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Synthesis of σ-Heterocyclic Iron Complexes Based on [3+3] Cycloaddition to 1,3-Dipolar Reagents

Valery N. Kalinin,* Marina A. Yakovleva and Vladimir V. Derunov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085

Treatment of iron complex $(\eta^5\text{–}C_5H_5)Fe(CO)_2CH_2C{\equiv}CPh$ **1** with nitrogen-containing 1,3-dipolar reagents (nitrile oxides and azomethine ylide) yields six-membered σ-heterocyclic iron complexes, due to cycloaddition and subsequent 1,2-migration of the $(\eta^5\text{–}C_5H_5)_2Fe(CO)$ group.

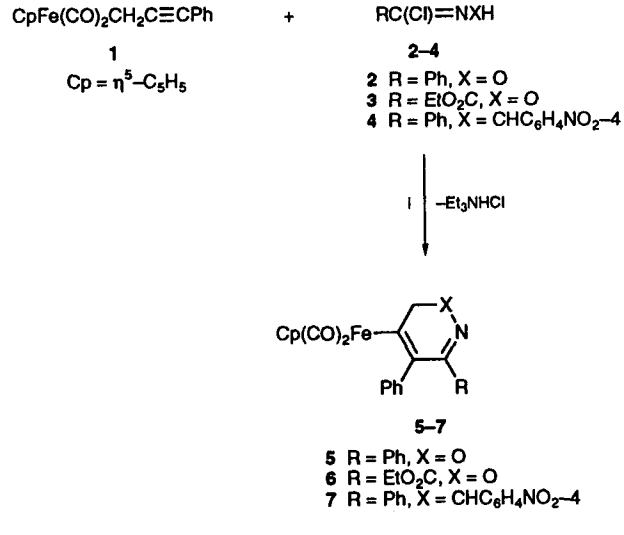
Cycloaddition reactions of transition metal σ-complexes with unsaturated ligands are known to provide useful methods for the synthesis of organometallic compounds with σ-carbo- and σ-heterocyclic ligands.[1–5]

It has been found previously that σ-propargyl iron complex $(\eta^5\text{–}C_5H_5)Fe(CO)_2CH_2C{\equiv}CPh$ **1** in reactions with 1,2-dipoles gives the products of [3 + 2] cycloaddition with subsequent 1,2-migration of the organometallic group.[1] The reactions of transition metal propargyl complexes with 1,3-dipoles were previously unknown.

We have carried out the reactions of **1** with nitrogen-containing 1,3-dipolar compounds generated *in situ*: benzonitrile oxide (from **2**), ethoxycarbonylnitrile oxide (from **3**) and benzonitrile(4-nitrobenzyl) ylide (from **4**). We have found that all these reactions proceed as [3 + 3] cycloadditions giving six-membered heterocycles, σ-bonded with the iron atom (Scheme 1).

One may suggest that migration of the $CpFe(CO)_2$ group proceeds on formation of the products and, apparently, π-allene intermediate **A** is formed and subsequently cyclizes into σ-oxazines **5** and **6** or σ-dihydropyridine **7** derivatives of iron (Scheme 2).

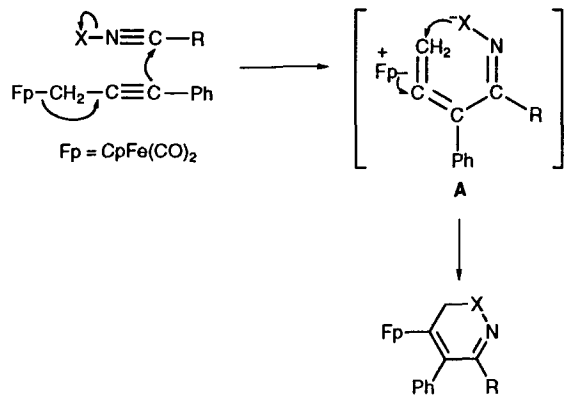
We failed to observe the formation of five-membered rings as possible isomeric products in these reactions; this would be characteristic of [3 + 2] interactions of 1,3-dipolar reagents with the triple bond in **1**, as is well-known for simple alkynes.[6] It is known that complex $CpFe(CO)_2C{\equiv}CPh$, in which migration of the $Cp(CO)_2Fe$ group is impossible, reacts with nitrile oxides to give isoxazole derivatives of iron.[7,8]



