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On the reactivity of $[IrCl(N_2)(PPh_3)_2]$ with alkynylsilanes – A new route to vinylidene iridium(I) complexes

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Abstract

The iridium dinitrogen complex $[IrCl(N_2)(PPh_3)_2]$ (**1**) was found to react with alkynylsilanes $RC{\equiv}CSiR'_3$ to form the vinylidene iridium(I) complexes *trans*-$[IrCl\{{=}C{=}CR(SiR'_3)\}(PPh_3)_2]$ (R/R′ = Ph/Me, **2**; Me/Me, **3**; Bn/Me, **4**; $SiMe_3$/Me, **5**; $SiEt_3$/Et, **6**; ^{i}Pr/Me, **7**) and with $Me_3SiC{\equiv}CC(O)R$ to yield the iridium η^2-alkyne complexes *trans*-$[IrCl\{\eta^2\text{-}Me_3SiC{\equiv}CC(O)R\}(PPh_3)_2]$ (R = OEt, **9**; Me, **11**). Complex **9** was found to isomerize upon heating or upon UV irradiation yielding the vinylidene complex *trans*-$[IrCl\{{=}C{=}C(SiMe_3)\text{-}CO_2Et\}(PPh_3)_2]$ (**10**). The reaction of **1** with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ yielded the complex *trans*-$[IrCl\{{=}C{=}C(SiMe_3)C{\equiv}CSiMe_3\}(PPh_3)_2]$ (**8**), whereas with $MeO_2CC{\equiv}CCO_2Me$ the iridacyclopentadiene complex $[Ir\{C_4(CO_2Me)_4\}Cl(PPh_3)_2]$ (**13**) was formed. The complexes were characterized by means of ^1H, ^{13}C and ^{31}P NMR spectroscopy as well as by IR spectroscopy and microanalysis.

Keywords: Iridium; Alkynylsilane; Vinylidene complexes; η^2-Alkyne complexes; Iridacyclopentadiene

1. Introduction

It is well-known that vinylidenes – the thermodynamically less stable isomers of alkynes – can be effectively stabilized via coordination to a transition metal center [1] and that vinylidene transition metal complexes play an important role as intermediates in some homogeneously catalyzed reactions [2]. Square-planar vinylidene iridium(I) complexes *trans*-$[IrCl({=}C{=}CHR)(P^iPr_3)_2]$ have been firstly prepared by Werner et al. [3] as shown in Scheme 1 (X = H). The substitution reactions of terminal alkynes $RC{\equiv}CH$ with the cyclooctene complex **a** (generated in situ from $[\{IrCl(C_8H_{14})_2\}]_2$ and P^iPr_3 [4]) gave the alkyne complexes **b**, which were found to isomerize via hydrido(alkynyl)iridium(III) complexes **c** yielding the vinylidene complexes **d** [3,5]. Alternatively, the dihydridoiridium(III) complex **e** underwent, with the reductive elimination of H_2, the oxidative addition of terminal alkynes to provide the intermediate complexes **c**, which isomerized to the vinylidene complexes **d** [6]. Furthermore, alkynylsilanes $RC{\equiv}CSiMe_3$ were found to react analogously with ${\equiv}C{-}Si$ bond activation (Scheme 1, X = $SiMe_3$), likely also via type **c** intermediate complexes [7,8]. However, all these reactions proceeded with triisopropylphosphine as coligands [3,5–8]. Other phosphines could be used only in special cases. Thus, $[IrCl({=}C{=}CH_2)(PMe^tBu_2)_2]$ was obtained from the reaction of $[IrCl(H)_2(PMe^tBu_2)_2]$ with acetylene, but reactions using $PMePh_2$, PMe_2^tBu, PMe_2Ph or PPh_3 failed [9]. The only complex having PPh_3 coligands $[IrCl({=}C{=}CH_2)(PPh_3)_2]$ was isolated in the elimination reaction of CO from $[Ir(C{\equiv}CH)Cl(H)(CO)(PPh_3)_2]$ with Me_3NO [9]. Furthermore, some vinylidene type **d** complexes with bifunctional phosphines $P(CH_2CH_2OMe)(^iPr)_2$ or $P(CH_2CO_2Me)(^iPr)_2$ have also been obtained [10].

