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

## Helmut Fischer\* and Peter A. Scheck

Fakultät für Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany. E-mail: hfischer@dg6.chemie.uni-konstanz.de

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

Novel indenylvinylidene iron complexes are formed in the reaction of alkynyl( $\eta^{5}$ -indenyl)iron complexes with phosphites and phosphanes in large excess by an intermolecular transfer of the indenyl ligand from iron to the C<sub> $\beta$ </sub> 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.<sup>2</sup> The conversion of  $\eta^5$ - to isolable  $\eta^3$ - or even  $\eta^1$ -cyclopentadienyl or indenyl complexes has also been observed.<sup>3</sup> The cleavage of the cyclopentadienyl ligand as  $[C_5H_5]^-$  from  $[(\eta^5-Cp)(CO)(NO)Re-Me]$  or mer- $[(\eta^1-Cp)(NO)(PMe_3)_3Re-Me]$  in the reaction with PMe<sub>3</sub> in large excess to give ionic trans-[(NO)(PMe<sub>3</sub>)<sub>4</sub>Re–Me]<sup>+</sup>[C<sub>5</sub>H<sub>5</sub>]<sup>-</sup> has also been described.<sup>4</sup> Finally, the loss of the indenyl ligand formally as a cation and the formation of  $[R_3P(Ind)]^+$  in the reaction of  $[Cp(\eta^5-Ind)(CO)_2Mo]^{2+}$  with PR<sub>3</sub> 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<sup>5</sup>-indenyl)iron complexes with phosphites and phosphanes, (ii) the novel transformation of (alkynyl)(n5-indenyl)iron complexes into vinylidene complexes by reaction with PR<sub>3</sub>, and (iii) the first evidence for the release of the indenvl ligand as a radical.

The alkynyl(dicarbonyl)( $\eta^5$ -indenyl)iron complexes [( $\eta^5$ -Ind)(CO)<sub>2</sub>Fe–C≡CR] (R = Ph **1a**, C<sub>6</sub>H<sub>4</sub>Me-*p* **1b**, Me **1c**, SiMe<sub>3</sub> **1d** or C≡CBu<sup>n</sup> **1e**) react in refluxing Bu<sub>2</sub>O with a slight excess of P(OMe)<sub>3</sub> within a few minutes by substitution of P(OMe)<sub>3</sub> for one CO ligand to form a racemic mixture of [( $\eta^5$ -Ind)(CO){P(OMe)<sub>3</sub>}Fe–C≡CR] **2a–e**. However, when **1a–e** is heated in neat P(OMe)<sub>3</sub> 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<sub>3</sub>}-Fe=C=C(inden-1-yl)R] **3a–e** (Scheme 1).† The complexes **3a–e** 



 $R = Ph(a), C_6H_4CH_3(b), Me(c), SiMe_3(d), C \equiv CBu^n(e)$ 

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  $C_\beta$  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  $C_\delta$  atom of the butadiynyl ligand could not be detected.

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)<sub>3</sub> the alkynyl complexes 2a-d are also transformed into the vinylidene complexes 3a-d.

When the nucleophilicity of the alkynyl  $C_{\beta}$  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  $C_{\beta}$ 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)<sub>3</sub> than with P(OMe)<sub>3</sub>. When the even bulkier P(OPr<sup>i</sup>)<sub>3</sub> or PPh<sub>3</sub> are employed in the reaction with **1a** no monocarbonyl-vinylidene complex analogous to **3a**-**e** is formed but rather a dicarbonyl-vinylidene complex [(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub>Fe=C=C(inden-1-yl)Ph] (R = OPr<sup>i</sup> **4** or Ph **5** in addition to the substitution product [( $\eta^5$ -Ind)-(CO)(PR<sub>3</sub>)Fe-C=CPh] (Scheme 2). The latter cannot be transformed into a vinylidene complex.

Labelling studies show that the Fe/C<sub>β</sub> migration of the indenyl ligand proceeds by an intermolecular pathway. The reaction of a 1:1 mixture of undeuterated **1a** and  $[(\eta^{5}-1,3-C_9H_5D_2)(CO)_2Fe-C\equiv C-C_6D_5]$  ([D<sub>7</sub>]-**1a**) with P(OMe)<sub>3</sub> at 70 °C affords [D<sub>0</sub>]-, [D<sub>2</sub>]-, [D<sub>5</sub>]- and [D<sub>7</sub>]-**3a** in a  $\approx$  1:1:1:1 ratio as determined by mass spectrometry.

