Synthesis and Characterization of *cis*-[$Cp^*W(CO)_2(MeCN)Me$] and Its Stereospecific Substitution Reactions with Phosphines

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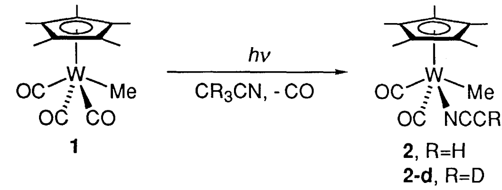
Photolysis of [$Cp^*W(CO)_3Me$] ($Cp^*=\eta^5$-C_5Me_5) in MeCN gave *cis*-[$Cp^*W(CO)_2(MeCN)Me$] in a high yield. Stereospecific substitution reactions of the acetonitrile complex with PR_3 (R=Me, Ph) took place under mild conditions to produce *cis*-[$Cp^*W(CO)_2(PR_3)Me$]. Reactions of M[$Cp^*W(CO)_2(PR_3)$] (M=Li, R=Me; M=K, R=Ph) with MeI afforded *trans*-[$Cp^*W(CO)_2(PR_3)Me$] as major products, which isomerized to the more stable cis isomers.

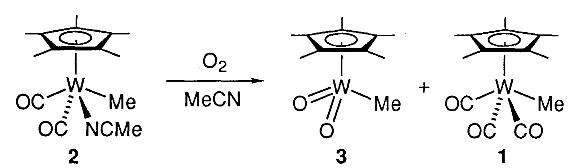
Transition-metal complexes having a labile solvent ligand such as tetrahydrofuran, acetonitrile, etc. are very useful for synthesizing a wide variety of complexes. One such complex [$CpW(CO)_2(MeCN)Me$] ($Cp=\eta^5$-C_5H_5) is formed in the photolysis of [$CpW(CO)_3Me$] in MeCN.[1] Several attempts to isolate it, however, were unsuccessful because of its instability.[1,2] Substitution of a Cp ligand by a Cp* ligand often enhances the kinetic and thermodynamic stability of the complexes and provides the opportunity to study their structure and reactivity in detail. Thus, we set out to synthesize the corresponding Cp* complex [$Cp^*W(CO)_2(MeCN)Me$] (**2**). We report here synthesis and spectroscopic characterization of **2** and its substitution reactions with phosphines. The isomerization of the substitution products *cis*-[$Cp^*W(CO)_2(PR_3)Me$] and their trans isomers is also described.

A CD_3CN solution (0.05 M) of [$Cp^*W(CO)_3Me$] (**1**) in a pyrex NMR tube was irradiated with a 100 W medium-pressure Hg lamp at ambient temperature and the reaction was monitored by ^1H NMR. After 15 min, **1** disappeared and new intense Cp* (δ 1.89) and W-Me (δ -0.25) signals attributed to *cis*-[$Cp^*W(CO)_2(CD_3CN)Me$] (**2-d**) were observed in 89% yield. In C_6D_6, **2-d** showed the Cp* and W-Me signals at δ 1.80 and 0.31, respectively. Similar photolysis of **1** in MeCN gave the corresponding MeCN complex **2**, which showed three signals at δ 1.80, 0.80, and 0.31 in C_6D_6. Thus, the signal at δ 0.80 is reasonably assigned to the coordinated MeCN, shifted downfield by 0.15 ppm from the resonance of free MeCN in C_6D_6.[3]

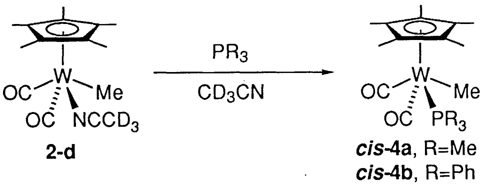


The cis configuration of the acetonitrile complex is shown by the ^{13}C NMR spectral data. In the spectrum of **2-d** in CD_3CN, two CO signals were observed at δ 259.9 and 248.6 together with a singlet at δ 136.0 and a septet at δ 4.4 (J_{CD} = 21.1 Hz) assignable to the coordinated CD_3CN.[4] The IR spectrum of **2** in MeCN shows two ν_{CO} absorptions at 1902 (vs) and 1804 (s) cm^{-1}. For the related Cp complexes, similar preferential formation of cis-substituted products *cis*-[$CpM(CO)_2LR$] (M=Mo, L=N_2, R=Me;[5] M=W, L=C_2H_4, R=Ph[6]) has been observed in low-temperature photolyses of [$CpM(CO)_3R$] in matrices containing N_2 and C_2H_4. A very weak absorption attributable to the ν_{CN} of the coordinated MeCN is also observed at 2259 cm^{-1} in C_6H_6. Upon standing at ambient temperature, the ν_{CN} absorption was replaced by the absorptions of free MeCN.[3]

Although under an inert atmosphere **2** is fairly stable in CH_3CN solution at ambient temperature, it easily reacts with oxygen to give the known dioxo complex[7] **3** (43% by ^1H NMR) together with small amounts of **1** and unidentified minor products. **1** was probably formed by the reaction of **2** with release of CO.

