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Michael addition of *N*-bonded enolato ligands to acrylonitrile in iron and ruthenium complexes†

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Treatment of the *N*-bonded enolatoiron(II) complex [M(H)(NCCHCO$_2$R)(L)$_2$] [1a, M = Fe, R = Me, L = depe {1,2-bis(diethylphosphino)ethane}; 1b, M = Fe, R = Et, L = depe; 2, M = Ru, L = dppe] with acrylonitrile results in mono-Michael addition to give [M(H)-{NCC(C$_2$H$_4$CN)CO$_2$R}(L)$_2$], which is found to be an active intermediate for the catalytic double-Michael reaction of cyanoacetate with acrylonitrile.

Transition-metal enolates have attracted considerable attention as key compounds in chemo-, regio- and stereospecific C–C bond forming reactions under neutral and mild conditions.[1] We previously reported the isolation of zwitterionic *N*-bonded enolate complexes of ruthenium[2] and rhenium[3] as active intermediates in catalytic Michael and Knöevenagel reactions. In these catalyses enhanced nucleophilicity of the enolato moiety by the zwitterionic structure was considered to be responsible for the driving force of the chemoselective C–C bond formations. Here we report the isolation of the mono-Michael adducts of the enolato-iron and -ruthenium complexes to acrylonitrile as active intermediates for the Michael reaction. The role of these adducts in the catalytic double-Michael reaction of cyanoacetate with acrylonitrile is also described.

The enolatoiron(II) complexes [Fe(H)(NCCHCO$_2$R)-(depe)$_2$]† (**1a**, R = Me; **1b**, R = Et) were newly prepared by the oxidative addition of cyanoacetate to a dinitrogen complex of iron(0) [Fe(N$_2$)(depe)$_2$][4] in 81 and 90% yields, respectively [eqn. (1)].

$$[Fe(N_2)(depe)_2] \xrightarrow{+\ NCCH_2CO_2R} [Fe(H)(NCCHCO_2R)(depe)_2] \quad (1)$$

1a R = Me
b R = Et

The molecular structure of **1b**[5] revealed that the structure of the enolato ligand is similar to those in other isolated enolato-ruthenium(II)[2] and -rhenium(I)[3] complexes, showing its delocalised zwitterionic character as suggested by the planarity of the O(1)–C(3)–C(2)–C(1) linkage [dihedral angle = 177.4(5)°] and linear structure of Fe(1)–N(1)–C(1)–C(2) [bond angles Fe–N(1)–C(1) = 173.3(4)°, N(1)–C(1)–C(2) = 178.6(5)°].

The ^{1}H and ^{31}P{^{1}H} NMR spectra of **1a** and **1b** indicate the presence of two isomers due to (*E*)- and (*Z*)-enolato ligands as observed for *N*-bonded ruthenium[2] and rhenium[3] enolates. The major : minor ratio for **1a** and **1b** at 23 °C was estimated as 4 : 1 and 3 : 1, respectively.

Treatment of **1b** with an equimolar amount of acrylonitrile in benzene in the absence of ethyl cyanoacetate at room temperature resulted in mono-Michael addition to the enolato ligand giving *trans*-[Fe(H){NCC(C$_2$H$_4$CN)CO$_2$Et}(depe)$_2$] (**3**) in 44% yield (Scheme 1).[6] The ^{1}H and ^{31}P{^{1}H} NMR spectra of **3** indicate the presence of two isomers (major : minor = 3 : 1 at 24 °C), probably due to (*E*)- and (*Z*)-isomerism of the enolato ligand. The ^{31}P{^{1}H} NMR spectrum of the major species shows two singlets at δ 84.3(s) and 89.4(s) and the ^{1}H NMR spectrum shows two quintets at δ − 25.70 and −25.61, suggesting that the hydrido and enolato ligands are *trans* to each other and all phosphorus atoms located in an equatorial plane. Methylene protons of the cyanoethyl group in **3** were observed as two multiplets at δ 2.4 (m, 2 H) and 2.5 (m, 2 H), as confirmed by COSY and homo-decoupling experiments.

