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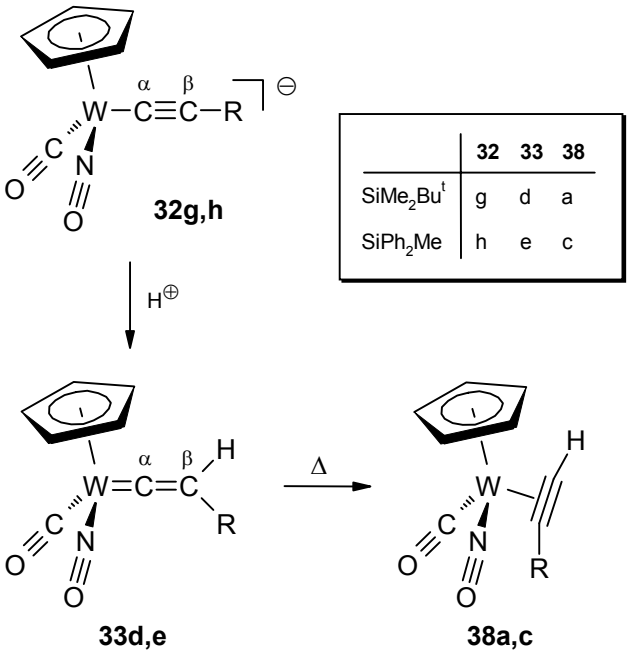
Mechanistic Studies of the η^1-Vinylidene → η^2-Alkyne Isomerization and Synthetic Application of Carbonyl-Vinylidene Complexes of Tungsten

Abstract

Part 1: η^1-Vinylidene → η^2-Alkyne Isomerization

In the first part the synthesis, characterization and isomerization of tungsten vinylidene complexes containing a silyl group at the β-carbon atom is described. Protonation of lithium tungsten acetylides [W(−C≡C−R)Cp(CO)(NO)]Li [R = $SiMe_2Bu^t$ (**32g**), R = $SiPh_2Me$ (**32h**)] lead to the formation of the corresponding vinylidene complexes [W(=C=CHR)Cp(CO)(NO)] (**33d,e**). It is shown that contrary to the general prediction, these monosubstituted vinylidenes convert thermally into the corresponding η^2-alkyne complexes [W(η^2-H−C≡C−R)Cp(CO)(NO)] (**38a,c**). Kinetic studies on the transformation of **33d** to **38a** provided following activation parameters: $\Delta H^{\ddagger}$ = 27.2 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −9.7 ± 1.1 eu. These values, the measured kinetic isotope effect of **33d** → **38a** and the synthetic data are consistent with the isomerization mechanism via a sigmatropic 1,2-shift of the silyl group.



	32	33	38
$SiMe_2Bu^t$	g	d	a
$SiPh_2Me$	h	e	c

Part 2: Nucleophilic Addition to Carbonyl-Vinylidene Complexes

Primary and secondary amines have been found to react in THF at room temperature with vinylidene complexes [W(=C=CHR)Cp(CO)(NO)] [R = $C(CH_3)_3$ (**33a**), R = $SiMe_2Bu^t$ (**33d**)] affording aminocarbene derivatives [W{=C(NR^1R^2)$CH_2C(CH_3)_3$}Cp(CO)(NO)] and [W{=C(NR^1R^2)$CH_2SiMe_2Bu^t$}Cp(CO)(NO)] [R^1 = H, R^2 = n-C_4H_9 (**90a**, **91a**); R^1 = H, R^2 = $CH(CH_3)_2$ (**90b**, **91b**); R^1 = H, R^2 = $C(CH_3)_3$ (**90c**, **91c**); R^1 = R^2 = $(CH_2)_4$ (**90d**, **91d**)]. At short reaction time the nuclophilic addition of both primary and secondary amines to **33a** occurs at the carbonyl carbon atom leading stereoselectively to the thermodynamically less stable η^2-carbamoyl-(*Z*)-vinyl complexes [W{σ-(*Z*)-CH=CH$C(CH_3)_3$}{η^2-C(O)NR^1R^2}Cp(NO)] [R^1 = H, R^2 = n-C_4H_9 (**92a**); R^1 = H, R^2 = $CH(CH_3)_2$ (**92b**); R^1 = H, R^2 = $C(CH_3)_3$ (**92c**); R^1 = R^2 = $(CH_2)_4$ (**92d**)]. At higher amine concentration and prolonged reaction time **92a–d** form the

corresponding aminocarbene complexes **90a-d**. The structure of **92b** has been authenticated by a single X-ray diffraction analysis.

The outcome of the additions depends on the vinylidene precursor leading stereoselectively to η^2-carbamoyl-(*Z*)-vinyl complexes **92a–d** in a short reaction time when a *tert*-butyl substituted vinylidene complex is used as a precursor. In the presence of an excess of the appropriate amine the complexes **92a–d** are not stable and undergo an elimimination reaction to generate the starting materials. With a longer reaction time the amine attacks again the complex **33a** and leads via addition to the C_α of the vinylidene moiety to the aminocarbenes **90a–d**. These results show a novel reactivity pattern in the nucleophilic addition of amines to vinylidene complexes bearing carbonyl ligands as competive electrophilic sites.