Unexpected migration of the indenyl ligand in the reaction of alkynyl(η^5-indenyl)iron complexes with phosphanes and phosphites from iron to the alkynyl group

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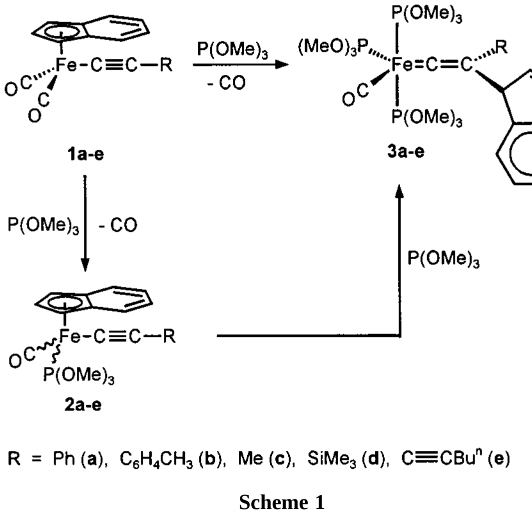
Received (in Cambridge, UK) 8th April 1999, Accepted 29th April 1999

Novel indenylvinylidene iron complexes are formed in the reaction of alkynyl(η^5-indenyl)iron complexes with phosphites and phosphanes in large excess by an intermolecular transfer of the indenyl ligand from iron to the C_β atom of the alkynyl ligand; mechanistic studies indicate that the reaction proceeds by a radical pathway.

Many associative substitution reactions of coordinatively saturated cyclopentadienyl and indenyl complexes have been documented.[1] These reactions have been interpreted as proceeding *via* an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage.[2] The conversion of η^5- to isolable η^3- or even η^1-cyclopentadienyl or indenyl complexes has also been observed.[3] The cleavage of the cyclopentadienyl ligand as $[C_5H_5]^-$ from $[(\eta^5\text{-Cp})(CO)(NO)Re–Me]$ or *mer*-$[(\eta^1\text{-Cp})(NO)(PMe_3)_3Re–Me]$ in the reaction with PMe_3 in large excess to give ionic *trans*-$[(NO)(PMe_3)_4Re–Me]^+[C_5H_5]^-$ has also been described.[4] Finally, the loss of the indenyl ligand formally as a cation and the formation of $[R_3P(Ind)]^+$ in the reaction of $[Cp(\eta^5\text{-Ind})(CO)_2Mo]^{2+}$ with PR_3 was recently proposed by Romão and coworkers.[5] We now report on (i) an unusual temperature-controlled product selectivity in the reaction of (alkynyl)(η^5-indenyl)iron complexes with phosphites and phosphanes, (ii) the novel transformation of (alkynyl)(η^5-indenyl)iron complexes into vinylidene complexes by reaction with PR_3, and (iii) the first evidence for the release of the indenyl ligand as a radical.

The alkynyl(dicarbonyl)(η^5-indenyl)iron complexes $[(\eta^5\text{-Ind})(CO)_2Fe–C{\equiv}CR]$ (R = Ph **1a**, C_6H_4Me-*p* **1b**, Me **1c**, $SiMe_3$ **1d** or $C{\equiv}CBu^n$ **1e**) react in refluxing Bu_2O with a slight excess of $P(OMe)_3$ within a few minutes by substitution of $P(OMe)_3$ for one CO ligand to form a racemic mixture of $[(\eta^5\text{-Ind})(CO)\{P(OMe)_3\}Fe–C{\equiv}CR]$ **2a–e**. However, when **1a–e** is heated in neat $P(OMe)_3$ for *ca*. 4 h at 70 °C, the complexes **2a–e** are formed in only minor amounts. The major products are the novel monocarbonyl-vinylidene complexes $[CO\{P(OMe_3\}_3\text{-}Fe{=}C{=}C(\text{inden-1-yl})R]$ **3a–e** (Scheme 1).† The complexes **3a–e** are derived from **1a–e** by substitution of $P(OMe)_3$ for one CO ligand, addition of two more molecules of $P(OMe)_3$ and an unusual transfer of the indenyl group from iron to the C_β atom of the alkynyl ligand. Such a migration is without precedence. The migration is highly selective. In the reaction of **1e** with $P(OMe)_3$, in addition to **2e**, only the vinylidene complex **3e** is observed. The alternative butatrienylidene complex that would have been formed by migration of the indenyl ligand to the C_δ atom of the butadiynyl ligand could not be detected.