We also carried out the reaction of the analogous enolato-ruthenium complex *trans*-[Ru(H)(NCCHCO$_2$Et)(dppe)$_2$][2a] (**2**) with acrylonitrile giving *trans*-[Ru(H){NCC(C$_2$H$_4$CN)-CO$_2$Et}(dppe)$_2$] (**4**) in quantitative yield.[7] The NMR spectra of **4** also show the presence of two isomers in 1 : 1 ratio, where the cyanoethyl group appears as a couple of A$_2$B$_2$ patterns at δ 1.84 (t, 2 H, J = 6 Hz) and 2.43 (t, 2 H, J = 6 Hz), and δ 2.28 (t, 2 H, J = 6 Hz) and 2.50 (t, 2 H, J = 6 Hz) in the same intensities.

The formation of these adducts **3** and **4** was further confirmed by the following chemical reactions. Acidolysis of **3** and **4** by excess dry HCl released the mono-Michael product NCCH(C$_2$H$_4$CN)CO$_2$Et in 48% and quantitative yields, respectively [eqn. (2)].

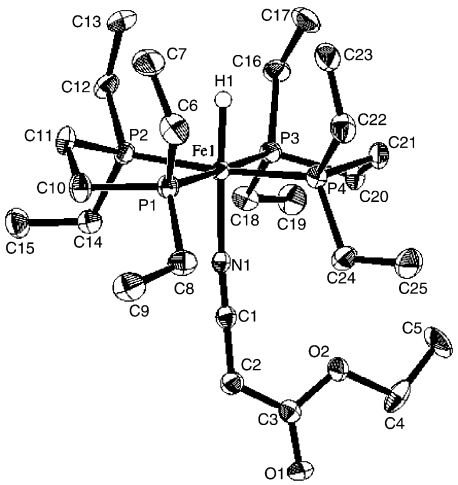
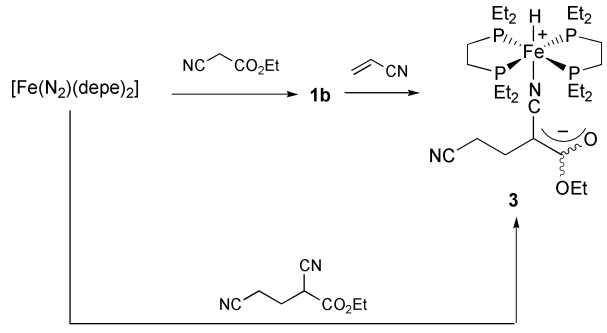


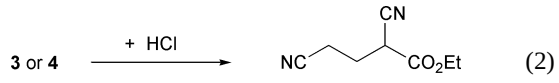
Fig. 1 Molecular structure of [Fe(H)(NCCHCO$_2$Et)(depe)$_2$] (**1b**). All hydrogen atoms except hydride and incorporated solvents are omitted for clarity. Ellipsoids represent 50% probability.



Scheme 1

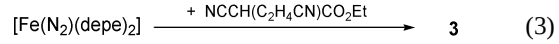
† Electronic supplementary information (ESI) available: physical and spectroscopic data for **1a** and **1b**. See http://www.rsc.org/suppdata/cc/b0/b004099l/

DOI: 10.1039/b004099l

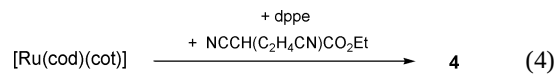


(2)

Reactions of $NCCH(C_2H_4CN)CO_2Et$[8] with $[Fe(N_2)(depe)_2]$ and with [Ru(cod)(cot)]/dppe also gave **3** and **4** in 61 and 62% yields, respectively [eqns. (3) and (4)].



