



Heterodinuclear TiMo and TiW complexes bridged by the (dimethylsilanediyl) dicyclopentadienyl ligand†

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Abstract—Reactions of the tricarbonyl-molybdenum and -tungsten complexes $[M(\text{CO})_3(\text{MeCN})_3]$ ($M = \text{Mo}, \text{W}$) or $[\text{Mo}(\text{CO})_3(\text{mesitylene})]$ with equimolar amounts of $[\text{Ti}(\eta^5\text{-Cp}')\{(\eta^5\text{-C}_5\text{H}_3)(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\}\text{Cl}_2]$ ($\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$) lead to the heterodinuclear compounds $[\text{Ti}(\eta^5\text{-Cp}')\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]\}\text{MH}(\text{CO})_3]$. These dinuclear complexes are isolated as single *cis*- and *trans*-isomers or as mixtures of both depending on the starting complex and the reaction conditions. The molar ratio of the two resulting isomers is controlled by thermodynamic and kinetic factors which prevent the application of stereoselective methods for some of the products. Reaction of the hydrido *cis*- and *trans*-complexes with CCl_4 in CH_2Cl_2 allows the isolation of chloro complexes $[\text{Ti}(\eta^5\text{-Cp}')\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]\}\text{MCl}(\text{CO})_3]$ of the same configuration. All of the new heterodinuclear compounds reported were characterized by their analytical composition, IR and NMR spectroscopy and the molecular structure of *cis*- $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]\}\text{WH}(\text{CO})_3]$ was studied by X-ray diffraction methods. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: heterodinuclear complexes; titanium-molybdenum; titanium-tungsten; cyclopentadienyl

Heterodinuclear organometallic complexes containing two metals with very different reactivity in close proximity have received considerable attention [1] because they may produce cooperative effects and new reactivity patterns when used in stoichiometric and catalytic reactions. Particular efforts have focused on complexes containing both early electron-deficient and middle or late electron-rich transition metals. Several strategies using different bridging groups have been used to prepare complexes of this type with and without metal-metal bonds. One of the most intensively studied [2] groups of compounds is that formed by using cyclopentadienylphosphine systems as bridging groups which are η^5 -coordinated to the early or middle group 4–6 transition metal and phosphorus-coordinated to the late transition metal. However most of the reported heterodinuclear compounds

involving group 4 metals are phosphido- [3a–c] and carbonyl- [3d–g] bridged complexes.

In recent years many dinuclear complexes containing bridging cyclopentadienyl systems have been described. They include fulvalene [4a–e] derivatives and those containing cyclopentadienyl rings singly bridged by different alkyl [5] and silyl [6] groups. Some similar trinuclear compounds have also been reported [7]. Although numerous homodimetallic complexes of this type have been synthesized and investigated, the range of synthetic methods available to isolate heterodinuclear compounds is limited mainly to the late transition metal derivatives.

We reported [8] the use of dilithium or dithallium salts of the $[\{1,1':2,2'\text{-bis}(\text{dimethylsilanediyl})\}\text{bis}(\eta^5\text{-cyclopentadienyl})]$ (CpSi_2Cp) dianion to prepare homodinuclear group 4 and 6 metal complexes containing the dicyclopentadienyl system as a bridging ligand. Related reactions using the monolithium salt of the ligand prepared as reported elsewhere [9] gives access to complexes containing only one of the cyclopentadienyl rings η^5 -coordinated to the group 4 metal center, leading to mono- and mainly mixed dicyclo-

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† Dedicated to Prof. Dr W. A. Herrmann on the occasion of his 50th birthday.

‡ X-ray diffraction studies.

pentadienyl-type derivatives $[M(\eta^5\text{Cp}')(\eta^5\text{-CpSi}_2\text{C}_5\text{H}_4)\text{Cl}_2]$ [10]. In these complexes the other cyclopentadiene moiety remains available for further reactions with a second different metal complex. Herein we report the application of this strategy to study migration reactions of the acidic cyclopentadiene ring proton to molybdenum and tungsten carbonyls as a method to prepare heterodinuclear compounds of the type *cis*- and *trans*- $[\text{TiCp}'\text{Cl}_2\{\mu\text{-(CpSi}_2\text{Cp)}\} \text{MH}(\text{CO})_3]$ ($\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$; $\text{CpSi}_2\text{Cp} = (\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2$) containing one titanium and one group 6 metal fragment. Conversion of the hydrido into the chloro complexes and the structural characterization of all these compounds is also reported.

RESULTS AND DISCUSSION

Reactions of the mixed dicyclopentadienyl titanium complexes $[\text{Ti}(\eta^5\text{-Cp}')\{\eta^5\text{-C}_5\text{H}_3\}(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\text{Cl}_2]$ [$\text{Cp}' = \text{C}_5\text{H}_5$ (**1**), C_5Me_5 (**2**)] with equimolar amounts of $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ ($\text{M} = \text{Mo}, \text{W}$) or $[\text{Mo}(\text{CO})_3(\text{mesitylene})]$ resulted in migration of the acidic ring hydrogen of the cyclopentadiene moiety to the group 6 metal with elimination of the acetonitrile or mesitylene ligands, which were replaced by the η^5 -coordinated cyclopentadienyl ring to give the hydrido tricarbonyl complexes $[\text{TiCp}'\text{Cl}_2\{\mu\text{-(CpSi}_2\text{Cp)}\} \text{MH}(\text{CO})_3]$ [$\text{Cp}' = \text{C}_5\text{H}_5, \text{M} = \text{Mo}$ (**3**), W (**4**); $\text{Cp}' = \text{C}_5\text{Me}_5, \text{M} = \text{Mo}$ (**5**), W (**6**)], as shown in Scheme 1.

