cis-Stereochemistry on Nucleophilic Addition to a Cationic η^2-Alkyne Complex, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(Ph\text{–}C{\equiv}C\text{–}Ph)]BF_4$

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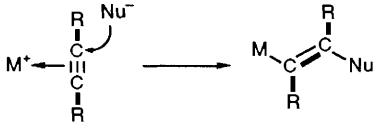
Treatment of a coordinatively saturated cationic η^2-alkyne iron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(Ph\text{–}C{\equiv}C\text{-}Ph)]BF_4$ with various nucleophiles (Nu: *O*-, *S*- and *N*-nucleophiles) does not afford a *trans*-alkenyl complex but alkenic products with *cis*-structure, *i.e.* a *cis*-alkenyl complex, *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}C(Ph){=}C(Ph)\text{–}Nu$ and/or a metallacycle, $(\eta^5\text{-}C_5H_5)(OC)Fe\text{–}[C(Ph){=}C(Ph)\text{–}C(=O)\text{–}Nu]$ or $(\eta^5C_5H_5)(OC)Fe\text{–}[C(Ph){=}C(Ph)\text{–}Cl{=}O)\text{–}Nu]$.

It has been generally accepted that nucleophilic addition to an η^2-alkyne metal complex with an 18e configuration results in the formation of a *trans*-alkenyl complex *via* an attack from the side opposite to the metal centre with respect to the alkyne ligand (*exo*-side attack),[1,2] [eqn. (1)]. As a typical example,



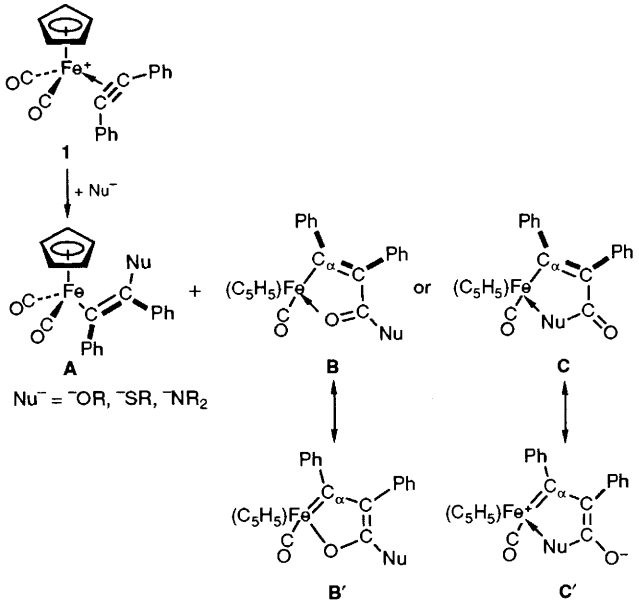
(1)

Reger and coworkers[3] have established the *trans*-stereochemistry for a wide variety of nucleophilic addition reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)(\eta^2\text{-}R'\text{–}C{\equiv}C\text{–}R'')]^+$-type complexes. This *trans-addition rule* has been widely applied to systems where the stereochemistry of the product cannot be determined by means of spectroscopic methods. On the other hand, in our previous study on the chemical properties of cationic *dinuclear* μ-alkynyl iron complexes, $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}C\text{–}R)]BF_4$, formation of the alkenic products has been interpreted in terms of an apparent *cis*-addition mechanism.[4] These results prompted us to examine if the *cis*-addition would be observed for a *mononuclear* system $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}Ph\text{–}C{\equiv}C\text{–}Ph)]BF_4$ **1**, which was related to Reger's system.

