Pergamon

Tetrahedron Letters, Vol. 37, No. 36, pp. 6543-6546, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01446-3

Transition Metal Complexes in Organic Synthesis, Part 32.[1]

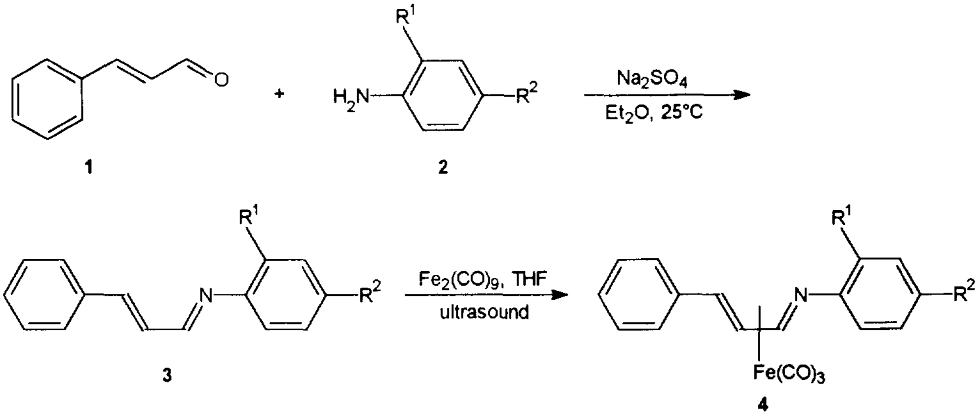
Fluxionality of (η^4-1-Aza-1,3-butadiene)tricarbonyliron Complexes

Hans-Joachim Knölker,[a]* *Helmut Goesmann*,[b] and *Peter Gonser*[a]

[a]Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, 76131 Karlsruhe, Germany
[b]Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstraße, 76128 Karlsruhe, Germany

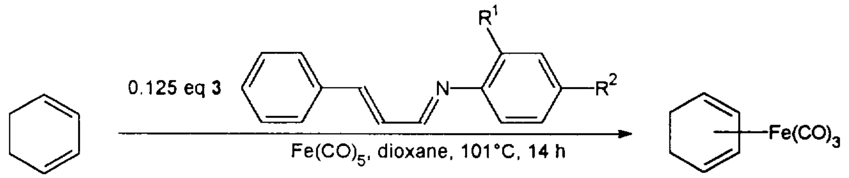
Abstract: The fluxionality of tricarbonyliron transfer reagents was investigated and the free enthalpy of activation for the rotation of the tricarbonyliron fragment of (η^4-1-*p*-anisyl-4-phenyl-1-aza-1,3-butadiene)tricarbonyliron **4b** was determined to 13.8 ± 0.5 kcal/mol.

Tricarbonyl(η^4-1,3-diene)iron complexes have found many useful applications in organic synthesis.[2] In order to achieve high yields in the complexation of labile diene systems tricarbonyliron transfer reagents have been developed.[3] Such reagents, which can deliver the tricarbonyliron fragment under mild reaction conditions onto diene systems, are the (η^4-benzylideneacetone)tricarbonyliron[4] synthesized by Lewis and Brookhart and the tricarbonylbis(η^2-*cis*-cyclooctene)iron[5] prepared by Grevels. Some time ago, we reported that (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes are highly efficient reagents for the transfer of the tricarbonyliron fragment.[6,7] The 1-aza-1,3-butadienes **3** and their tricarbonyliron complexes **4** are readily available by condensation of cinnamaldehyde **1** with the corresponding arylamine **2** followed by ultrasound-mediated complexation with the tricarbonyliron fragment (Scheme 1).[6,7,8]



Scheme 1

The advantage of these novel reagents is, that the 1-aza-1,3-butadienes **3** can be used in catalytic amounts on complexation of 1,3-dienes with either pentacarbonyliron or nonacarbonyldiiron (Scheme 2). This feature of the 1-aza-1,3-butadienes was utilized by us to develop the first asymmetric catalytic complexation of prochiral 1,3-dienes by the tricarbonyliron fragment.[9,10]