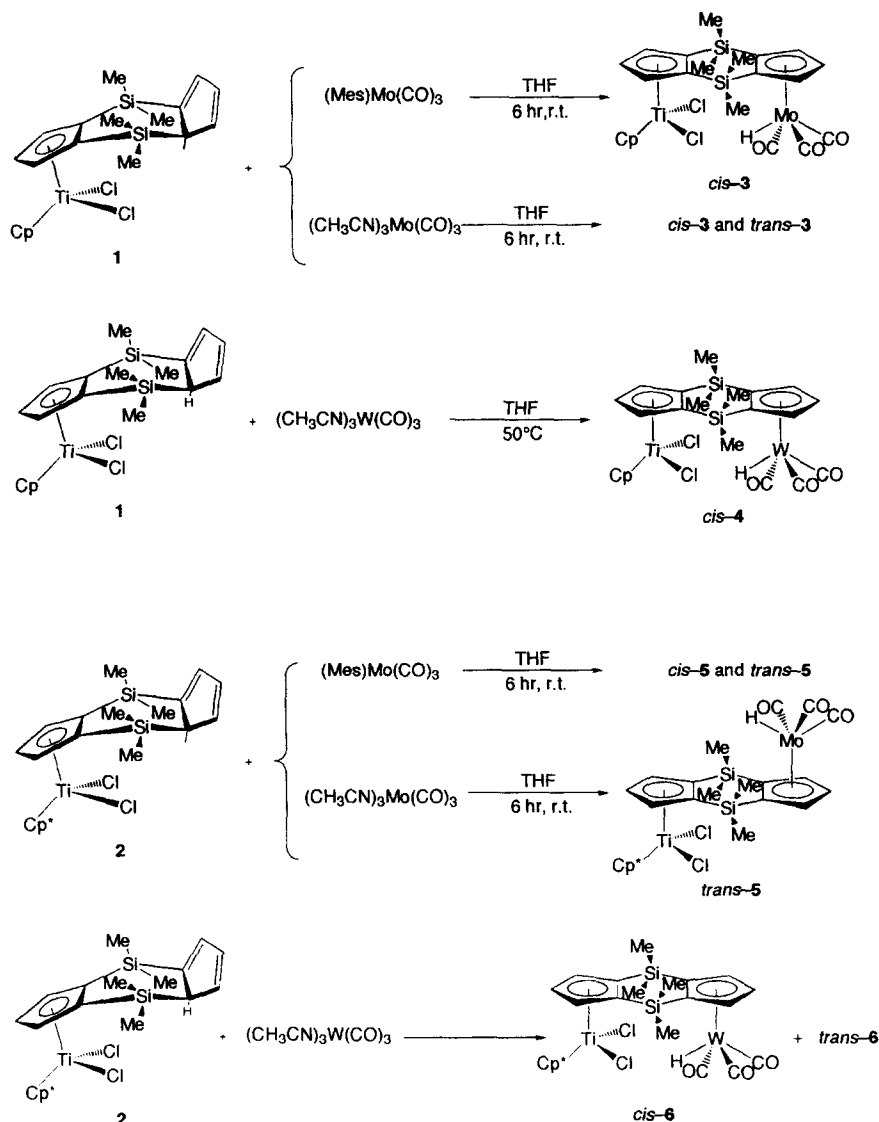
The rigidity of the bridging dicyclopentadienyl ligand is responsible for the formation of different stereoisomers in this type of dinuclear compound for which six different structural dispositions have been found in the solid by X-ray diffraction studies. Two were reported [11] to belong to a *trans*-configuration of the two metal centers with the central six-membered ring of the ligand exhibiting either a boat or an essentially planar conformation, and the other two show the metal fragments in a *cis*-disposition occupying either the internal or the external faces of the boat configuration of the central ring of the ligand. In addition we have recently reported [8f] two new configurations: one *cis*-configuration showing an almost planar disposition of the central ring of the ligand and a *trans*-configuration with the ligand exhibiting a chair disposition. It is not easy to explain the preferential formation of one of these structures when the two metals are not connected either by metal–metal bonds or through additional ligand bridges, because it results from the contribution of many different factors including the conformation of the starting complex and the mechanism followed by the reaction leading to the final product.

It has been reported [9] that the monoalkali-metal derivatives of the ligand exist at low temperature as a mixture of two stable enantiomers which show fluxional behavior being interconverted at higher temperatures through a silatropic rearrangement. Solutions of the starting titanium complexes **1** and **2** may

contain an enantiomeric mixture of two stereoisomers, showing the cyclopentadiene proton in *cis*- and *trans*-disposition with respect to the metal fragment in variable molar ratios of both stereoisomers at different temperatures. It must be expected that hydrogen transfer to the group 6 metal in the *cis*- and *trans*-isomers should lead, respectively, to the heterodinuclear complex with the same *cis*- or *trans*-disposition of the metal fragments. However this transformation which is thermodynamically and kinetically controlled may give different molar ratios of the resulting stereoisomers for each reaction and under different conditions even assuming that the hydrogen transfer process follows the same mechanism. For these reasons, using the pure solid complexes **1** and **2**, we observed that the *cis*- or *trans*-configuration of the resulting final heterodimetallic product depends on the solvent, the temperature and time of reaction and the nature of the carbonyl derivative $\text{M}(\text{CO})_3(\text{MeCN})_3$ or $\text{Mo}(\text{CO})_3(\text{mesitylene})$ used as the starting compound. Both *cis*- and *trans*-isomers can be easily distinguished by ^1H NMR spectroscopy because, although both show the same pattern of resonances due to an ABB' spin system for both nonequivalent cyclopentadienyl rings bonded to the different metal fragments, the difference between the chemical shifts of the two nonequivalent silyl-methyl singlets is larger for the *cis*- than for the *trans*-isomer (see Experimental).

