Unusually High Reactivity of *cis*-Cp*W(CO)$_2$(MeCN)Me to CO Insertion Reaction with Isocyanide

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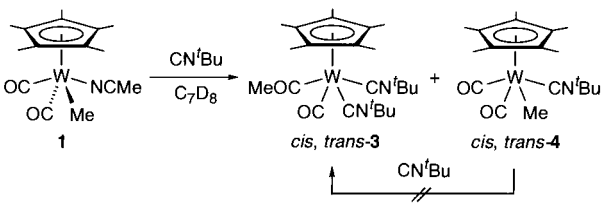
The reaction of *cis*-Cp*W(CO)$_2$(MeCN)Me with CN^{t}Bu gave a mixture of the acetonitrile substitution products *cis*- and *trans*-Cp*W(CO)$_2$(CN^{t}Bu)Me and the CO insertion products *cis*- and *trans*-Cp*W(CO)(CN^{t}Bu)$_2$(COMe). The substitution was favored at room temperature, while the insertion was favored at low temperature.

Recently we reported the synthesis of *cis*-Cp*W(CO)$_2$(MeCN)Me (**1**) by photolysis of Cp*W(CO)$_3$Me (**2**) in MeCN and its substitution reaction with phosphines to give *cis*-Cp*W(CO)$_2$(PR$_3$)Me.[1] In the course of further reactivity studies of **1** with two-electron donors, we have found that it shows unusually high reactivity toward CO insertion reaction with isocyanides, contrary to a general tendency for tungsten alkyl complexes to be rather unreactive to insertion reactions compared with the corresponding molybdenum complexes.[2]

When **1** was treated with CN^{t}Bu (3 equiv) in toluene-d_8 at room temperature, the rapid formation of the unexpected CO insertion products *cis*- and *trans*-Cp*W(CO)(CN^{t}Bu)$_2$(COMe) (*cis*-**3**:*trans*-**3** = 1.3:1)[3] was observed in addition to the substitution products *cis*- and *trans*-Cp*W(CO)$_2$(CN^{t}Bu)Me (*cis*-**4**:*trans*-**4** = 1.3:1)[4] in a ratio of **3**:**4** = 25:75 (almost quantitative yields). From a preparative reaction, **3** and **4** were isolated by column chromatography in 13 and 64% yields, respectively.



Complexes **3** show characteristic acetyl signals at δ 2.90 (*cis*-**3**) and 2.78 (*trans*-**3**) in the ^{1}H NMR spectrum. Recrystallization of **3** from hexane at –20 °C gave single crystals of *cis*-**3**, whose structure was determined by X-ray crystallography.[5] The ORTEP drawing of the molecule shows a four-legged piano-stool structure with the cis arrangement of two isocyanide ligands (Figure 1). The bonding parameters of the acetyl ligand shown in Figure 1 are very similar to those of the structurally related acetyl complex *trans*-CpW(CO)$_2$(PPh$_3$)(COMe).[6] The isocyanide ligands are essentially linear, although the one trans to the acetyl group is slightly more bent (C4–N1–C5 = 169(1)°) than the other (C9–N2–C10 = 178(1)°).

The most straightforward explanation of the formation of **3** is isocyanide-induced CO insertion in **4**. This possibility, however, is excluded from the fact that no reaction was observed in the presence of excess CN^{t}Bu in toluene-d_8 at room temperature, and the reaction under severe conditions (90 °C) gave the η^3-1-azaallyl complex Cp*W(CO)$_2$(η^3-CH$_2$CHN^{t}Bu) as a major product as reported by Carmona.[7] In this relation, the reactivity of **2** to CN^{t}Bu was also examined in toluene-d_8 and CD$_3$CN, but no product was observed in both solutions at room temperature in accordance with the general tendency of tungsten alkyl complexes in insertion reactions.[2,8] These results emphasize the unusually high reactivity of **1** to insertion as a tungsten alkyl complex, and its quite interesting reactivity is further demonstrated by low-temperature experiments.

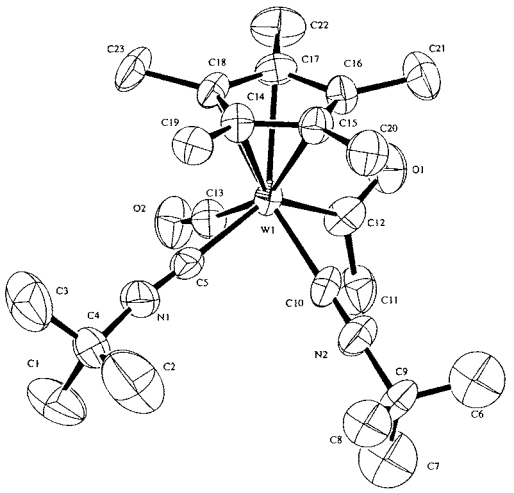
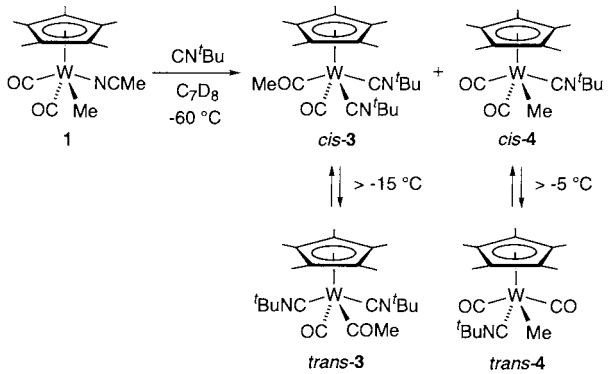


