Inorganica Chimica Acta, 96 (1985) L83–L85

Neutral Isocyanide Complexes containing Tungsten in a High Oxidation State: Synthesis and Susceptibility to Nucleophilic Attack

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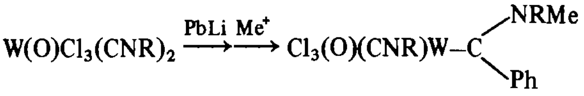
Received August 28, 1984

Tungsten alkylidene complexes which contain tungsten in a high oxidation state have been shown to behave as active olefin metathesis catalysts [1]. As with most metathesis catalysts, these complexes are unable to transalkylidenate alkenes containing heteroatoms attached on or near the carbon-carbon double bond [2]. Since olefin metathesis is generally considered to involve a metal alkylidene intermediate it is unclear whether the heteroatom-containing metal alkylidene is unable to form, or whether it is simply too stable to undergo further reaction. The synthesis of a tungsten alkylidene complex similar to those described above containing a heteroatom attached to the alkylidene carbon would serve to resolve the dilemma since such a complex should either catalyze metathesis, supporting the former hypothesis, or be unreactive, supporting the latter.

The catalytic high-valent tungsten alkylidenes have been synthesized by Schrock *et al.* [1] in a unique ligand exchange reaction between Ta($CHCMe_3$)(PEt_3)$_2$$Cl_3$ and W(O)($OCMe_3$)$_4$, but probable difficulties with alpha hydride abstraction from a heteroatom-containing tantalum alkyl complex to produce the parent alkylidene led us to seek a more direct route to the desired products. While isocyanide ligands attached to metals in low oxidation states do not appear to be susceptible to nucleophilic attack [3], those bonded to higher-valent metals are often attacked by even relatively weak bases such as methanol and dimethylamine [4]. Based on this we postulated a synthetic scheme which parallels the well known preparation of tungsten carbonyl carbene complexes [5] in which a strong nucleophile reacts with coordinated carbon, followed by methylation:

$$WCl_6 + THF(xs) \longrightarrow W(O)Cl_3(THF)_2 \quad [6]$$

$$W(O)Cl_3(THF)_2 + 2CNR \longrightarrow W(O)Cl_3(CNR)_2$$



$$W(O)Cl_3(CNR)_2 \xrightarrow{\text{PbLi}\ \text{Me}^+} Cl_3(O)(CNR)W{-}C\begin{smallmatrix}\diagup NRMe\\ \diagdown Ph\end{smallmatrix}$$

We report here the details of the synthesis and characterization of these new neutral high-valent tungsten isocyanide complexes and results of their reactions with phenyllithium.

Experimental

W(O)Cl_3(THF)$_2$ was prepared as described by Fowles and Frost [6]. Cyclohexylisocyanide was obtained from Aldrich Chemical Co. and used without further purification. *p*-Tolylisocyanide and t-butylisocyanide were prepared and purified using previously published methods [7]. All operations were carried out under dry nitrogen using standard Schlenck techniques and all solvents were distilled under N_2 prior to use. The isocyanides were added as solutions in CH_2Cl_2 via syringe to a stirred suspension of W(O)Cl_3(THF)$_2$ in toluene. IR spectra were obtained as KBr pellets using a Nicolet MX1 FTIR spectrometer and ^{13}C NMR spectra were recorded in C_6D_6 or CH_2Cl_2 on a Bruker WH-250 NMR Spectrometer. Chemical shifts were referenced to CH_2Cl_2 or C_6D_6 and standardized to TMS.

Compounds of the general formula W(O)Cl_3(CNR)$_2$ were prepared by adding a solution of 4.4 mmol of the appropriate isocyanide in 20 ml of CH_2Cl_2 to a stirred suspension of W(O)Cl_3(THF)$_2$ (2.2 mmol) in 40 ml of toluene. After an induction period of approximately 15 min. the reaction mixtures changed from blue to dark green. The solutions were allowed to stir for 18 additional hours with no noticeable change. Solvent volume was reduced by ½ *in vacuo*, and 45 ml of hexane was added to aid in the precipitation. In each case the entire mixture was cooled to –20 °C, filtered, and washed with hexane, yielding the disubstituted isocyanide complex in approximately 70% yield.