Reaction of complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_3\}(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\text{Cl}_2]$ (**1**) with $[\text{Mo}(\text{CO})_3(\text{mesitylene})]$ in THF at room temperature for 6 h led to *cis*- $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]\text{MoH}(\text{CO})_3\}]$ (*cis*-**3**) isolated as a red solid in 95% yield whereas the same reaction carried out with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ under the same conditions led to mixtures of *cis*-**3** and *trans*-**3** in different molar ratios, the *trans*-isomer always being the main component. Separation of the isomers was not possible. The reaction of complex **1** with $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ at 50°C for 4 h led to the stereoselective formation of *cis*- $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_3)_2]\text{WH}(\text{CO})_3\}]$ (*cis*-**4**) isolated as a red solid in 95% yield. In contrast, reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_3\}(\text{SiMe}_2)_2(\text{C}_5\text{H}_4)\text{Cl}_2]$ (**2**) with $[\text{Mo}(\text{CO})_3(\text{mesitylene})]$ in THF at room temperature gave a mixture of *cis*-**5** and *trans*-**5** with the *cis*-isomer being the main product, whereas use of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ under the same conditions resulted in the stereoselective formation of *trans*- $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\{\mu\text{-}[(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_3)_2]\text{MoH}(\text{CO})_3\}]$ (*trans*-**5**), isolated as a red solid in 85% yield. In the reaction of $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ with compound **2** we sometimes obtained *cis*-**6** and sometimes a mixture of *cis*-**6** and *trans*-**6**, *cis*-**6** being the main product. This reaction was carried out under various conditions: in THF or dichloromethane at room temperature for 24 h or in THF at 50°C for 4 h but the results of the reactions were unpredictable.

Complexes **3–6** are air stable for short periods, insoluble in alkanes but soluble in aromatic solvents,

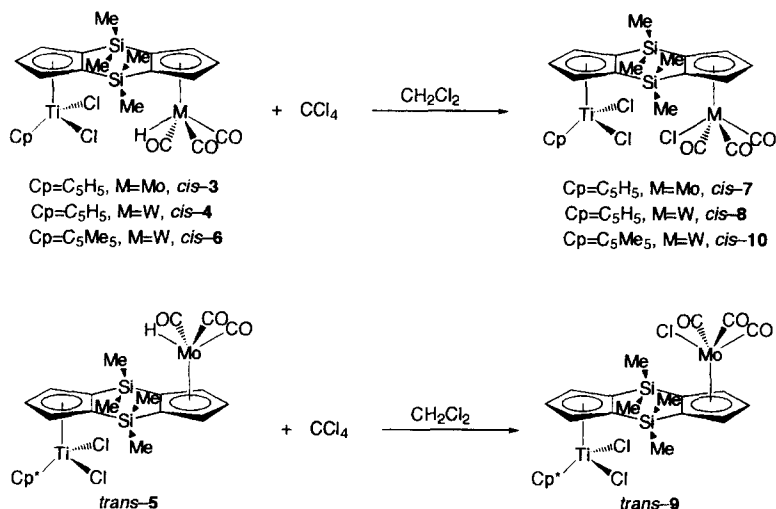


Scheme 1.

ethers and dichloromethane. They react with CCl_4 (see Scheme 2) at room temperature to be transformed into the related chlorotricarbonyl derivatives $\text{cis-}[\text{TiCp}'\text{Cl}_2\{\mu\text{-Si}_2(\eta^5\text{-Cp})_2\}\text{MCl}(\text{CO})_3]$ ($\text{Cp}' = \text{Cp}$, $\text{M} = \text{Mo}$ *cis-7*, W *cis-8*, $\text{Cp}' = \text{Cp}^*$, $\text{M} = \text{Mo}$ *trans-9*, $\text{Cp}' = \text{Cp}^*$, $\text{M} = \text{W}$ *cis-10*) in yields higher than 90%. These compounds are air stable red solids insoluble in alkanes and in toluene but soluble in ethers and dichloromethane.

All of the new heterodinuclear complexes were identified by elemental analysis and IR, ^1H and ^{13}C NMR spectroscopy. All of the compounds show the presence of one dicyclopentadienyl-type titanium fragment and one pseudo-square pyramidal hydrido or chloro tricarbonyl group 6 metal fragment, each bonded to one of the two cyclopentadienyl rings of the bridging ligand, with no interaction between the

metal centers. The IR spectra of all the complexes show the expected two absorption bands between 2054 and 1914 cm^{-1} . The high field resonance due to the hydrido ligand in complexes 3–6 was observed between $\delta -4.86$ and $\delta -7.48$ ppm. The ^1H NMR spectra of all of the complexes show the presence of two nonequivalent cyclopentadienyl rings each with the expected ABB' spin system proton resonances. Two pairs of nonequivalent silyl-methyl groups provide two additional singlets with a difference in their chemical shifts for the *cis*-isomers (0.25 ppm) larger than that observed for the *trans*-isomers (less than 0.06 ppm). The ^{13}C NMR spectra show the expected two singlets for the silyl-methyl carbon atoms and six resonances due to the nonequivalent two C_β and two pairs of C_{ipso} and C_α ring atoms, together with one or two singlets for the additional cyclopentadienyl or



Scheme 2.

pentamethylcyclopentadienyl ring carbons respectively and two low field resonances due to the CO ligands, which could not be observed for some of the complexes (see Experimental).