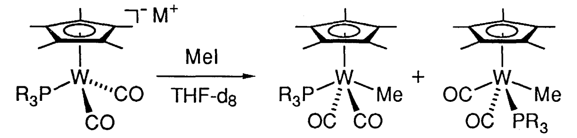


The lability of the acetonitrile ligand in **2** is also demonstrated by clean substitution reactions with phosphines. Reaction of **2-d** with PMe_3 (2.5 eq) in CD_3CN was complete within 8 min at ambient temperature to give the phosphine complex ***cis*-4a** in 98% ^1H NMR yield. Similar reaction of **2-d** with PPh_3 afforded ***cis*-4b** in 96% yield. Interestingly, the configuration of the products is retained through the reactions. In preparative reactions, which were carried out by adding the phosphines to CH_3CN solutions of **2** obtained by the photolyses of **1**, the phosphine complexes ***cis*-4a** and ***cis*-4b** were isolated as yellow solids in respective yields of 76 and 84% based on **1**. The cis configurations of ***cis*-4a,b** are required by the observation of two CO resonances in the ^{13}C NMR spectra.[8,9]



The phosphine complex ***cis*-4a** is cofigurationally stable and isomerization to the trans isomer was not observed in CD_3CN after 2 days at ambient temperature. To get information on the isomerization of [$Cp^*W(CO)_2(PMe_3)Me$], we prepared ***trans*-4a** according to the literature.[10] When the reaction of Li[$Cp^*W(CO)_2(PMe_3)$] (**5a**) with MeI in THF-d_8 was monitored by ^1H NMR, a 96:4 mixture of ***trans*-4a** and ***cis*-4a** was observed. The configuration of ***trans*-4a** was established by a single CO resonance at δ 234.2 in the ^{13}C NMR spectrum (THF-d_8, -20 °C), and less intense symmetric and more intense antisymmetric ν_{CO} bands at 1910 and 1821 cm^{-1}, respectively, in the IR spectrum. On monitoring the THF-d_8 solution by ^1H NMR, the isomerization of ***trans*-4a** to ***cis*-4a** was observed ($t_{1/2}$ $\approx$ 6 h at 30 °C) and only a trace amount (1-2%) of ***trans*-4a** was detected in the equilibrium mixture. Similar isomerization

($t_{1/2}$ ≈ 9 h at 30 °C) was also observed for *trans*-[Cp*W(CO)$_2$(PPh$_3$)Me] (***trans*-4b**)[12] prepared by methylation of K[Cp*W(CO)$_2$(PPh$_3$)] (**5b**) in THF-d_8 and gave a ca. 5:95 equilibrium mixture of ***trans*-4b** and ***cis*-4b**. These results clearly indicate the cis isomers are thermodynamically more stable than the trans isomers.



5a, R=Me, M=Li *trans*-**4a**, R=Me *cis*-**4a**, R=Me

5b, R=Ph, M=K *trans*-**4b**, R=Ph *cis*-**4b**, R=Ph

A number of studies have been carried out on the isomerization of CpM(CO)$_2$LR type complexes. Although the factors controlling the relative stability of cis and trans isomers are not always clear, it was pointed out that the equilibrium might be mainly on a delicate balance between the trans influence of the ligands and the steric interaction between the ligands L and R.[13] It was reported that *trans*-[CpW(CO)$_2$(PR$_3$)Me] (R=Me, Ph) are more stable than the cis isomers.[14] In the case of the corresponding Cp* complexes, however, the cis isomers are more stable as described above. There must be another factor favoring the cis isomer in the Cp* complexes and it might be ascribed to the angular trans influence proposed recently by Poli; a π-neutral ligand R (R=hydride, alkyl, etc.) has a tendency to decrease the Cp(centroid)-M-R and Cp(centroid)-M-L(trans) angles compared with the Cp(centroid)-M-L(cis) angle in CpML$_3$R complexes, where L(trans) and L(cis) are a π-acceptor ligand (CO, PR$_3$, etc.) trans to R and that cis to R, respectively.[15] Decrease in the Cp*(centroid)-M-PR$_3$ angle in [Cp*M(CO)$_2$(PR$_3$)Me] causes a larger repulsive interaction between the phosphine and the Cp* ligand compared with the corresponding interaction in the Cp analogues. It will shift the equilibrium between *cis*- and *trans*-[Cp*M(CO)$_2$(PR$_3$)Me] to the cis isomer, because the Cp*(centroid)-M-PR$_3$ angle in the cis isomer is expected to be larger than that in the trans isomer and hence the steric repulsion between the phosphine and the Cp* ligand will be reduced in the cis isomer.

The predominant formation of the cis isomers **2** and ***cis*-4a,b** in the present reactions is quite interesting. A high activation barrier suppressing the isomerization of ***cis*-4a,b** to ***trans*-4a,b** apparently makes a significant contribution to the observed predominance in the substitution reactions of **2**. However, essential questions concerning the site-selectivity in the photo-induced CO dissociation in **1** and the stereochemical rigidity of the coordinatively unsaturated [Cp*W(CO)$_2$Me] are not yet resolved. Mechanistic studies on the present reactions as well as exploration of the reactivity of **2** are currently being pursued.