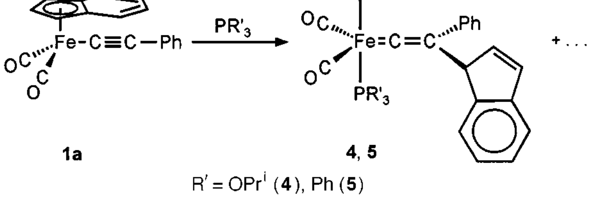
Scheme 1

The product ratio **2a–e**:**3a–e** is strongly temperature dependent. With increasing temperature it is shifted towards the substitution product **2**. On prolonged heating at 70 °C in neat $P(OMe)_3$ the alkynyl complexes **2a–d** are also transformed into the vinylidene complexes **3a–d**.

When the nucleophilicity of the alkynyl C_β atom is changed by variation of its substituent (R = Me, C_6H_4OMe-*p*, C_6H_4Me-*p*, Ph, C_6H_4Br-*p*, $SiMe_3$) the product distribution and the reaction rate are only slightly influenced. Therefore, a bimolecular mechanism *via* a nucleophilic attack of the alkynyl C_β atom at an indenyl ligand is unlikely. In contrast, the steric requirements of the P-donors considerably influence the reaction rate and the product distribution. For instance, **1a** reacts significantly more slowly with $P(OEt)_3$ than with $P(OMe)_3$. When the even bulkier $P(OPr^i)_3$ or PPh_3 are employed in the reaction with **1a** no monocarbonyl-vinylidene complex analogous to **3a–e** is formed but rather a dicarbonyl-vinylidene complex $[(CO)_2(PR_3)_3Fe{=}C{=}C(\text{inden-1-yl})Ph]$ (R = OPr^i **4** or Ph **5** in addition to the substitution product $[(\eta^5\text{-Ind})(CO)(PR_3)Fe–C{\equiv}CPh]$ (Scheme 2). The latter cannot be transformed into a vinylidene complex.

Labelling studies show that the Fe/C_β migration of the indenyl ligand proceeds by an intermolecular pathway. The reaction of a 1 : 1 mixture of undeuterated **1a** and $[(\eta^5\text{-}1,3\text{-}C_9H_5D_2)(CO)_2Fe–C{\equiv}C–C_6D_5]$ ([D$_7$]-**1a**) with $P(OMe)_3$ at 70 °C affords [D$_0$]-, [D$_2$]-, [D$_5$]- and [D$_7$]-**3a** in a ≈ 1 : 1 : 1 : 1 ratio as determined by mass spectrometry.

In the reaction of **1a** with PPh_3, complex **5** is formed independent of whether the reaction is carried out in toluene, EtOH or EtOH–H_2O (20 : 1). Therefore, the formation of $[C_7H_9]^+$ and $[(CO)_2(PPh_3)_2Fe–C{\equiv}CPh]^-$ or of $[C_7H_9]^-$ and $[(CO)_2(PPh_3)_2Fe–C{\equiv}CPh]^+$ as intermediates is unlikely. Since $[(CO)_2(PPh_3)_2Fe–C{\equiv}CPh]^-$ and $[C_7H_9]^-$ are rapidly trapped in a large excess of EtOH–H_2O as $[(CO)_2(PPh_3)_2Fe{=}C{=}C(H)Ph]$ and indene, respectively, complex **5** should not be formed.