Figure 1. ORTEP drawing of *cis*-**3**. All hydrogen atoms are omitted for clarity, and only one part (C6, C7, C8) of the disordered methyl groups is shown. Selected bond lengths (Å) and angles (deg): W1–C5, 2.051(8); W1–C10, 2.049(9); W1–C12, 2.199(9); W1–C13, 1.942(8); N1–C4, 1.43(1); N1–C5, 1.14(1); N2–C9, 1.48(2); N2–C10, 1.13(1); O1–C12, 1.20(1); O2–C13, 1.17(1); C11–C12, 1.53(2); C5-W1-C10, 77.7(3); C5-W1-C13, 79.3(3); C10-W1-C12, 77.1(4); C12-W1-C13, 72.3(3); W1–C12–O1, 124.2(8); W1-C12-C11, 122.1(7); O1-C12-C11, 113.6(9).

When the reaction of **1** with CN^{t}Bu (3 equiv) was carried out in toluene-d_8 at –50 °C, the product ratio **3**:**4** changed dramatically from 25:75 at room temperature to 95:5, showing the CO insertion is favored at low temperature. Considering the observation that the exchange between the labile CD$_3$CN ligand and free CH$_3$CN occurs above ca. –30 °C in a toluene-d_8 solution of *cis*-Cp*W(CO)$_2$(CD$_3$CN)Me and CH$_3$CN, it is suggested that the substitution favored at room temperature may be via dissociation of MeCN from **1**, while the insertion favored at low temperature may proceed via interaction of **1** with CN^{t}Bu. To examine this mechanistic hypothesis, the reactions of **1** with CN^{t}Bu (3 equiv) were carried out in the presence of CH$_3$CN (ca. 27–30 equiv). The reaction at room temperature produced a 64:36 mixture of **3** and **4**, while the corresponding reaction at –50 °C gave a 93:7 mixture. A qualitative support for the hypothesis is provided by the facts that a considerably large decrease in the relative ratio of **4** to **3** was observed in the presence of CH$_3$CN (**3**:**4** = 64:36)

compared with in the absence (25:75) at room temperature, and that no essential change in the ratio of **3**:**4** was detected in the absence (95:5) and in the presence (93:7) of CH_3CN at –50 °C.

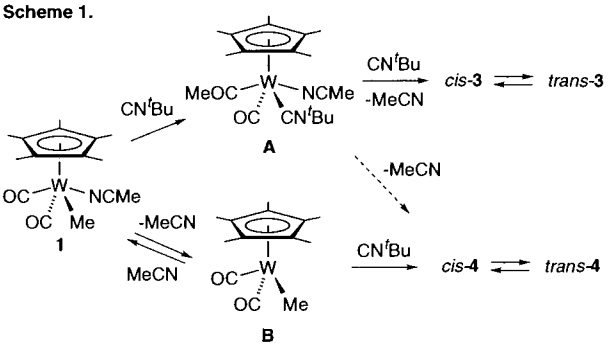
To get further information on the CO insertion process, low-temperature NMR studies were carried out. An NMR tube containing a toluene-d_8 solution of **1** and CN^{t}Bu (14 equiv) cooled at –78 °C was inserted into a precooled probe (–80 °C), and the reaction was monitored. Interestingly, the insertion reaction proceeded smoothly even at –60 °C ($t_{1/2} \approx 70$ min) and stereospecifically gave *cis*-**3** (> 95%) along with a trace amount of *cis*-**4** (< 5%). When the temperature was gradually raised, cis-trans isomerizations of *cis*-**3** and *cis*-**4** to form their isomeric mixtures were observed at ca. –15 °C and –5 °C, respectively.