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References and Notes

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3 Although **2** has enough stability to take the ^{1}H NMR and IR spectra in C$_6$D$_6$ and C$_6$H$_6$, respectively, at ambient temperature, it gradually decomposes to give free MeCN, [Cp*W(CO)$_2$]$_2$, and **1** as major products, and a weak signal assignable to methane is also detected by ^{1}H NMR.

4 The full ^{13}C NMR data of **2** is as follows. ^{13}C{^{1}H} NMR (126 MHz, CD$_3$CN) δ 259.9 (s, CO), 248.6 (s, CO), 136.0 (s, CD$_3\underline{C}$N), 102.8 (s, $\underline{C}_5$Me$_5$), 10.6 (s, C$_5\underline{Me}_5$), 4.4 (septet, J_{CD} = 21.1 Hz, $\underline{C}$D$_3$CN), -12.6 (s, WMe)

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8 ***cis*-4a**: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 1.71 (d, $^4J_{HP}$ = 0.5 Hz, 15H, C$_5$Me$_5$), 1.01 (d, $^2J_{HP}$ = 8.3 Hz, 9H, PMe$_3$), 0.01 (d, $^3J_{HP}$ = 12.9 Hz, 3H, WMe); ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$) δ 251.8 (d, $^2J_{CP}$ = 19.8 Hz, CO), 234.7 (d, $^2J_{CP}$ = 8.4 Hz, CO), 100.6 (s, $\underline{C}_5$Me$_5$), 16.7 (d, 9H, J_{CP} = 29.8 Hz, PMe$_3$), 10.8 (s, C$_5\underline{Me}_5$), -21.6 (d, $^2J_{CP}$ = 19.1 Hz, WMe); IR (C$_6$D$_6$) ν_{CO} = 1910 (vs), 1821 (s) cm^{-1}; Anal. Found: C, 41.28; H, 5.64%. Calcd for C$_{16}$H$_{27}$O$_2$PW: C, 41.22; H, 5.84%. The cis configuration was also confirmed by X-ray crystallography and the details will be published elsewhere.

9 ***cis*-4b**: ^{1}H NMR (90 MHz, C$_6$D$_6$) δ 7.67–6.93 (m, 15H, PPh$_3$), 1.69 (s, 15H, C$_5$Me$_5$), 0.02 (d, $^3J_{HP}$ = 12.9 Hz, 3H, WMe); ^{13}C{^{1}H} NMR (68 MHz, C$_6$D$_6$) δ 249.3 (d, $^2J_{CP}$ = 18.9 Hz, CO), 235.2 (d, $^2J_{CP}$ = 5.4 Hz, CO), 135.4(d, $^2J_{CP}$ = 41.7 Hz, ArC), 134.2 (s, ArC), 134.1 (s, ArC), 129.7 (s, ArC), 100.8 (s, $\underline{C}_5$Me$_5$), 10.5 (s, C$_5\underline{Me}_5$), -15.4 (d, $^2J_{CP}$ = 16.1 Hz, WMe); IR (C$_6$D$_6$) ν_{CO} = 1914 (vs), 1833 (s) cm^{-1}; Anal. Found: C, 56.88; H, 4.94%. Calcd for C$_{31}$H$_{33}$O$_2$PW: C, 57.07; H, 5.08%.

10 [Cp*W(CO)$_2$(PMe$_3$)Me] has been synthesized by the reaction of Li[Cp*W(CO)$_2$(PMe$_3$)] (**5a**) with MeI and a single CO resonance in the reported ^{13}C NMR data suggests the trans configuration.[11] However, we observed different NMR data from the reported one for the initial product, which was assigned to ***trans*-4a** and isomerized to ***cis*-4a** as described in text. The reported NMR data are rather close to those of ***cis*-4a** except for a single CO resonance. ***trans*-4a**: ^{1}H NMR (90 MHz, C$_6$D$_6$) δ 1.67 (s, 15H, C$_5$Me$_5$), 1.30 (d, $^2J_{HP}$ = 8.6 Hz, 9H, PMe$_3$), 0.66 (d, $^3J_{HP}$ = 2.6 Hz, 3H, WMe); ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$, -20 °C) δ 234.2 (d, $^2J_{CP}$ = 17.2 Hz, CO), 100.3 (s, $\underline{C}_5$Me$_5$), 21.3 (d, J_{CP} = 32.3 Hz, PMe$_3$), 10.7 (s, C$_5\underline{Me}_5$), -23.0 (d, $^2J_{CP}$ = 8.6 Hz, WMe); IR (C$_6$D$_6$) ν_{CO} = 1910 (s), 1821 (vs) cm^{-1}.

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12 ***trans*-4b**: ^{1}H NMR (90 MHz, C$_6$D$_6$) δ 7.80-6.80 (m, 15H, PPh$_3$), 1.57 (s, 15H, C$_5$Me$_5$), 0.87 (d, $^3J_{HP}$ = 2.2 Hz, 3H, WMe); IR (C$_6$D$_6$) ν_{CO} = 1918 (s), 1835 (vs) cm^{-1}.

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