As a result, reaction of **1** with nucleophiles (Nu^-) gives two types of alkenic products with *cis*-structure depending on the nature of the nucleophile. (Scheme 1). One of the alkenic products is a *cis*-alkenyl complex, *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}C(Ph){=}C(Ph)\text{–}Nu$ **A**, and the other is a metallacyclic complex, $(\eta^5\text{-}C_5H_5)(OC)Fe\text{–}C(Ph){=}C(Ph)\text{–}C(=O)\text{–}Nu$ **B** or $(\eta^5\text{-}C_5H_5)(OC)Fe\text{–}C(Ph)\text{–}C(Ph)\text{–}C){=}O)\text{–}Nu$ **C**. While $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$ is occasionally formed as a byproduct, a *trans*-alkenyl complex has never been isolated from the reaction mixtures. The structures of **B** and **C** are readily assigned on the basis of a single ν(C≡O) absorption and a ^{13}C NMR signal of the α carbon observed in lower field ($\delta > 220$) owing to the contribution of the carbene structures (**B′** and **C′**) as well as the presence or absence of ν(C=O) absorption. On the other hand, since the stereochemistry of **A** cannot be determined by spectroscopic methods alone, the structures of representative products were confirmed by X-ray crystallography. The results of individual cases are illustrated below.

Reaction of **1** with an oxygen nucleophile, NaOMe, in CH_2Cl_2 gave a metallacycle **2B** (Nu = OMe) in 31% yield (NMR) along with $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$ as reported earlier.[4b]

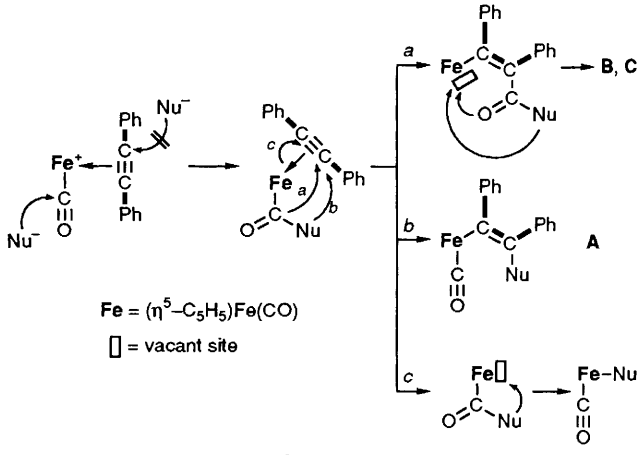
Treatment of **1** with a sulfur nucleophile, $NaSBu^t$, in CH_2Cl_2 resulted in the formation of a mixture of products, from which a pair of alkenyl complexes **3A** and **3A′** (Nu =



Scheme 1

S-Bu^t) and a metallacycle **3C** (Nu = S-Bu^t)†‡ were isolated in low yields after chromatographic separation on alumina. However, just after the reaction **3A** was formed as a sole alkenyl complex [**3A**:55, **3A′**:0, **3C**:21, {(η^5-C_5H_5)-Fe(CO)$_2$}$_2$:14%] as revealed by ^{1}H NMR analysis of the reaction mixture, and **3A′** was formed with the consumption of **3A** during work up. Since the *cis*-structure of **3A** was confirmed by X-ray crystallography (Fig. 1),§ **3A′** was assigned to the *trans*-isomer. Thus, the reaction with $^-$S-Bu^t affords the *cis*-isomer **3A** as a kinetic product.

The distribution of products arising from reaction of **1** with amines depends on substituents on the amine as shown in Table 1.[5] In general, primary amines tend to give metallacycles **B**, whereas secondary amines afford *cis*-alkenyl complexes **A**. The results may be interpreted in terms of a steric as well as an electronic nature of amine, *i.e.* sterically congested, basic amines tend to produce **B**. However, the fact that a primary amine with a bulky substituent such as Bu^{t}NH$_2$ affords the *cis*-alkenyl complex **5A** and that a compact secondary amine such as pyrrolidine affords the metallacycle **8B** suggest that the steric effect appears to be dominant over the electronic one.



Scheme 2

Table 1 Distribution of products obtained by the reaction of **1** with amines[a]

Amine	Yield (%) A	Yield (%) B
Pr^{n}NH$_2$	0[b]	64 (**4B**)
Pr^{i}NH$_2$	0[b]	51 (**5B**)
Bu^{t}NH$_2$	53 (**6A**)	0[b]
Et$_2$NH	61 (**7A**)	0[b]
Pr$^i_2$NH	58 (**8A**)	0[b]
c-C_4H_8NH[c]	0[b]	39 (**9B**)
c-C_5H_{10}NH[d]	71 (**10A**)	0[b]

[a] Reactions were carried out in CH_2Cl_2 on a 0.2 mmol scale. Yields were determined by ^{1}H NMR by using dimethyl terephthalate as an internal standard. [b] Not detected by ^{1}H NMR and IR spectroscopy. [c] Pyrrolidine. [d] Piperidine.