Crystals suitable for X-ray study were obtained for complex *cis*-6 whose molecular structure is shown in Fig. 1 together with the atomic labeling scheme. Selected bond distances and angles are given in Table 1.

The structure of **6** shows a *cis*-disposition of the two metal fragments bonded to the external faces of the cyclopentadienyl rings in order to place the two metal centers farther apart (6.298 Å), in the asymmetric molecule. Both cyclopentadienyl rings are

planar and bound to the titanium and tungsten atoms in a slightly asymmetric η^5 -fashion [the W—C distances range from 2.327(9) to 2.340(8) Å with a W—Cp(centroid) distance of 1.99 Å; the Ti—C distances range from 2.347(8) to 2.496(8) Å]. The dihedral angle between the two bridging cyclopentadienyl rings is 37.7(3)°. The central ring formed by the two silicon and the four carbon-*ipso* atoms is not planar in such a way that the dihedral angles between the mean planes containing Si(1), Si(2), C(11), C(12) and Si(1), Si(2), C(21), C(22) and the corresponding cyclopentadienyl ring are 13.7(3)° and 12.3(2)°, respectively, and the Si(1) and Si(2) atoms

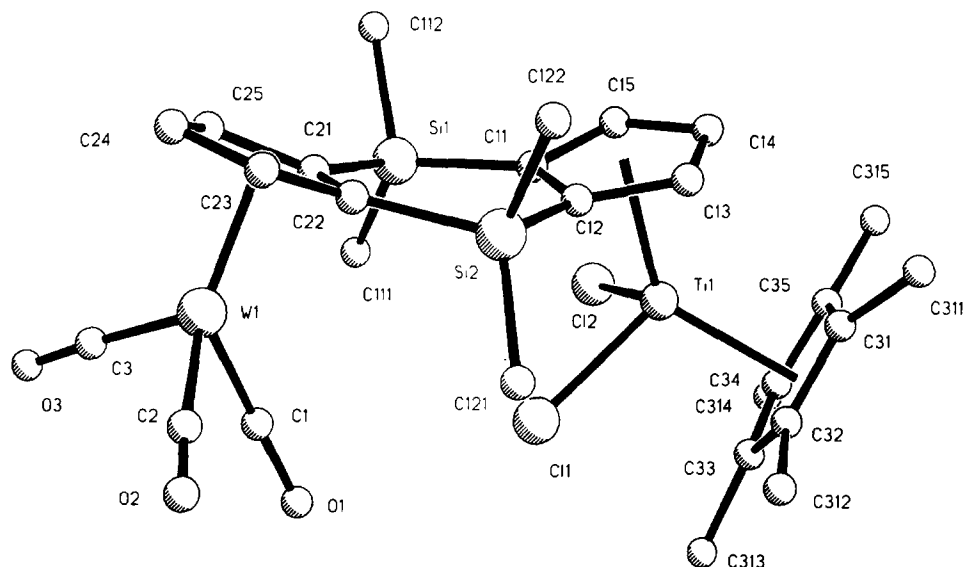
Fig. 1. Perspective view of complex *cis*-6 with the atomic labeling scheme.

Table 1. Selected bond lengths (Å) and angles (°) for *cis*-6

W(1)—C(3A)	1.88(4)	W(1)—C(1)	1.89(2)
W(1)—C(3)	1.89(3)	W(1)—C(1A)	1.91(4)
W(1)—C(2A)	1.92(4)	W(1)—C(2)	2.01(3)
W(1)—C(23)	2.327(9)	W(1)—C(25)	2.331(9)
W(1)—C(24)	2.333(9)	W(1)—C(21)	2.339(8)
W(1)—C(22)	2.340(8)	Ti(1)—C1(1)	2.324(3)
Ti(1)—C(14)	2.347(8)	Ti(1)—C1(2)	2.355(3)
Ti(1)—C(13)	2.367(8)	Ti(1)—C(32)	2.386(8)
Ti(1)—C(15)	2.400(8)	Ti(1)—C(35)	2.400(8)
Ti(1)—C(31)	2.411(8)	Ti(1)—C(33)	2.421(8)
Ti(1)—C(34)	2.456(8)	Ti(1)—C(11)	2.486(8)
Ti(1)—C(12)	2.496(8)	Si(1)—C(111)	1.844(8)
Si(1)—C(11)	1.866(8)	Si(1)—C(112)	1.874(9)
Si(1)—C(21)	1.878(8)	Si(2)—C(121)	1.843(9)
Si(2)—C(122)	1.873(9)	Si(2)—C(12)	1.874(8)
Si(2)—C(22)	1.875(8)	C(11)—C(15)	1.424(11)
C(11)—C(12)	1.442(10)	C(12)—C(13)	1.396(11)
C(13)—C(14)	1.386(11)	C(14)—C(15)	1.411(11)
C(21)—C(25)	1.416(11)	C(21)—C(22)	1.452(11)
C(22)—C(23)	1.422(11)	C(23)—C(24)	1.383(12)
C(24)—C(25)	1.432(12)	C(31)—C(35)	1.412(12)
C(31)—C(32)	1.415(12)	C(31)—C(311)	1.499(11)
C(32)—C(33)	1.432(11)	C(32)—C(312)	1.507(12)
C(33)—C(34)	1.394(11)	C(33)—C(313)	1.491(12)
C(34)—C(35)	1.410(11)	C(34)—C(314)	1.496(11)
C(35)—C(315)	1.504(12)	C(1A)—C(1)	0.70(3)
C(1A)—O(1A)	1.22(4)	C(1A)—O(1)	1.43(4)
C(1A)—C(3)	2.03(4)	O(1A)—O(1)	1.02(3)
O(1A)—C(1)	1.50(3)	C(2A)—C(2)	0.66(4)
C(2A)—O(2A)	1.13(4)	C(2A)—O(2)	1.47(4)
O(2A)—O(2)	0.91(3)	O(2A)—C(2)	1.20(3)
C(3A)—C(3)	1.13(4)	C(3A)—(3A)	1.23(4)
C(3A)—O(3)	1.93(4)	O(3A)—O(3)	1.38(3)
O(3A)—C(3)	1.52(4)	C(1)—O(1)	1.17(2)
C(2)—O(2)	1.08(3)	C(3)—O(3)	1.20(3)
C(1)—W(1)—C(3)	82.4(10)	C(1)—W(1)—C(2)	75.2(9)
C(3)—W(1)—C(2)	109.6(10)	C1(1)—Ti(1)—C1(2)	94.57(10)
C(111)—Si(1)—C(11)	116.8(4)	C(111)—Si(1)—C(112)	109.0(4)
C(11)—Si(1)—C(112)	106.5(4)	C(111)—Si(1)—C(21)	113.1(4)
C(11)—Si(1)—C(21)	105.6(4)	C(112)—Si(1)—C(21)	105.2(4)
C(121)—Si(2)—C(122)	108.3(5)	C(121)—Si(2)—C(12)	117.9(4)
C(122)—Si(2)—C(12)	104.9(4)	C(121)—Si(2)—C(22)	113.7(4)
C(122)—Si(2)—C(22)	105.9(4)	C(12)—Si(2)—C(22)	105.3(3)
O(1A)—C(1A)—W(1)	177(3)	O(3A)—C(2A)—W(1)	166(4)
O(3A)—C(3A)—W(1)	153(3)	O(1)—C(1)—W(1)	177(2)
O(2)—C(2)—W(1)	173(3)	O(3)—C(3)—W(1)	176(3)