In the reaction of **1a** with PPh<sub>3</sub>, complex **5** is formed independent of whether the reaction is carried out in toluene, EtOH or EtOH–H<sub>2</sub>O (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<sub>2</sub>O as  $[(CO)_2(PPh_3)_2Fe=C=C(H)Ph]$ and indene, respectively, complex **5** should not be formed.





The most probable mechanism involves dissociation of the indenvl ligand as a radical and subsequent addition of  $[C_7H_9]$  to the alkynyl  $C_{\beta}$  atom of either [(CO)(PR'\_3)\_3Fe-C=CR] or [(CO)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>Fe-C=CR]. This mechanistic proposal is supported by two observations: (i) addition of the radical-scavenger galvinoxyl to the reaction mixture of 1a and P(OMe)<sub>2</sub> 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  $C_{\beta}$  atom is hindered by the sterically demanding mesityl (Mes) substituent. Then, only small amounts of the corresponding complex,  $[CO{P(OMe)_3}_3Fe=C=C(inden$ vinylidene 1-yl)Mes], are formed. In addition, small amounts of 1,4-bis-(mesityl)butadivne are obtained. The butadivne 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<sub>3</sub> is well known.<sup>6</sup> The resulting phosphoranyl radical [R<sub>3</sub>P(Ind)] would then act as a mediator. The assumption is supported by the following observation: when the *methyl* indenyl complex  $[(\eta^{5}-1-Me-Ind)(CO)_2Fe-C\equiv CPh]$  is treated with P(OMe)<sub>3</sub> in the presence of a mixture of P(Ind)<sub>3</sub> and P(Ind)<sub>2</sub>OMe, both [CO{P(OMe)\_3}\_3Fe=C=C(1-Me-inden-1-yl)Ph] *and* [CO{P(OMe)\_3}\_3Fe=C=C(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,<sup>4,5</sup> 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)<sup>7</sup> 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<sub>2</sub>Cl<sub>2</sub>): ν(CO): 1906 (**3a**), 1917 (**3b**), 1917 (**3c**), 1902 (**3d**), 1918 (**3e**), 1907, 1974 (**4**), 1896, 1962 cm<sup>-1</sup> (**5**); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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**); <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  177.54 (**3a**), 177.68 (**3b**), 178.93 (**3c**), 180.16 (**3d**), 175 (**3e**), 165.05 (**4**), 73.54 (**5**).

- See, for example: J. A. S. Howell and P. M. Burkinshaw, *Chem. Rev.*, 1983, **83**, 557; F. Basolo, *Inorg. Chim. Acta*, 1985, **100**, 33; J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307; F. Basolo, *Polyhedron*, 1990, **9**, 1503.
- 2 A. J. Hart-Davis and R. J. Mawby, J. Chem. Soc. A, 1969, 2403
- 3 See, for example:  $\eta^5 \rightarrow \eta^3$ : T. C. Forschner, A. R. Cutler and R. K. Kullnig, *Organometallics*, 1987, **6**, 889;  $\eta^5 \rightarrow \eta^1$ : H. Werner and A. Kühn, *Angew. Chem.*, 1979, **91**, 416; *Angew. Chem., Int. Ed. Engl.*, 1979, **91**, 447; C. P. Casey and W. D. Jones, *J. Am. Chem. Soc.*, 1980, **102**, 6154.
- 4 C. P. Casey, J. M. O'Connor and K. J. Haller, J. Am. Chem. Soc., 1985, 107, 1241.
- 5 C. A. Gamelas, E. Herdtweck, J. P. Lopes and C. C. Romão, *Organometallics*, 1999, **18**, 506.
- 6 See, for example: W. G. Bentrude, *Phosphorus Sulfur*, 1977, 3, 109; B. P. Roberts, *Adv. Free Radical Chem.*, 1980, 6, 225.
- 7 H. Kandler, C. Gauss, W. Bidell, S. Rosenberger, T. Bürgi, I. L. Eremenko, D. Veghini, O. Orama, P. Burger and H. Berke, *Chem. Eur. J.*, 1995, **1**, 541.
- 8 C. Bianchini, F. Laschi, D. Masi, F. M. Ottaviani, A. Pastor, M. Peruzzini, P. Zanello and F. Zanobini, J. Am. Chem. Soc., 1993, **115**, 2723.

Communication 9/02785H