Detailed mechanistic studies on typical CO insertion reactions of the structurally related $CpMo(CO)_3Me$ with PR_3 to give $CpMo(CO)_2(PR_3)(COMe)$ have shown that two competing mechanisms are operative: a solvent-assisted mechanism including the preequilibrium formation of solvent complex $CpMo(CO)_2$-(solv)(COMe) followed by the replacement of the coordinated solvent with PR_3 favored in a nucleophilic coordinating solvent such as THF and a direct interaction mechanism between the alkyl complex and the phosphine favored in a non-coordinating solvent such as toluene.[9] Although, considering the solvent used in the above reactions, the direct interaction mechanism seems more likely for the insertion reaction of **1**, a reaction via this type of mechanism is generally rather slow and some interaction to cause a significant rate enhancement is required for **1**. As one such interaction, a donor–acceptor interaction between an alkyl complex and an incoming ligand to form a molecular complex might be conceivable. This type of interaction has recently been proposed for CO insertion reactions of CpML(CO)R (M = Fe, Ir) and related complexes with phosphines and isocyanides.[10] Although remarkable rate enhancements have not been observed in these systems, significant acceleration of an insertion reaction would be expected if a strong oxidative effect on an alkyl complex results from such an interaction. In this regard, it is interesting to note that **1** has a very electron-rich metal center (ν_{CO} = 1902, 1804 cm^{-1}) compared to **2** (ν_{CO} = 2002, 1904 cm^{-1}).

A possible mechanism is outlined in Scheme 1. In the CO insertion reaction favored at low temperature, intermediate **A** is presumed to be formed by the interaction between **1** and CN^{t}Bu,[11] where the donor–acceptor interaction might be included, and then the MeCN ligand of **A** is replaced by CN^{t}Bu to form *cis*-**3**. A major route to **4** in the room temperature reactions seems to be via intermediate **B**. However, a decarbonylation path from **A** via dissociation of MeCN ligand might be also operative, especially in

Scheme 1.



the formation of a trace amount of *cis*-**4** in the low-temperature reactions. In the reaction of **1** with phosphines, only substitution reaction occurred at room temperature,[1] and no reaction was observed at low temperature. Although steric reasons are responsible for no reactivity to CO insertion reaction with phosphines, systematic studies are needed to clarify essential features causing the unusually high reactivity of **1** toward isocyanide.

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References and Notes

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3 **3**: ^{1}H NMR (400 MHz, C_6D_6) *cis*-**3**: δ 1.13 (9H, ^{t}Bu), 1.20 (9H, ^{t}Bu), 2.03 (15H, Cp*), 2.90 (3H, COMe); *trans*-**3**: δ 1.15 (18H, ^{t}Bu), 2.05 (15H, Cp*), 2.78 (3H, COMe); ^{13}C{^{1}H}NMR (100 MHz, C_6D_6) *cis*-**3**: δ 10.91 ($C_5\mathit{Me}_5$), 31.2 (CNCMe_3), 31.7 (CNCMe_3), 54.7 (COMe), 57.0 (CNCMe_3), 58.2 (CNCMe_3), 103.1 (C_5Me$_5$), 177.8 (CNCMe$_3$, J_{CW} = 147 Hz), 188.3 (CNCMe$_3$, J_{CW} = 121 Hz), 242.3 (CO, J_{CW} = 163 Hz), 259.2 (COMe); *trans*-**3**: δ 10.88 ($C_5\mathit{Me}_5$), 31.2 (CNCMe_3), 53.3 (COMe), 57.7 (CNCMe_3), 102.8 (C_5Me$_5$), 182.9 (CNCMe$_3$, J_{CW} = 139 Hz), 247.7 (CO, J_{CW} = 148 Hz), 262.6 (COMe); HRMS Calcd for $C_{23}H_{36}N_2O_2W$ 556.2287, found 556.2322.
4 Complexes *cis*- and *trans*-**4** have been synthesized by the reaction of Na[Cp*W(CO)$_2$(CN^{t}Bu)] with MeI.[7]
5 Crystal data for *cis*-**3**: $C_{23}H_{36}N_2O_2W$, MW = 556.40, monoclinic, space group $P2_1/c$ (No. 14), a = 17.593(2), b = 8.510(3), c = 17.872(2) Å, β = 104.557(7)°, V= 2589.9(9) Å^3, Z = 4, D_{calc} = 1.427 g/cm^3, μ(Cu-Kα) = 83.92 cm^{-1}, R = 0.037 (R_W = 0.039) for 3367 observed reflections [$I > 3.00\sigma(I)$]. The *t*-Bu group including C9 atom is disordered in two parts, in which six Me carbon atoms were refined isotropically at half occupancy rate. All hydrogen atoms except for those on the disordered carbons, calculated geometrically, were not refined, but included in the refinement.
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11 The stereochemistry of **A** is tentatively shown on the supposition that the methyl group migrates to the CO ligand cis to the methyl and that the incoming isocyanide occupies the cis position to the acetyl group, and the selective formation of *cis*-**3** is also explained by the occupancy of the trans position to the acetyl group by CN^{t}Bu followed by stereospecific substitution of the MeCN ligand by CN^{t}Bu.