lie 0.348(2) Å and 0.291(2) Å, respectively, above the plane of the ring bonded to tungsten, and 0.195(2) Å and 0.479(2) Å above the plane of the ring bonded to titanium.

The titanium fragment shows the typical disposition of a bent dicyclopentadienyl system with an angle between the rings of 52.9(3)° with normal Ti—C1 distances [average 2.341(3) Å]. The tungsten fragment shows a pseudo-square pyramidal coordination in

which the hydrido ligand, which could not be localized, presumably occupies the fourth position between the two C(2)O(2) and C(3)O(3) carbonyl ligands for which the C(2)—W(1)—C(3) angle is more open [109(1)°] than the other two [C(1)—W(1)—C(2) of 82(1)° and C(1)—W(1)—C(3) of 75(1)°] although the disorder found for the positions occupied by the carbonyl ligands prevents a rigorous assignment of their bonding situation.

EXPERIMENTAL

Reagents and general techniques

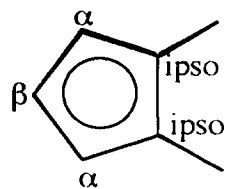
All reactions were carried out in dried Schlenk tubes under argon or nitrogen, and the manipulations were carried out using syringes or cannulas through Sub-seals. Solvents were dried and distilled under nitrogen: tetrahydrofuran from sodium benzophenone ketyl; hexane and pentane from sodium and potassium amalgam; dichloromethane from P_2O_5 and carbon tetrachloride from $CaCl_2$. Unless otherwise stated, reagents were obtained from commercial sources and used as received. IR spectra were recorded in Nujol mulls for solids over the range 4000–200 cm^{-1} or in solution over the range 2500–1500 cm^{-1} on a Perkin–Elmer 583 spectrophotometer. IR data are given in cm^{-1} . The 1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz respectively on a Gemini 200 spectrometer, at 299.95 and 75.43 MHz respectively on a Varian Unity 300 spectrometer and at 499.85 and 125.7 MHz on a Varian Unity 500 Plus spectrometer; chemical shifts, in ppm, are positive downfield relative to external $SiMe_4$, and coupling constants are in Hz. C, H, and N analyses were performed with a Perkin–Elmer 240-B instrument.

The compounds $[Ti(\eta^5-C_5H_5)Cl_2\{(\eta^5-C_5H_3)[Si(CH_3)_2(C_5H_4)]\}]$ and $[Ti(\eta^5-C_5Me_5)Cl_2\{(\eta^5-C_5H_3)[Si(CH_3)_2(C_5H_4)]\}]$ were prepared as reported elsewhere [10b].

Synthesis of cis-[Ti($\eta^5-C_5H_5$)Cl₂{($\eta^5-C_5H_3$)₂[Si(CH₃)₂]}MoH(CO)₃] (cis-3)

THF (50 ml) was added to a mixture of $[Ti(\eta^5-C_5H_5)Cl_2\{(\eta^5-C_5H_3)[Si(CH_3)_2(C_5H_4)]\}]$ (1.43 g, 3.35 mmol) and $[Mo(CO)_3(mesitylene)]$ (1.01 g, 3.35 mmol). After stirring for 6 h at room temperature the resulting red solution was concentrated to dryness *in vacuo* leaving a red solid which was washed with pentane and identified as complex *cis-3* (1.93 g, 95%). Anal. calc. for $C_{22}H_{24}Cl_2MoO_3Si_2Ti$: C, 43.51; H, 3.98. Found: C, 43.87; H, 4.06. 1H NMR (300 MHz, C_6D_6): δ -4.91 (s, 1H, Mo-H), 0.10 (s, 6H, Si-Me), 0.61 (s, 6H, Si-Me), 4.98 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$), 5.10 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 5.44 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 5.94 (s, 5H, C_5H_5), 6.52 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): 3.1 (Si-CH₃), 3.4 (Si-CH₃), 95.9 ($C_\beta C_5H_3$), 96.8 ($C_\alpha C_5H_3$), 109.1 ($C_{ipso} C_5H_3$), 113.3 ($C_\beta C_5H_3$), 119.8 (C_5H_5), 133.2 ($C_\alpha C_5H_3$), 138.7 ($C_{ipso} C_5H_3$), 223.8 (CO). IR (nujol): ν_{CO} 2015, 1915 cm^{-1} . IR (THF): ν_{CO} 2020, 1928 cm^{-1} .