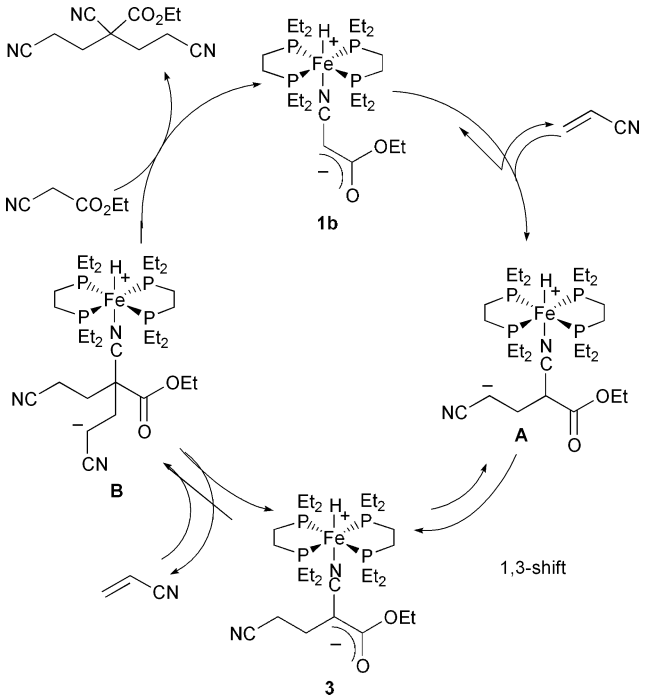
(3)



(4)

It is interesting to note that treatment of **3** (or **4**) with excess of either acrylonitrile or ethyl cyanoacetate resulted in no reaction, even at 50 °C, whilst the **3** (or **4**) catalysed double-Michael reaction of ethyl cyanoacetate with acrylonitrile exclusively gave ethyl 2,2-bis(cyanoethyl)cyanoacetate. Both enolate complexes **1b** and the mono-Michael adduct **3** (1.0 mol%) smoothly catalysed this double-Michael addition at room temperature for 36 h in 88 and 79% yields, respectively.[9] Similarly, complexes **2** and **4** also catalysed this reaction in 88 and 75% yields, respectively, under the same conditions.

By taking into account these facts, the possible reaction mechanism for the double-Michael reaction is illustrated in Scheme 2.



Scheme 2

The *N*-bonded enolate complex **1b** is nucleophilic enough to react with acrylonitrile to give **A**. The intermediate **A** rapidly converts to **3** by 1,3-proton migration. This process is probably driven by the high acidity of the methine proton in **A** and thermodynamic stability of the resulting oxo-π-allyl structure in **3**. This system exclusively affords the double-Michael product regardless of the amount of Michael acceptor and no trace of signals due to the mono-Michael product were detected by NMR. Thus, the direct formation of **1b** from **3** is negligible. Whereas compound **3** catalyses the double-Michael reaction, it remained unreacted with acrylonitrile or ethyl cyanoacetate. This fact suggests that the protonolysis of intermediate **B** took place by ethyl cyanoacetate to reproduce **1b**. When the isotopic labeled $FeD(NCCDCO_2Et)(depe)_2$ (**1b**-d_2) (45 atom% D for Fe–D) was employed in this reaction, the deuteride ligand in **1b**-d_2 remained intact during the catalytic Michael reaction of ethyl cyanoacetate with acrylonitrile (41 atom% D for Fe–D after TON = 3). This is good evidence for this double-Michael product being released from the catalyst, not by reductive elimination, but by protonation.

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Notes and references

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5 *Crystal data* for **1b**·Et_2O·H_2O: $C_{29}H_{67}FeNO_4P_4$ monoclinic, *C*2/*c* (No. 15), *a* = 32.31(2), *b* = 13.63(1), *c* = 17.54(1) Å, β = 111.68(4)°, *V* = 7179(8) Å^3, *Z* = 8, *T* = −160.0 °C, D_{calc} = 1.246 g cm^{-3}, Total reflections = 6421, Unique reflection = 6302, F_{000} = 2928.00, μ = 6.30 cm^{-1}, $R(R_w)$ = 0.054 (0.098). Goodness of Fit Indicator = 1.03. The hydride in **1b** was found in the differential Fourier map and was refined isotropically. CCDC 182/1729. See http://www.rsc.org/suppdata/cc/b0/b004099l/ for crystallographic files in .cif format.