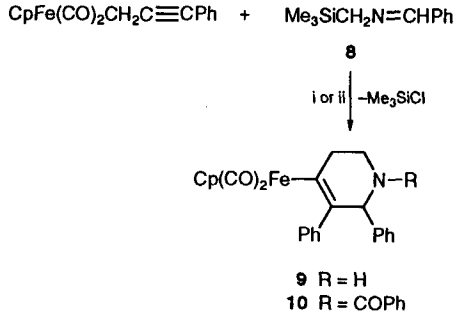
Scheme 1 *Reagents and conditions*: i, Et_3N, C_6H_6, 40–45 °C, 1 h.

We have also found that complex **1** reacts with 1,3-dipolar ylide reagents (generated *in situ* from *N*-[(trimethylsilyl)methyl]imine **8** under the action of HCl or PhCOCl) to give σ-tetrahydropyridine complexes of iron (Scheme 3).

Recently it has been shown[9] that this ylide reacts with simple alkynes to form five-membered *N*-substituted heterocycles.



Scheme 2



Scheme 3 *Reagents and conditions*: i, HCl/Et_2O, THF, 20 °C, 0.5 h; ii, PhCOCl, THF, 20 °C, 0.5 h.

The ability of the σ-propargylic ligand to play the role of a three-carbon component in reactions with 1,3-dipolar compounds depends on the high tendency of the organometallic group to migration and π-complexation. The reactions investigated are the first examples of [3 + 3] cycloaddition for transition-metal propargyl complexes.

All the new complexes gave satisfactory analytical and spectroscopic data.†

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† **5:** yield 15%; m.p. 114–115 °C; MS: *m/z* 306 $[M-CO, Ph]^+$; IR ν/cm^{-1}: 2050, 2005 (C≡O); ^1H NMR (200 MHz) (C_6D_6): δ 2.15 (s, 2 H, CH_2), 4.04 (s, 5 H, C_5H_5), 7.2–7.6 (m, 10 H, 2 Ph).

6: yield 21%; m.p. 110–111 °C; MS: *m/z* 306 $[M-CO, CO_2Et]^+$; IR ν/cm^{-1}: 2053, 2005 (C≡O), 1740 (C=O); ^1H NMR (200 MHz) (C_6D_6): δ 0.85 (t, 3 H, Me, *J* 7.3 Hz), 3.95 (q, 2 H, CH_2, *J* 7.3 Hz), 2.90 (s, 2 H, CH_2), 4.04 (s, 5 H, C_5H_5), 7.10–7.40 (m, 5 H, Ph).

7: yield 27%; m.p. 117–118 °C; MS: *m/z* 410 $[M-C_6H_4NO_2]^+$; IR ν/cm^{-1}: 2050, 2010 (C≡O), ^1H NMR (200 MHz) (C_6D_6): δ 3.99 (m, 1 H, CH), 4.13–4.21 (m, 2 H, CH_2), 4.04 (s, 5 H, C_5H_5), 6.8–7.9 (m, 14 H, 3Ph).

9: yield 45%; m.p. 102–103 °C; MS: *m/z* 410 $[M-H]^+$; IR ν/cm^{-1}: 2050, 2005 (C≡O), ^1H NMR (200 MHz) (C_6D_6): δ 1.44 (m, 2 H, $CH_2C=C$), 2.84 (s, 1 H, CH), 3.08 (m, 2 H, CH_2N), 4.02 (s, 5 H, C_5H_5), 5.65 (s, sh, 1 H, NH), 7.19–7.50 (m, 10–2 Ph).

10: yield 50%; m.p. 122–123 °C; MS: *m/z* 410 $[M-C(O)Ph]^+$; IR ν/cm^{-1}: 2060, 2010 (C≡O), 1730 (C=O); ^1H NMR (200 MHz) (C_6D_6): δ 1.87 (m, 2 H, $CH_2C=C$), 2.69 (s, 1 H, CH), 2.89 (m, 2 H, CH_2N), 4.04 (s, 5 H, C_5H_5), 7.2–7.8 (m, 15 H, 3 Ph).