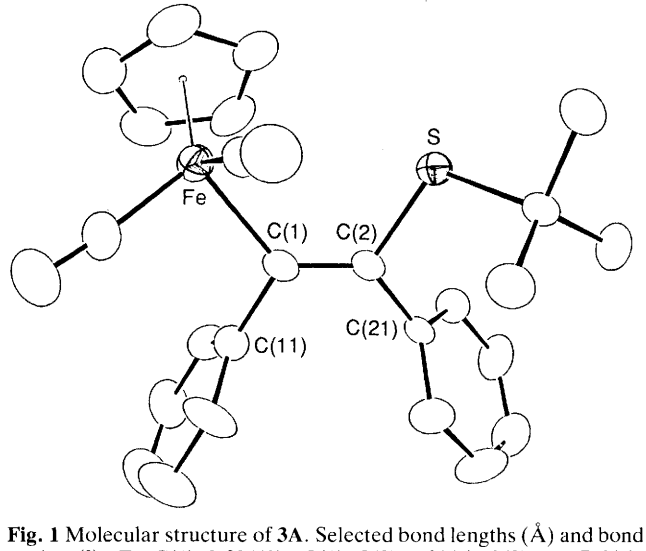
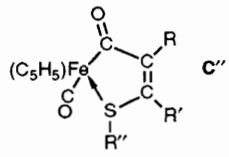


Fig. 1 Molecular structure of **3A**. Selected bond lengths (Å) and bond angles (°): Fe–C(1) 2.024(8), C(1)–C(2) 1.30(1) C(2)–S 1.790(7), C(1)–C(11) 1.53(1), C(2)–C(21) 1.51(1); Fe–C(1)–C(2) 127.5(6), C(11)–C(1)–C(2) 120.2(7), C(1)–C(2)–S 121.7(6), C(1)–C(2)–C(21) 123.3(7).