5

6, Yield

	no catalyst	0.7%
3a	$R^1 = R^2 = H$	41%
3b	$R^1 = H$; $R^2 = OMe$	50%
3c	$R^1 = OMe$; $R^2 = H$	83%

Scheme 2

Recently, we described for the first time the dynamic behaviour of the (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes with respect to migration of the metal fragment from one face of the organic ligand to the other.[11] In this paper, we report our investigation concerning the fluxionality of these complexes due to the rotation of the tricarbonyliron fragment. This process is sufficiently slow on the NMR time scale at temperatures below 260 K to allow the observation of three signals for the CO ligands in the ^{13}C NMR spectrum.

Table. Characteristic IR and ^{13}C NMR data of the (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes **4**.

	R^1	R^2	**3**, Yield [%]	**4**, Yield [%]	ν_{CO} [cm^{-1}] [a]	δ_{CO} [ppm] (T[K]) [b]
a	H	H	81	81	2055, 1988, 1977	206.1, 209.6, 212.8 (261)
b	H	OCH_3	81	88	2049, 1987, 1963	206.6, 209.8, 213.1 (237)
c	OCH_3	H	86	80	2058, 2000, 1970	206.5, 210.1, 213.8 (261)

[a] Wave numbers of the CO bands in the IR spectrum (KBr) at room temperature

[b] Chemical shifts of the carbonyl ligands in the ^{13}C NMR spectrum at low temperature; solvent: [D_8]toluene

Almost all of the (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes which were prepared by us during the development of these novel tricarbonyliron transfer reagents did show no signals for the CO ligands in their ^{13}C NMR spectra in $CDCl_3$ at room temperature. However, the IR spectra in KBr show the typical bands for the CO ligands at 1960-2060 cm^{-1} (Table). Generally, (η^4-1,3-carbadiene)tricarbonyliron complexes exhibit fluxionality by turnstile rotation of the tricarbonyliron fragment: the ^{13}C NMR spectrum at room temperature shows one singlet for the CO ligands at 210-212 ppm, while at low temperatures two peaks with an intensity ratio of 2 : 1 (symmetrical ligands) or three peaks of equal height (unsymmetrical ligands) are observed.[13] In the low temperature ^{13}C NMR spectra of **4a** and **4c** three sharp signals for the carbonyl ligands are already observed at 261 K, while for a similar spectrum of complex **4b** 237 K are required (Table). We concluded that the dynamic equilibrium for the rotation of the tricarbonyliron fragment in 1-aza-1,3-butadiene complexes must have a coalescence temperature slightly above room temperature and therefore, a significantly higher activation energy. This assumption was confirmed by dynamic ^{13}C NMR spectroscopy of **4b** (Figure 1). The stepwise increase of the temperature provides at 338 K a single signal for the three CO ligands at 209.9 ppm, which still at 363 K shows some line broadening. The free enthalpy of activation $\Delta G^{\#}$ was determined by using the formula $\Delta G^{\#} = R \cdot T_C\,[22.96 + \ln (T_C/\delta\nu)]$.[12] With the coalescence temperature $T_C = 313 \pm 10$ K and by taking the value $\delta\nu = 649$ Hz from the low temperature spectrum the free enthalpy of activation for complex **4b** in [D_8]toluene can be calculated: $\Delta G^{\#} = 13.8 \pm 0.5$ kcal/mol.