Nucleophilic attack studies were initially performed on W(O)Cl_3(CNtBu)$_2$ since it provided the best CHN analysis. Theoretical: C, 25.42%; H, 3.84%; N, 5.93%. Found: C, 25.47%, H, 3.51%; N, 5.69%. The other isocyanide complexes contained small amounts of strongly adsorbed isocyanide and we have been unable to obtain them in sufficient purity for analysis. 0.25 ml (6 mmol) of phenyllithium was added to a suspension of 0.55 g of W(O)Cl_3($CNC_6H_4CH_3$)$_2$ (5 mmol) in 10 ml of toluene. The solution changed from purple to dark green in about 20 sec, then to dark brown after 3 min. Solvent was removed *in vacuo* and an extremely air sensitive brown precipitate was isolated.

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0020-1693/85/$3.30

Discussion

$W(O)Cl_3(THF)_2$ reacts readily with *p*-tolylisocyanide, cyclohexylisocyanide and t-butylisocyanide to yield the corresponding bis-substituted isocyanide complexes. These complexes are sensitive to moisture but can be stored under dry N_2 for months. All are dark brown solids which are insoluble in most common organic solvents.

The CN stretching frequencies for the coordinated and free isocyanide ligands are given in Table I, and the ^{13}C chemical shifts are listed in Table II. Upon coordination each ligand experiences an unusually large increase in ν_{CN}: 102, 53, and 42 cm^{-1} for the t-butyl, cyclohexyl, and *p*-tolyl isocyanides, respectively. This effect parallels that observed when isocyanide coordinates to positive metal centers such as Cr^{+n} ($n = 1, 2, 3$) or Pt^{+4} [8] and supports the notion that tungsten is relatively electron deficient in these neutral complexes. It is likely that there is comparatively little π back donation to the isocyanide carbons, since one would expect a decrease in the CN stretching frequencies in such a case, and it follows that contribution **I** (below) should be predominant in the metal–ligand bonding scheme:

$$\underset{\textbf{I}}{M{-}C{\equiv}N{-}R} \longleftrightarrow \underset{\textbf{II}}{M{=}C{=}N{-}R}$$

TABLE I. CN Stretching Frequencies for $W(O)Cl_3(CNR)_2$ and the Free Isocyanide Ligand.

R	Free ligand	Coordinated ligand
t-butylNC	2135	2236, 2191
p-tolylNC	2126	2166, 2136
cyclohexylNC	2140	2193, 2131

TABLE II. ^{13}C Chemical Shifts for $W(O)Cl_3(CNR)_2$.

Complex	ppm (TMS)	
$W(O)Cl_3(CNC(CH_3)_2)$	27.05	t-carbon
	25.06	methyl
$W(O)Cl_3(CNC_6H_4CH_3)_2$	21.73	methyl
	123.96	phenyl
	132.03	phenyl
	142.11	phenyl
	149.47	phenyl
$W(O)Cl_3(CNC_6H_{11})_2$	22.9	
all resonances multiplets	25.6	
due to various configurations	32.7	
	38.8	

For each complex a strong absorption in the 960 cm^{-1} region of the infrared spectrum is observed which is consistent with W=O stretch. As is often the case, the isonitrile ^{13}C resonances were not observed, due in large part to the inherent insolubility of the complexes and the lack of an effective relaxation mechanism for the isocyanide carbon.

Treatment of $W(O)Cl_3(CNC(CH_3)_3)_2$ with one equivalent of phenyllithium produces an extremely air-sensitive compound which exhibits an IR spectrum with a broad absorption at 2134 cm^{-1} and a shoulder at 2048 cm^{-1}. This large decrease in the CN stretching frequency strongly implies that the bond order of the coordinated isocyanide has been reduced, suggesting that nucleophilic attack has occured at the isocyanide ligand. The W=O stretching frequency is essentially unchanged at 961 cm^{-1}, indicating that bonding at the metal center has not been significantly perturbed as would be expected if the $C_6H_5^-$ ion was bonded directly to the metal center. The bis-*p*-tolyl complex suspended in toluene reacts with phenyllithium in an analogous manner with an immediate color change from light green to dark green, followed by a slow change to brown. Subsequent methylation yields a brown powder which has yet to be isolated with purity. An IR spectrum of the product mixture displays a CN stretching frequency at 2180 cm^{-1} which is significantly broadened with respect to the starting complex. Again, a peak at 970 cm^{-1} is evidence that the W=O bond remains essentially unchanged.

In contrast to isocyanides coordinated to metals in low oxidation states, the isocyanides coordinated to tungsten(V) appear to undergo facile nucleophilic attack and further reaction with CH_3^+. It follows that these new tungsten(V) isocyanide complexes are ideal candidates as potential intermediates for the synthesis of high-valent carbene/alkylidene complexes which contain a heteroatom bonded directly to the carbene carbon.

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