When the reaction was carried out under the same experimental conditions using the equimolar amount of $[Mo(CO)_3(MeCN)_3]$ a mixture of *cis-3* and *trans-3* was obtained after concentrating the resulting red solution to dryness. The complex *trans-3* could not be isolated. 1H NMR (300 MHz, C_6D_6): δ -5.43 (s, 1H,



Mo-H), 0.40 (s, 6H, Si-Me), 0.44 (s, 6H, Si-Me), 5.06 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 5.09 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$), 5.45 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 5.92 (s, 5H, C_5H_5), 6.48 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$).

Synthesis of cis-[Ti($\eta^5-C_5H_5$)Cl₂{($\eta^5-C_5H_3$)₂[Si(CH₃)₂]}WH(CO)₃] (cis-4)

THF (50 ml) was added to a mixture of $[Ti(\eta^5-C_5H_5)Cl_2\{(\eta^5-C_5H_3)[Si(CH_3)_2(C_5H_4)]\}]$ (1.14 g, 2.91 mmol) and $[W(CO)_3(MeCN)_3]$ (1.24 g, 2.91 mmol). After stirring for 4 h at 50°C the resulting red solution was concentrated to dryness *in vacuo* leaving a red solid which was washed with pentane and identified as complex *cis-4* (1.91 g, 94%). Anal. calc. for $C_{22}H_{24}Cl_2O_3Si_2TiW$: C, 38.01; H, 3.48. Found: C, 37.74; H, 3.55. 1H NMR (300 MHz, $CDCl_3$): δ -6.82 (s, 1H, W-H), 0.32 (s, 6H, Si-Me), 0.57 (s, 6H, Si-Me), 5.58 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$), 5.74 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 6.40 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 6.54 (s, 5H, C_5H_5), 7.10 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 3.1 (Si-CH₃), 3.6 (Si-CH₃), 94.7 ($C_\beta C_5H_3$), 95.6 ($C_\alpha C_5H_3$), 106.2 ($C_{ipso} C_5H_3$), 113.8 ($C_\beta C_5H_3$), 120.1 (C_5H_5), 133.4 ($C_\alpha C_5H_3$), 139.2 ($C_{ipso} C_5H_3$), CO was not observed. IR (nujol): ν_{CO} 2012, 1914 cm^{-1} ; IR (THF): ν_{CO} 2016, 1920 cm^{-1} .

Synthesis of trans-[Ti($\eta^5-C_5Me_5$)Cl₂{($\eta^5-C_5H_3$)₂[Si(CH₃)₂]}MoH(CO)₃] (trans-5)

THF (50 ml) was added to a mixture of $[Ti(\eta^5-C_5Me_5)Cl_2\{(\eta^5-C_5H_3)[Si(CH_3)_2(C_5H_4)]\}]$ (1.48 g, 2.97 mmol) and $[Mo(CO)_3(MeCN)_3]$ (0.9 g, 2.97 mmol). After stirring for a night at room temperature the resulting red solution was concentrated to dryness *in vacuo* leaving a red solid which was washed with pentane and identified as complex *trans-5* (1.88 g, 93%). Anal. calc. for $C_{27}H_{34}Cl_2MoO_3Si_2Ti$: C, 47.87; H, 5.06. Found: C, 47.59; H, 5.25. 1H NMR (300 MHz, C_6D_6): δ -5.54 (s, 1H, Mo-H), 0.47 (s, 6H, Si-Me), 0.59 (s, 6H, Si-Me), 1.70 (s, 15H, C_5Me_5), 5.05 (m, 3H, $C_\alpha C_5H_3 + C_\beta C_5H_3$), 5.68 (t, $J = 2.4$ Hz, 1H, $C_\beta C_5H_3$), 6.48 (d, $J = 2.4$ Hz, 2H, $C_\alpha C_5H_3$). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): 2.5 (Si-CH₃), 4.7 (Si-CH₃), 13.5 (C_5Me_5), 97.5 ($C_\beta C_5H_3$), 98.8 ($C_\alpha C_5H_3$), 105.2 ($C_{ipso} C_5H_3$), 117.4 ($C_\beta C_5H_3$), 129.6 (C_5Me_5), 131.5 ($C_\alpha C_5H_3$), 137.7 ($C_{ipso} C_5H_3$), 227.9 and 228.0 (CO).

IR (nujol): ν_{CO} 2016, 1920 cm^{-1} ; IR(THF): ν_{CO} 2018, 1928 cm^{-1} .

When the reaction was carried out with $\text{Mo}(\text{CO})_3$ (mesitylene) in the same conditions, a mixture of *cis-5* and *trans-5* was obtained after concentrating to dryness and washing with pentane. Complex *cis-5* could not be isolated. ^1H NMR (300 MHz, C_6D_6): δ -4.86 (s, 1H, Mo-H), 0.20 (s, 6H, Si-Me), 0.73 (s, 6H, Si-Me), 1.73 (s, 15H, C_5Me_5), 5.02 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 5.11 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.65 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.51 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$).