† *Selected spectral data*. Data for Ph parts are omitted. **3A**: ^{1}H NMR ($CDCl_3$) δ 1.09 (9H, s, Bu^t), 4.86 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 31.4 (q, *J* 127 Hz, CH_3), 46.6 (q, *J* 3.9 Hz, S–C), 86.9 (d, *J* 180 Hz C_5H_5, 143.5 (s, C=C), 155.6 (s, C=C), 215.8 (s, C≡O); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 2008, 1962. **3A′**: ^{1}H NMR ($CDCl_3$) δ 0.93 (9H, s, Bu^t), 4.45 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 31.4 (q, *J* 127 Hz, CH_3), 46.5 (s, S–C), 86.1 (d, *J* 181 Hz, C_5H_5), 136.5 (s, C=C), 155.6 (s, C=C), 214.8 (s, C=O); IR (CH_2Cl_2) ν(C=O)/cm^{-1} 2010, 1963. **3C**: ^{1}H NMR ($CDCl_3$) δ 1.50 (9H, s, Bu^t), 4.43 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 29.8 (q, *J* 127 Hz, CH_3), 52.0 (s, S–C), 84.4 (d, *J* 178 Hz, C_5H_5), 145.8 (s, Cβ), 196.0 (s, C=O), 219.8 (s, C≡O), 228.6 (t, *J* 3 Hz, Cα); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 1941, 1655. **4B**: ^{1}H NMR ($CDCl_3$) δ 0.82 (3H, t, *J* 7.3 Hz, CH_3), 1.32–1.43 (2H, m, CH_2), 2.98–3.05 (1H, m, CH_2), 3.16–3.26 (1H, m, CH_2), 4.35 (5H, s, C_5H_5), 5.64 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 11.5 (q, *J* 127 Hz, CH_3), 21.9 (t, *J* 128 Hz, CH_2), 41.7 (t, *J* 136 Hz, CH_2), 82.4 (d, *J* 176 Hz, C_5H_5), 134.0 (s, Cβ), 179.1 (s, C=O), 219.7 (s, C≡O), 223.8 (s, Cα); IR (CH_2Cl_2) ν(C≡O) 1909 cm^{-1}. **5B**: ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, d, *J* 6.8 Hz, CH_3), 1.08 (3H, d, *J* 6.4 Hz, CH_3), 3.92 (1H, sept, *J* 6.4 Hz, CH), 4.35 (5H, s, C_5H_5), 5.47 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 22.8 (q, *J* 126 Hz, CH_3), 42.0 (d, *J* 141 Hz, CH), 82.3 (d, *J* 176 Hz, C_5H_5), 134.0 (s, Cβ), 178.3 (s, C=O), 219.7 (s, C≡O), 223.9 (s, Cα); IR (CH_2Cl_2) ν(C≡O) 1921 cm^{-1}. **6A**: ^{1}H NMR ($CDCl_3$) δ 1.08 (9H, s, Bu^t), 4.87 (5H, s, C_5H_5); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 1998, 1952. **7A**: ^{1}H NMR ($CDCl_3$) δ 1.18 (6H, t, *J* 7.1 Hz, CH_3), 2.63 (4H, q, *J* 7.1 Hz, CH_2), 4.51 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 12.8 (q, *J* 126 Hz, CH_3), 47.7 (t, *J* 133 Hz, CH_2), 86.5 (d, *J* 178 Hz, C_5H_5),147.7 (s, C=C), 151.9 (s, C=C), 219.0 (s, C≡O); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 1993, 1946. **8A**: ^{1}H NMR ($CDCl_3$) δ 1.15–1.20 (12H, br, CH_3), 3.35–3.64 (2H, m, CH), 4.44 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 19.7–20.3 (br, CH_3), 48.5 (d, *J* 135 Hz, CH), 87.0 (d, *J* 180 Hz, C_5H_5), 145.2 (s, C=C), 156.3 (s, C=C), 217.2 (s, C≡O); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 1993, 1946. **9B**: ^{1}H NMR ($CDCl_3$) δ 1.4–2.0 (4H, m, CH_2 × 2), 2.6 (1H, m, NCH_2), 2.8 (1H, m, NCH_2), 3.4 (2H, m, NCH_2), 4.33 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 23.4 (t, *J* 132 Hz, CH_2), 26.4 (t, *J* 133 Hz, CH_2), 47.7 (t, *J* 143 Hz, NCH_2), 49.0 (t, *J* 144 Hz, NCH_2), 82.7 (d, *J* 177 Hz, C_5H_5), 135.2 (s, Cβ), 177.4 (s, C=O), 219.6 (s, C≡O), 227.7 (s, Cα); IR (CH_2Cl_2) ν(C≡O) 1919 cm^{-1}. **10A**: ^{1}H NMR ($CDCl_3$) δ 1.36 (2H, br, CH_2), 1.67 (4H, br, 2 × CH_2), 2.53 (4H, br, N(CH_2)$_2$), 4.77 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 25.1 (t, *J* 128 Hz, CH_2), 25.7 (t, *J* 129 Hz, 2 × CH_2), 53.2 (t, *J* 133 Hz, N(CH_2)$_2$), 85.8 (d, *J* 180 Hz, C_5H_5), 140.4 (s, C=C), 155.7 (s, C=C), 216.3 (s, C≡O); IR (CH_2Cl_2) ν(C≡O)/cm^{-1} 2004, 1955.

‡ The assignment of **3C** is based on the Cα signal coupled with the *ortho*-protons of the phenyl group (δ 228.6, t, $^3J_{CH}$ 3 Hz), whereas another isomeric metallacyclic structure C″ has been also reported. See, for example, K. Kergoat, M. M. Kubicki, L. C. G. de Lima, H. Scordia, J. E. Guerchais and P. L.'Haridon, *J. Organomet. Chem.*, 1989, **367**, 143; M. T. Ashby, J. H. Enemark, and D. L. Lichtenberger, *Inorg. Chem.*, 1988, **27**, 191.

§ *Crystal data*: **3A** $C_{25}H_{24}O_2SFe$, *M* = 444.38, monoclinic space group $P2_1/a$, *a* = 9.1931(37), *b* = 33.2006(82), *c* = 8.2722(29) Å, β = 115.117(82)°; *V* = 2286(3) Å^3; *Z* = 4; D_c = 1.29 g cm^{-3}; λ = 0.71069 Å; μ = 7.62; $2 < 2\theta < 55°$; $R(R_w)$ = 0.0724(0.0571) for 2792 data with $F > 3\sigma(F)$. The structure was solved by using the TEXSAN structure solving system. The non-hydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were confirmed by using isotropic thermal parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.



