7 s. Then, the $T_1^{(\text{iso})}(CH_2)$ value of 0.675 s can be obtained from eq 2.

The rate of the spin−lattice relaxation of a pair of protons is described by eq 3 in the fast motion regime,[26b] where $\gamma_H$ and h are the well-known constants, $\tau_C$ is the correlation time of isotropic motions and $r_{H-H}$ is the proton−proton distance.

$$1/T_1(H\cdots H) = {}^3/_2\,\gamma_H{}^4 h^2 [r_{H-H}]^{-6}\tau_C \qquad (3)$$

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**Table 4.** $^{1}H$ NMR Data for the Hydride Ligands in Complexes **4′a**, **3′a**, **4a**, **3a** and **4b**

| complex | $\delta_{WH}$ (ppm) | $J$(W−H) (Hz) | $J$(H−H) (Hz) | $T_1$(s) at 303 K, 80 MHz |
|---|---|---|---|---|
| **4′a** | −13.91 | 67.0 | 7.9 | 1.772 |
| | −18.27 | 72.0 | | 2.01 |
| **3′a** | −10.25 | 78.7 | 8.9 | 1.113 |
| | −10.86 | 76.8 | | 1.070 |
| **4a** | −16.99 | 67 | | 2.006 |
| **3a** | −11.43 | 73 | | 1.590 |
| **4b** | −14.33 | 67.6 | | |
| | | 14.8 | | |

Equation 3 written for the $WH_2$ and $CH_2$ protons with elimination of $\gamma_H$, $h$, and $\tau_C$ takes the form in (4), which makes

$$r_{WH\cdots H}/r_{CH\cdots H} = [T_1^{(iso)}(WH\cdots H)/T_1^{(iso)}(CH\cdots H)]^{1/6} \qquad (4)$$

it possible to determine the WH···H distance because the standard proton−proton distance in the $CH_3$ group is known as 1.78 Å.[27] This approach leads to the WH···H value of 2.0 or 2.1 Å if the $T_1$ value of 1.541 or 1.614 s (Table 1) is used.

Table 4 lists the $^{1}H$ NMR parameters collected for the hydride ligands of W/Cr compounds **3** and **4** in $C_6D_6$. The $T_1$ data correspond accurately to the classical nature of these complexes according to $T_1$ criterion of Hamilton and Crabtree.[24a] The H ligands of complex **3a** with the octahedral Cr center show a resonance with $^{1}J$(WH) = 73.0 Hz. The high field shift of 5.65 ppm accompanied by a decrease in the $^{1}J$(WH) value is observed for the H ligands when **3a** transforms to **4a**. Both spectroscopic effects can be attributed to H binding to the Cr center in complex **4a** in full accord with the above $^{13}C$ NMR data. Nevertheless the high value of the $^{1}J$(WH) coupling constant suggests that the W−H interactions remain strong in **4a**.[20b]

Table 4 shows the hydride signal to be a singlet in the $^{1}H$ NMR spectrum of **4a** and therefore structure **A** in Scheme 5 can be unambiguously rejected. Thus, the static symmetric structure **B** (global 2e H−W−H bridging moiety) and the nonrigid structure **C** (dynamic 2e monohydride bridge) seem to be the most reasonable for this complex. The formation of H bridges is consistent with the $C_6D_6$ $^{1}H$ NMR spectrum of complex **4b**, showing constants of 67.6 and 14.8 Hz. A similar effect was already reported for $Cp_2WH_2W(CO)_5$[4b] and we believe that such coupling constants can be interpreted in terms of the stronger W−H bonding interactions in the case of the tetrahedral W center. In addition, the significant $J$(HP) value of 3 Hz was found for the H ligands of **4b** and no W*H*−*P* coupling was resolved for compound **3b**. In our opinion, this fact supports the formation of W−H−W bridges in **4b**.

Unfortunately, the choice between two binding modes **B** and **C** is quite difficult in the case of symmetrical complexes **4a** and **4b**. Actually, in the $^{13}C$ NMR spectrum of **4a** with selective decoupling of the $PPh_2$ protons, we have found the additional *triplet* W$^{1}$*H*Cr−$^{13}$*C*O coupling of 2.3 Hz for the resonances of two equivalent CO groups located cis to the phosphorus and H ligands (Figure 2). However, the above triplet splittings can be interpreted in terms of both structural modes **B** and **C**. This is quite obvious for **B** and possible in the case of dynamic structure **C** because of equally-populated isomeric states. Therefore, this structural problem was solved in the present work on the basis of the NMR data collected for the 1−3-substituted complexes **3′a** and **4′a**.

The diastereotopic H ligands of **3′a** are manifested in the $^{1}H$ NMR spectrum as two resonances at −10.25 ($^{1}J$(WH) = 78.7 Hz) and −10.86 ($^{1}J$(WH) = 76.8 Hz) ppm with H-H coupling of 8.9 Hz (Table 4). If complex **4′a** had the structure **A**, it would give four W*H* resonances because of its plane chirality. However, none were observed in the variable-temperature $^{1}H$ NMR spectra of **4′a** in toluene-$d_8$ between 213 and 295 K. Moreover, the diastereotopic chemical shift difference for the H ligands increases from 0.61 to 4.36 ppm when **3′a** transforms to **4′a** (Table 4). Both spectral features conflict strongly with structure **A** containing the single W−H−Cr bridging bond and with symmetric structure **B**. At the same time, these NMR data can be rationalized in terms of dynamic structure **C** when populations of diastereomeric forms of **4′a** are unequal. To support this suggestion, the $C_6D_6$ $^{13}C$ NMR spectrum of **4′a** was obtained with selective decoupling of the $PPh_2$ protons. The carbonyl region of this spectrum in Figure 3 shows clearly additional *doublet* W$^{1}$*H*Cr−$^{13}$*C*O splittings of 5 Hz observed for the CO groups located cis to the phosphorus and H ligands. Thus, the last experiment provides accurate evidence for structure **C** which is probably valid for all the bridging complexes obtained in this work.

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**Supporting Information Available:** Tables providing full details of the X-ray structural determinations including crystal data, atomic coordinates and isotropic thermal parameters, non-essential bond lengths, and bond angles for complex **4a** (5 pages).

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