Synthesis of cis-[Ti(η^5 - C_5Me_5)Cl₂{(η^5 - C_5H_3)₂[Si(CH₃)₂]₂}WH(CO)₃] (cis-6)

THF (50 ml) was added to a mixture of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\{(\eta^5\text{-C}_5\text{H}_3)[\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4]\}]$ (1.38 g, 2.77 mmol) and $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ (1.08 g, 2.77 mmol). After stirring for 4 h at 50°C the resulting red solution was concentrated to dryness *in vacuo* leaving a red solid which was washed with pentane and identified as complex *cis-6* (1.95 g, 92%). Anal. calc. for $\text{C}_{27}\text{H}_{34}\text{Cl}_2\text{O}_3\text{Si}_2\text{TiW}$: C, 42.37; H, 4.48. Found: C, 42.59; H, 4.59. ^1H NMR (300 MHz, CDCl_3): δ -6.78 (s, 1H, W-H), 0.31 (s, 6H, Si-Me), 0.55 (s, 6H, Si-Me), 2.04 (s, 15H, C_5Me_5), 5.56 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 5.71 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.09 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.66 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): 2.8 (Si-CH₃), 4.9 (Si-CH₃), 13.8 (C_5Me_5), 95.0 ($\text{C}_\beta \text{C}_5\text{H}_3$), 95.7 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 106.0 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 116.0 ($\text{C}_\beta \text{C}_5\text{H}_3$), 130.1 (C_5Me_5), 131.8 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 139.0 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), CO was not observed. IR (nujol): ν_{CO} 2012, 1920 cm^{-1} ; IR(THF): ν_{CO} : 2016, 1922 cm^{-1} .

When the reaction yielded a mixture of isomers, we were unable to isolate complex *trans-6*. ^1H NMR (300 MHz, CDCl_3): δ -7.48 (s, 1H, W-H), 0.43 (s, 6H, Si-Me), 0.48 (s, 6H, Si-Me), 2.02 (s, 15H, C_5Me_5), 5.62 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 5.76 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.18 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.63 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$).

Synthesis of cis-[Ti(η^5 - C_5H_5)Cl₂{(η^5 - C_5H_3)₂[Si(CH₃)₂]₂}MoCl(CO)₃] (cis-7)

CCl_4 (2 ml) was added to a solution of complex *cis-3* (1 g, 1.65 mmol) in CH_2Cl_2 (40 ml). After stirring for a night, the solution was concentrated to dryness *in vacuo* leaving a red solid which was washed with pentane and recrystallized from a mixture CH_2Cl_2 : pentane 1 : 1 at -40°C to give *cis-7* as a red solid (0.95 g, 90%). Anal. calc. $\text{C}_{22}\text{H}_{23}\text{Cl}_3\text{MoO}_3\text{Si}_2\text{Ti}$: C, 41.17; H, 3.61. Found: C, 41.69; H, 4.19. ^1H NMR (300 MHz, CDCl_3): 0.33 (s, 6H, Si-Me), 0.57 (s, 6H, Si-Me), 5.55 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 6.25 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.40 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.56 (s, 5H, C_5H_5), 7.13 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): 1.8 (Si-

CH_3), 3.0 (Si- CH_3), 96.7 ($\text{C}_\beta \text{C}_5\text{H}_3$), 105.8 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 111.6 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 113.9 ($\text{C}_\beta \text{C}_5\text{H}_3$), 120.3 (C_5H_5), 133.5 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 139.1 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 222.8 and 242.5 (CO). IR (nujol): ν_{CO} 2045, 1946 cm^{-1} ; IR(CH_2Cl_2): ν_{CO} 2054, 1976 cm^{-1} .

Synthesis of cis-[Ti(η^5 - C_5H_5)Cl₂{(η^5 - C_5H_3)₂[Si(CH₃)₂]₂}WCl(CO)₃] (cis-8)

This complex was obtained by the same procedure described for *cis-7* starting from *cis-4* (1 g, 1.44 mmol) as a red solid (1 g, 95%). Anal. calc. for $\text{C}_{22}\text{H}_{23}\text{Cl}_3\text{O}_3\text{Si}_2\text{TiW}$: C, 36.21; H, 3.18. Found: C, 35.84; H, 3.15. ^1H NMR (300 MHz, CDCl_3): δ 0.36 (s, 6H, Si-Me), 0.60 (s, 6H, Si-Me), 5.57 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 6.41 (m, 2H, $2\text{C}_\beta \text{C}_5\text{H}_3$), 6.57 (s, 5H, C_5H_5), 7.13 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): 2.0 (Si- CH_3), 3.2 (Si- CH_3), 96.4 ($\text{C}_\beta \text{C}_5\text{H}_3$), 102.7 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 110.0 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 113.9 ($\text{C}_\beta \text{C}_5\text{H}_3$), 120.4 (C_5H_5), 133.4 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 139.2 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 214.2 and 232.4 (CO). IR (nujol): ν_{CO} 2013, 1952 cm^{-1} ; IR(CH_2Cl_2): ν_{CO} 2046, 1958 cm^{-1} .