Scheme 2

The most probable mechanism involves dissociation of the indenyl ligand as a radical and subsequent addition of $[C_7H_9]^{\cdot}$ to the alkynyl C_β atom of either $[(CO)(PR'_3)_3Fe{-}C{\equiv}CR]^{\cdot}$ or $[(CO)_2(PR'_3)_2Fe{-}C{\equiv}CR]^{\cdot}$. This mechanistic proposal is supported by two observations: (i) addition of the radical-scavenger galvinoxyl to the reaction mixture of **1a** and $P(OMe)_3$ efficiently inhibits the formation of **3a** but does not affect the formation of the substitution product **2a**; (ii) dimerization of the indenyl radical to give bisindenyl, $C_{14}H_{18}$, is preferentially observed when the addition of the indenyl radical to the alkynyl C_β atom is hindered by the sterically demanding mesityl (Mes) substituent. Then, only small amounts of the corresponding vinylidene complex, $[CO\{P(OMe)_3\}_3Fe{=}C{=}C(\text{inden-1-yl})Mes]$, are formed. In addition, small amounts of 1,4-bis(mesityl)butadiyne are obtained. The butadiyne is presumably formed by decomposition of the 17-electron intermediate $[CO\{P(OMe)_3\}_3Fe{-}C{\equiv}CMes]$.

The indenyl radical intermediates are very likely stabilized by addition to the phosphites or phosphanes which are present in the reaction mixture in a large excess. The reversible addition of radicals to PR_3 is well known.[6] The resulting phosphoranyl radical $[R_3P(Ind)]^{\cdot}$ would then act as a mediator. The assumption is supported by the following observation: when the *methyl*indenyl complex $[(\eta^5\text{-1-Me-Ind})(CO)_2Fe{-}C{\equiv}CPh]$ is treated with $P(OMe)_3$ in the presence of a mixture of $P(Ind)_3$ and $P(Ind)_2OMe$, both $[CO\{P(OMe)_3\}_3Fe{=}C{=}C(\text{1-Me-inden-1-yl})Ph]$ *and* $[CO\{P(OMe)_3\}_3Fe{=}C{=}C(\text{inden-1-yl})Ph]$ are formed in nearly equal amounts.

The results demonstrate a novel route to vinylidene complexes. Presumably, the transformation mode can also be extended to other complexes such as alkynyl(allyl) and alkynyl(fluorenyl) complexes. Based on previous results,[4,5] we initially assumed that the transformation most likely proceeds by an ionic pathway *via* either an indenyl anion or cation. However, all observations indicate a radical mechanism. Presumably, more organometallic reactions proceed by a radical mechanism than anticipated. There are some experimental hints that the proposed 17-electron intermediate is rather long-lived and can be intercepted also with other substrates. Recently, several other related 17-electron iron complexes $[(CO)_2(PR_3)_2FeX]$ (X = Br or I)[7] and $[\{P(CH_2CH_2PPh_2)_3\}FeC{\equiv}CR]$[8] have been isolated and structurally characterized.

Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Notes and references

† *Selected spectroscopic data*: IR (CH_2Cl_2): *ν*(CO): 1906 (**3a**), 1917 (**3b**), 1917 (**3c**), 1902 (**3d**), 1918 (**3e**), 1907, 1974 (**4**), 1896, 1962 cm^{-1} (**5**); ^{13}C NMR ($CDCl_3$, 0 °C): δ(Fe=C) 312.8 (q, *J* 42 Hz) (**3a**), 313.8 (q, *J* 42 Hz) (**3b**), 307.9 (q, *J* 42 Hz) (**3c**), 310.6 (q, *J* 41 Hz) (**3d**), 315.5 (q, *J* 41 Hz) (**3e**), 325.5 (t, *J* 63 Hz) (**4**), 325.2 (t, *J* 48 Hz) (**5**); ^{31}P NMR ($CDCl_3$): δ 177.54 (**3a**), 177.68 (**3b**), 178.93 (**3c**), 180.16 (**3d**), 175 (**3e**), 165.05 (**4**), 73.54 (**5**).

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Communication 9/02785H