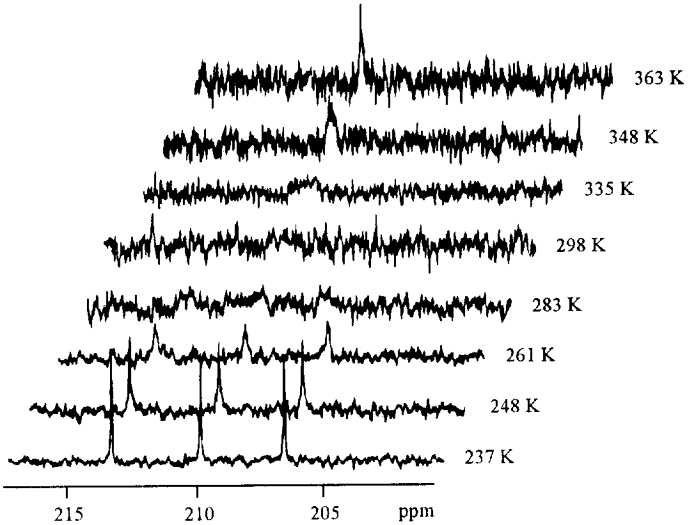


Figure 1. Dynamic ^{13}C NMR spectra of complex **4b** in the metal carbonyl region (100 MHz, [D_8]toluene).

From the low temperature ^{13}C NMR spectra of the complexes **4a** and **4c** it can be concluded that their coalescence temperature is about 20 K higher and therefore, the free enthalpy of activation for those complexes can be estimated: $\Delta G^{\#} \approx 14.8$ kcal/mol. While previous work on tricarbonyl(η^4-1-heterodiene)iron complexes gave similar results, Takats *et al.* found that the free enthalpy of activation for complex **6** in [D_6]DMSO/CS_2 was much lower: $\Delta G^{\#}_{298} = 8.8 \pm 0.5$ kcal/mol.[13]

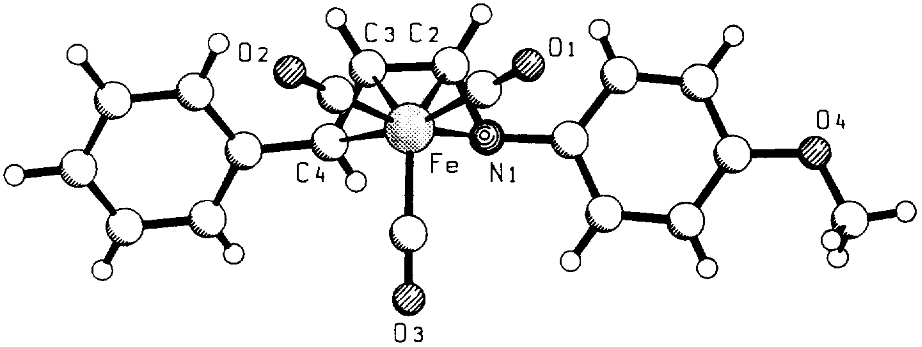


Figure 2. Molecular structure of complex **4b** in the crystal.
Selected bond lengths [Å]: Fe-N1 2.075(3), Fe-C2 2.074(4), Fe-C3 2.068(4), Fe-C4 2.167(4).

The X-ray crystal structure investigation of complex **4b** confirms the same preferred conformation of the tricarbonyliron fragment as observed for (η^4-1,3-carbadiene)tricarbonyliron complexes: one carbonyl ligand is arranged over each coordinated π-bond, representing the two basal CO ligands (Figure 2).[14,15]

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft (Gerhard-Hess Award) and the Fonds der Chemischen Industrie. We thank the BASF AG, Ludwigshafen, for a generous gift of pentacarbonyliron. We thank Dr. H. Röttele for the ^{13}C NMR spectra.