Reactions with carbanions and hydride were also examined. However, an adduct like **A–C** was not obtained. Instead, the action of Bu^nLi resulted in the formation of $(\eta^5\text{-}C_5H_4\text{-}Bu^n)Fe(CO)_2C(Ph)=C(Ph)\text{–}H$. While we also examined the reaction of the $\eta^5\text{-}C_5Me_5$ analogue of **1** with Bu^nLi in order to prevent the addition to the $\eta^5\text{-}C_5H_5$ ring, the Ph–C≡C–Ph ligand was replaced by the nucleophile to give $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(Bu^n)$. In addition, all reactions with borohydrides such as $NaBH_4$, $NaBH_3CN$ and $LiHBEt_3$ afforded $\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2$ as the sole organometallic product.

The formation of alkenic products with *cis*-structure (**A–C**) may be interpreted by Scheme 2. Nucleophiles do not attack the η^2-alkyne ligand but a terminal CO ligand to give an acyl intermediate. Then, migration of the whole acyl group to the η^2-alkyne ligand may produce an acyl-substituted *cis*-alkenyl intermediate with a 16e configuration. (path *a*) Successive coordination of either of the acyl oxygen atom or the Nu part to the Fe centre finally affords the metallacyclic adduct (**B** or **C**), respectively. On the other hand, migration of the Nu part to the η^2-alkyne ligand leads to the formation of the *cis*-alkenyl product **A**, (path *b*). In the case of the reaction with Bu^nLi and borohydrides the Ph–C≡C–Ph ligand dissociates to generate the coordinatively unsaturated acyl intermediate, which is finally converted to $(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}Nu$ (Path *c*).¶ Anyway, the initial reaction site of nucleophiles of the present reactions contrasts with that of Reger's system where the η^2-alkyne ligand is attacked from the *exo*-side.[6] A preliminary EHMO calculation on $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}H\text{–}C{\equiv}C\text{–}H)]^+$ and $[(\eta^5\text{-}C_5H_5Fe(CO)(PH_3)(\eta^2\text{-}H\text{–}C{\equiv}C\text{–}H)]^+$ has revealed that in both cases the CO carbon atoms are positively charged and the η^2-H–C≡C–H carbon atoms are slightly negatively charged and that on introduction of PH_3 no significant change in charge on the CO and H–C≡C–H carbon atoms has been observed. These results suggest that even for the PH_3 derivative the CO ligand is the preferable reaction site toward a nucleophile. A plausible explanation for the regiochemistry observed for Reger's system may be either the steric effect of the coexisting bulky PR_3 ligand which hinders a nucleophile from approaching the CO ligand from its lateral side or the unsymmetric electronic structure which should facilitate slippage of the side-bound alkyne ligand.[7]

In conclusion, the present work has revealed that, on nucleophilic addition to an η^2-alkyne metal complex having an η^1-bound π-acceptor ancillary ligand such as CO, a *cis*-alkenyl complex may arise from an initial attack at the π-acceptor ligand followed by migration from the inside.

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¶ $(\eta^5\text{-}C_5Me_5)(CO)_2$ Fe–H readily decomposes to give $\{(\eta^5\text{-}C_5Me_5)(CO)_2Fe\}_2$ during work up.

References

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4 (*a*) M. Akita, S. Oyama, M. Terada and Y. Moro-oka, *Organometallics*, 1990, **9**, 816; (*b*) M. Akita, S. Oyama, M. Terada and Y. Moro-oka, *Organometallics*, 1991, **10**, 1561; (*c*) M. Akita, M. Terada and Y. Moro-oka, *Organometallics*, 1991, **10**, 2961.
5 The molecular structure of **8a** and **9b** has been confirmed by X-ray crystallography. M. Akita and Y. Moro-oka, to be published.
6 Reaction at the $\eta^5\text{-}C_5H_5$ ligand is also observed, see references cited in ref. 3.
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