As early as 1967 Collman et al. reported the reactions of $[IrCl(N_2)(PPh_3)_2]$ (**1**) with internal alkynes having two electron-withdrawing substituents $RC{\equiv}CR'$ (R, R′ = CO_2Me, Ph,...) to form iridium η^2-alkyne [11] or

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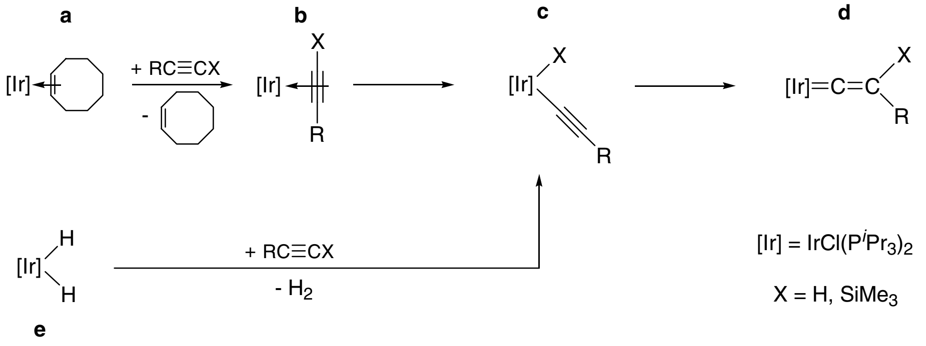


Scheme 1.

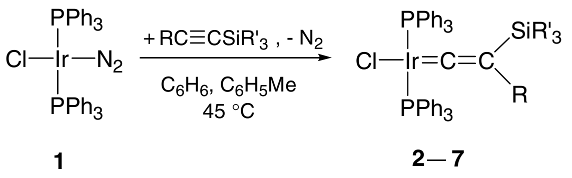
iridacyclopentadiene [12] complexes. Thus, it was shown that the dinitrogen ligand in **1** could be – in principle – substituted by alkynes. However, from the analogous reactions with acetylene and phenylacetylene it was not possible to isolate either the requisite alkyne or vinylidene complexes [9]. Within this paper we describe our investigations on the reactivity of the iridium dinitrogen complex **1** toward trialkylsilyl-substituted alkynes yielding η^2-alkyne complexes and/or, with ≡C—Si bond activation, square-planar iridium(I) vinylidene complexes having triphenylphosphine co-ligands.

2. Results and discussion

The dinitrogen iridium complex $[IrCl(N_2)(PPh_3)_2]$ (**1**) was found to react with $RC{\equiv}CSiR'_3$ in benzene or toluene at 45 °C yielding the iridium(I) vinylidene complexes *trans*-$[IrCl\{{=}C{=}CR(SiR'_3)\}(PPh_3)_2]$ (**2**–**7**) (Scheme 2). Monitoring the reactions NMR spectroscopically (^{13}C, ^{31}P) revealed that the complexes **2**–**7** were almost quantitatively formed within 1–6 h. Complexes **2**–**6** were isolated in yields of 53–78%; complex **7** has been characterized in C_6D_6 solution. The vinylidene complexes **2**–**6** are red-pink or orange, with the exception of **4**, moderately air-sensitive solids, which are well soluble in benzene and methylene chloride and sparingly soluble in methanol, hexane and diethyl ether. They undergo decomposition within 15 min up to 1 h on air but can be stored under argon at −40 °C at least for a few weeks without decomposition. Complex **4** (R = Bn) is air-sensitive in the solid state and it turns brownish within a few minutes.

The identities of the vinylidene complexes were confirmed by microanalyses, IR spectroscopy as well as ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^{13}C NMR resonances for vinylidene α-carbon atoms are strongly low-field shifted (244–264 ppm) exhibiting $^2J(P,C)$ coupling constants of 11–13 Hz, whereas the resonances for vinylidene β-carbon atoms were found at 82–103 ppm having $^3J(P,C)$ coupling constants of 2–4 Hz. The triplet patterns of these two signals give clear evidence for the *trans* configuration of the complexes. In accordance with that in the ^{31}P NMR spectra singlet resonances at 25–28 ppm were found. The NMR data are consistent with those reported by Werner et al. for analogous complexes with P^iPr_3 ligands (^{13}C NMR: 240–255 ppm (C_α); 80–100 ppm (C_β); ^{31}P NMR: 29–34 ppm) [7]. The IR spectra of complexes **2**–**6** revealed bands in the range 1587–1659 cm^{-1} that were assigned to the C=C stretching vibration. For comparison, in the IR spectra of alkenes C=C stretching vibrations usually appear in the range 1635–1690 cm^{-1} [13].

Complex **1** was found to react with excess of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ yielding the vinylidene complex *trans*-$[IrCl\{{=}C{=}C(SiMe_3)C{\equiv}CSiMe_3\}(PPh_3)_2]$ (**8**) (Scheme 3). This complex was isolated in 68% yield as a violet-brown powder that is stable on air in the solid state for about 1 h. The analogous reaction of **1** with only 0.5 equiv. of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ did not lead to the formation of a binuclear complex having a bridging bis(vinylidene) ligand μ-(=C=C($SiMe_3$)—C($SiMe_3$)=C=). The ^{13}C NMR spectrum of **8** gave clear evidence for its identity. The low-field shifted resonance for the vinylidene α-carbon atom was found as triplet at 261.5 ppm ($^2J(P,C)$ =



1 **2**—**7**

	R/R'
2	Ph/Me
3	Me/Me
4	Bn/Me
5	$SiMe_3$/Me
6	$SiEt_3$/Et
7*	^iPr/Me

* in solution

Scheme 2.