References and Notes

1. Part 31: H.-J. Knölker, H. Goesmann, C. Hofmann, *Synlett* **1996**, 734.
2. Reviews: A. J. Pearson, *Acc. Chem. Res* **1980**, *13*, 463. A. J. Pearson in *Comprehensive Organometallic Chemistry*; G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.; Pergamon Press: Oxford, **1982**; Vol. 8, Chap. 58. A. J. Pearson, *Metallo-organic Chemistry*; Wiley: Chichester, **1985**; Chap. 7 and 8. R. Grée, *Synthesis* **1989**, 341. H.-J. Knölker in *Organic Synthesis via Organometallics*; K. H. Dötz, R. W. Hoffmann, Eds.; Vieweg: Braunschweig, **1991**; p. 119. H.-J. Knölker, *Synlett* **1992**, 371. A. J. Pearson, *Iron Compounds in Organic Synthesis*; Academic Press: London, **1994**; Chap. 4 and 5. H.-J. Knölker in *Advances in Nitrogen Heterocycles*; C. J. Moody, Ed.; JAI Press: Greenwich (CT), **1995**; Vol. 1, p. 173.
3. For a compilation see: H.-J. Knölker in *Encyclopedia of Reagents for Organic Synthesis*; L. A. Paquette, Ed.; Wiley: Chichester, **1995**; Vol. 1, p. 333.
4. J. A. S. Howell, B. F. G. Johnson, P. L. Josty, J. Lewis, *J. Organomet. Chem.* **1972**, *39*, 329.
   M. Brookhart, G. O. Nelson, *J. Organomet. Chem.* **1979**, *164*, 193.
5. H. Fleckner, F.-W. Grevels, D. Hess, *J. Am. Chem. Soc.* **1984**, *106*, 2027.
6. H.-J. Knölker, P. Gonser, *Synlett* **1992**, 517.
7. H.-J. Knölker, P. Gonser, P. G. Jones, *Synlett* **1994**, 405.
8. For previous work on (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes, see: S. Otsuka, T. Yoshida, A. Nakamura, *Inorg. Chem.* **1967**, *6*, 20. A. M. Brodie, B. F. G. Johnson, P. L. Josty, J. Lewis, *J. Chem. Soc. Dalton Trans.* **1972**, 2031. T. N. Danks, S. E. Thomas, *J. Chem. Soc. Perkin Trans. 1* **1990**, 761.
9. H.-J. Knölker, H. Hermann, *Angew. Chem.* **1996**, *108*, 363; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 341.
10. H.-J. Knölker, P. Gonser, T. Koegler, *Tetrahedron Lett.* **1996**, *37*, 2405.
11. H.-J. Knölker, G. Baum, P. Gonser, *Tetrahedron Lett.* **1995**, *36*, 8191.
12. H. Günther, *NMR-Spektroskopie*, Thieme: Stuttgart, **1992**; p. 310.
13. Previous work on dynamic ^{13}C NMR spectra of $Fe(CO)_3$ complexes: L. Kruczinsky, J. Takats, *Inorg. Chem.* **1976**, *15*, 3140. D. Leibfritz, H. tom Dieck, *J. Organomet. Chem.* **1976**, *105*, 255; *et loc. cit.*
14. X-ray crystal structure determination of complex **4b**. Formula: $C_{19}H_{15}FeNO_4$; M = 377.17; crystal size: $0.54 \cdot 0.12 \cdot 0.12$ mm^3; monoclinic; space group: $P2_1/c$; a = 11.975(5), b = 15.735(8), c = 9.439(4) Å; β = 101.07(3)°; V = 1745.5(14) Å^3, Z = 4, ρ_{calcd} = 1.435 g/cm^3, T = 293(2) K, μ = 0.862 mm^{-1}; λ = 0.71069 Å; $2\theta_{max}$ = 56.3°; independent reflections: 4111; refinement method: full-matrix least squares on F^2; R_1 = 0.0583, wR_2 = 0.1376 [$I > 2\sigma(I)$]; maximal residual electron density: 0.467 e/Å^3. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59410.
15. X-ray crystal structure of **4a**, see: A. De Cian, R. Weiss, *J. Chem. Soc. Chem. Commun.* **1968**, 348. For the X-ray analysis of (η^4-1-*o*-anisyl-4-*p*-anisyl-1-aza-1,3-butadiene)tricarbonyliron, *cf.* [7]

(*Received in Germany* 20 *June* 1996; *accepted* 23 *July* 1996)