Synthesis of trans-[Ti(η^5 - C_5Me_5)Cl₂{(η^5 - C_5H_3)₂[Si(CH₃)₂]₂}MoCl(CO)₃] (trans-9)

This complex was obtained by the same procedure described for *cis-7* starting from *trans-5* (1 g, 1.47 mmol) as a red solid (0.97 g, 93%). Anal. calc. for $\text{C}_{27}\text{H}_{33}\text{Cl}_3\text{O}_3\text{Si}_2\text{TiMo}$: C, 45.55; H, 4.67. Found: C, 44.65; H, 4.47. ^1H NMR (300 MHz, CDCl_3): δ 0.42 (s, 6H, Si-Me), 0.46 (s, 6H, Si-Me), 2.01 (s, 15H, C_5Me_5), 5.57 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 6.21 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.24 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.58 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3): 0.5 (Si- CH_3), 3.5 (Si- CH_3), 13.7 (C_5Me_5), 103.3 ($\text{C}_\beta \text{C}_5\text{H}_3$), 104.4 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 108.8 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 118.2 ($\text{C}_\beta \text{C}_5\text{H}_3$), 129.5 (C_5Me_5), 130.4 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 137.0 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 224.7 and 243.4 (CO). IR (nujol): ν_{CO} 2039, 1956 cm^{-1} ; IR(CH_2Cl_2): ν_{CO} 2050, 1970 cm^{-1} .

Synthesis of cis-[Ti(η^5 - C_5Me_5)Cl₂{(η^5 - C_5H_3)₂[Si(CH₃)₂]₂}WCl(CO)₃] (cis-10)

This complex was obtained by the same procedure described for *cis-7* starting from *cis-6* (1 g, 1.30 mmol) as a red solid (0.94 g, 90%). Anal. calc. for $\text{C}_{27}\text{H}_{33}\text{Cl}_3\text{O}_3\text{Si}_2\text{TiW}$: C, 40.55; H, 4.16. Found: C, 40.22; H, 4.05. ^1H NMR (300 MHz, CDCl_3): δ 0.35 (s, 6H, Si-Me), 0.62 (s, 6H, Si-Me), 2.06 (s, 15H, C_5Me_5), 5.49 (d, $J = 2.4$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$), 6.10 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.37 (t, $J = 2.4$ Hz, 1H, $\text{C}_\beta \text{C}_5\text{H}_3$), 6.68 (d, $J = 3$ Hz, 2H, $\text{C}_\alpha \text{C}_5\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): 2.5 (Si- CH_3), 2.7 (Si- CH_3), 13.8 (C_5Me_5), 97.1 ($\text{C}_\beta \text{C}_5\text{H}_3$), 103.1 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 109.2 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 116.2 ($\text{C}_\beta \text{C}_5\text{H}_3$), 130.4 (C_5Me_5), 131.9 ($\text{C}_\alpha \text{C}_5\text{H}_3$), 138.8 ($\text{C}_{\text{ipso}} \text{C}_5\text{H}_3$), 214.9 (CO), 232.9 (CO). IR

Table 2. Crystal, experimental data and structure refinement procedures for compound *cis-6*

Formula	C ₂₇ H ₃₄ Cl ₂ O ₃ Si ₂ TiW
Crystal habit	Prismatic
Color	Red
Crystal size	0.20 × 0.25 × 0.30 mm
Symmetry	Monoclinic, <i>P</i> 2 ₁ / <i>a</i>
Unit cell dimensions	
<i>a</i> (Å)	16.150(10)
<i>b</i> (Å)	12.021(3)
<i>c</i> (Å)	17.04(2)
β (°)	112.87(4)
<i>V</i> (Å ³)	3048(4)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.668
<i>M</i> _w	765.37
<i>F</i> (000)	1512
μ (cm ⁻¹)	43.13
Scan mode	ω/2θ 2.13 < θ < 24.01
No. of reflections	
Measured	4783
Independent observed	3297
Range of <i>h</i> , <i>k</i> , <i>l</i>	-18 < <i>h</i> < 16, 0 < <i>k</i> < 13, 0 < <i>l</i> < 19
Standard reflections	3 every 200 refl.
Refinement method	Full matrix least squares on <i>F</i> ²
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>)) ^a	<i>R</i> ₁ = 0.0419, <i>wR</i> ₂ = 0.0902
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1019, <i>WR</i> ₂ = 0.1288
Weighting scheme	Calc. ω = 1/[σ ² (<i>F</i> _o ²) + (0.0352 <i>P</i>) ² + 14.9107 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Maximum peak in final diff. map (e/Å ³)	0.826
Minimum peak in final diff. map (e/Å ³)	-0.851
Goodness of fit on <i>F</i> ²	1.107

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|; wR_2 = \{[\sum \omega((F_o^2 - F_c^2) / [\sum \omega(F_o^2)])^2]\}^{1/2}.$$

(*nujol*): ν_{CO} 2039, 1952 cm⁻¹. IR(CH₂Cl₂): ν_{CO} 2046, 1958 cm⁻¹.

X-ray structural determination for 6

Red crystals of compound **6** were obtained by crystallization from THF and a suitable sized crystal in a Lindemann tube was mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXL 90) [12] and refined by least squares against *F*² (SHELXL 93) [13]. A severe disorder appeared in the coordination sphere of the W atom and two different sets of carbonyl groups with similar occupancies were found. Unfortunately the second set shows the angle of one carbonyl group with an important deviation from linearity. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced from geometrical calculations and refined using

a riding model with thermal parameters equivalent to those of the atoms to which they are bonded. It was not possible to find the hydrogen atom bonded to W due to the disorder and this atom could not be included in any way. Calculations were carried out on an ALPHA AXP (Digital) workstation.

Supplementary material—Tables of positional parameters and their estimated standard deviations (Table 1), full list of bond lengths (Å) and angles (°) (Table 2), anisotropic displacement parameters (Table 3), hydrogen coordinates and isotropic displacement parameters (Table 4), and structure factors (Table 5) are available from author P.R. upon request.

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