6 *Spectroscopic data* for **3**: major isomer: ^{1}H NMR (300.4 MHz, C_6D_6): δ −25.70 (qnt, *J* = 46.5 Hz, 1 H, Fe-*H*), 0.75 (br, 12 H, PCH_2CH_3), 0.98 (sext, *J* = 7.2 Hz, 4 H, PCH_2CH_3), 1.00 (sext, *J* = 7.2 Hz, 4 H, PCH_2CH_3), 1.08 (br, 12 H, PCH_2CH_3), 1.27 (t, *J* = 7.5 Hz, 3 H, OCH_2CH_3), 1.59 (sext, *J* = 7.7 Hz, 4 H, PCH_2CH_3), 1.61 (sext, *J* = 8.1 Hz, 4 H, PCH_2CH_3), 2.06 (sext, *J* = 8.1 Hz, 2 H, PC_2H_4P), 2.09 (sext, *J* = 7.7 Hz, 2 H, PC_2H_4P), 2.4 (m, 2 H, C_2H_4CN), 2.5 (m, 2 H, C_2H_4CN), 4.39 (q, *J* = 6.9 Hz, 2 H, OCH_2CH_3); ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 89.2; Minor isomer: ^{1}H NMR (300.4 MHz, C_6D_6); δ −25.61 (qnt, *J* = 46.8 Hz, 1 H, Fe-*H*), 4.26 (q, *J* = 6.3 Hz, 2 H, OCH_2CH_3); ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 89.4; IR (KBr, ν/cm^{-1}): 2162 (νN≡C), 1831 (νFe–H), 1608 (νC=O); Anal. Calcd for $C_{28}H_{58}FeN_2O_2P_4$: C, 53.00; H, 9.21; N, 4.41%. Found: 53.75; H, 9.58; N, 5.56%.

7 *Spectroscopic data* for **4**: compound **4** is insoluble in most of organic solvents such as methanol or dmso. However, the initial stage of the reaction in an NMR tube afforded the following NMR spectra: isomer A; ^{1}H NMR (300.4 MHz, C_6D_6): δ −16.44 (qnt, *J* = 19.6 Hz, 1 H, Ru-*H*), 1.44 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 1.84 (t, *J* = 6 Hz, 2 H, C_2H_4CN), 1.9–2.1 (br, 4 H, PC_2H_4P), 2.43 (t, *J* = 6 Hz, 2 H, C_2H_4CN), 2.5 (br, 2 H, PC_2H_4P), 2.8 (br, 2 H, C_2H_4CN), 4.58 (q, *J* = 6 Hz, 2 H, OCH_2CH_3), 6.8 (m, 12 H, *Ph*), 7.0 (m, 12 H, *Ph*), 7.1 (m, 8 H, *Ph*), 7.4 (m, 8 H, *Ph*); ^{31}P{^{1}H} (121.6 MHz, C_6D_6): δ 58.9 or 62.3 (s); isomer B: ^{1}H NMR (300.4 MHz, C_6D_6): δ −16.29 (qnt, *J* = 18.3 Hz, 1 H, Ru-*H*), 1.46 (t, *J* = 6 Hz, 3 H, OCH_2CH_3), 2.28 (t, 2 H, *J* = 6 Hz, C_2H_4CN), 2.50 (t, 2 H, *J* = 6 Hz, C_2H_4CN), 4.6 (q, *J* = 6 Hz, 2 H, OCH_2CH_3); ^{31}P{^{1}H} (121.6 MHz, C_6D_6): δ 62.3 or 58.9 (s); IR (KBr, ν/cm^{-1}): 2165 (νN≡C), 1933 (νRu–H), 1621 (νC=O).

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9 *Conditions*: [ethyl cyanoacetate] = 0.81 M, [acrylonitrile] = 1.6 M, [catalyst] = 0.0081 M, solvent = thf (2.0 cm^3), temp. = r.t., time = 36 h.