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C–C coupling and C–H activation occurring in reactions of $FeRu(CO)_6({}^iPr\text{-}Pyca)$ (${}^iPr\text{-}Pyca = C_5H_4N\text{-}2\text{-}CH{=}N\text{-}{}^iPr$) with activated alkynes $RC{\equiv}CR'$ ($R = R' = C(O)OMe$; $R = H$, $R' = C(O)Me$)

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Abstract

Reaction of $FeRu(CO)_6({}^iPr\text{-}Pyca)$ (**5**) with the alkynes $RC{\equiv}CC(O)OMe$ ($R = C(O)OMe$ (**a**); $R = H$ (**b**)) leads to the formation of $FeRu(CO)_5({}^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}MeOC(O)C{=}C(R){-}C(O))$ ($R = C(O)OMe$ (**6a**); $R = H$ (**6b**)). In the case of the monosubstituted alkyne $HC{\equiv}CC(O)OMe$ (**b**) the C–C coupling reaction between the alkyne and the carbonyl ligand proved to be highly regioselective. However, in contrast to literature reports, the C–C coupling exclusively takes place at the unsubstituted alkyne C atom, which indicates that substituent effects are dominant. An X-ray single crystal structure of complex **6a** has been determined. Red crystals of **6a** are monoclinic, space group $P2_1/n$, $Z = 4$, with unit cell dimensions $a = 9.277(2)$, $b = 20.112(4)$, $c = 15.964(2)$ Å and $\beta = 99.267(15)°$. The structure refinement converged to $R = 0.040$ for 4123 observed reflections. Thermal conversion of the complexes **6a, b** leads to the formation of $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}RC{=}CHR')$ ($R = R' = C(O)OMe$ (**7a**); $R = H$, $R' = C(O)OMe$ (**7b**); $R = C(O)OMe$, $R' = H$ (**7b′**)) in which, as a result of H migration of the isopropyl H atom from the ${}^iPr$-Pyca ligand to the alkyne, a μ,η^2-vinyl fragment is present which is σ-bonded to Ru and η^2-bonded to Fe. The former imine C atom is σ-bonded to the Fe centre. The conversion of **6b** leads to an unseparable mixture of the complexes **7b** and **7b′** suggesting that during the H migration reaction the alkyne C atoms may change their positions and are both capable of abstracting a proton from the ${}^iPr$-Pyca ligand. Given the fact that the formation of **7b** is strongly favoured over the formation of **7b′** substituent effects appear to be important in determining the product distribution of the H migration reaction.

Introduction**

In the past two decades the preparation and reactivity of complexes containing α-diimine ligands has been studied extensively [1–10], and in particular compounds $M_2(CO)_6(L)$ ($M = Fe_2$, FeRu, Ru_2; L = R-DAB, R-Pyca), containing the 6e bridging σ-N, μ_2-N′, η^2-C=N′ bonded α-diimine ligand, proved to be excellent starting compounds for a large number of interesting reactions with small molecules owing in many cases to the activation of the η_2-bonded imine moiety by the bimetallic core [1, 4–6, 8]. For the preparation of $Fe_2(CO)_6(L)$ (L = R-DAB, R-pyca) [4–6] and $Ru_2(CO)_6(L)$ (L = R-DAB, R-Pyca) [4, 6] several synthetic routes were known, as well as a synthetic route for the preparation of $FeRu(CO)_6$(R-DAB) [3], whereas a synthetic pathway for the preparation of complexes $FeRu(CO)_6$(R-Pyca) has only very recently become available [11].

In order to explain the observed reactivity of $FeRu(CO)_6({}^iPr\text{-}DAB)$ towards DMADC an intermediate (**X1**) has been proposed containing a μ_2-N,μ_2-N′-coordinated ${}^iPr$-N-CH=CH-N-${}^iPr$ ligand [9] (Scheme 1). Due to the presence of the aromatic ring this intermediate cannot be formed starting from $FeRu(CO)_6({}^iPr\text{-}Pyca)$. Moreover $FeRu(CO)_6({}^iPr\text{-}DAB)$ reacted with MP to yield products containing a DAB ligand in a 8e donating σ-N,σ-N′,η^2-C=N,η^2-C=N′ coordination mode [9], which would not be possible for a ${}^iPr$-Pyca ligand.

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**Abbreviations: R-DAB = 1,4-diaza-1,3-butadiene, R–N=CHCH=N–R; R-Pyca = pyridine-2-carbaldiimine, C_5H_4N-2-CH=N–R; DMADC = $MeOC(O)C{\equiv}CC(O)OMe$; MP = $HC{\equiv}CC(O)OMe$; AIB = ${}^iPr$-N=CHCH(N^{i}Pr)C(R)=C(R); R = C(O)OMe.

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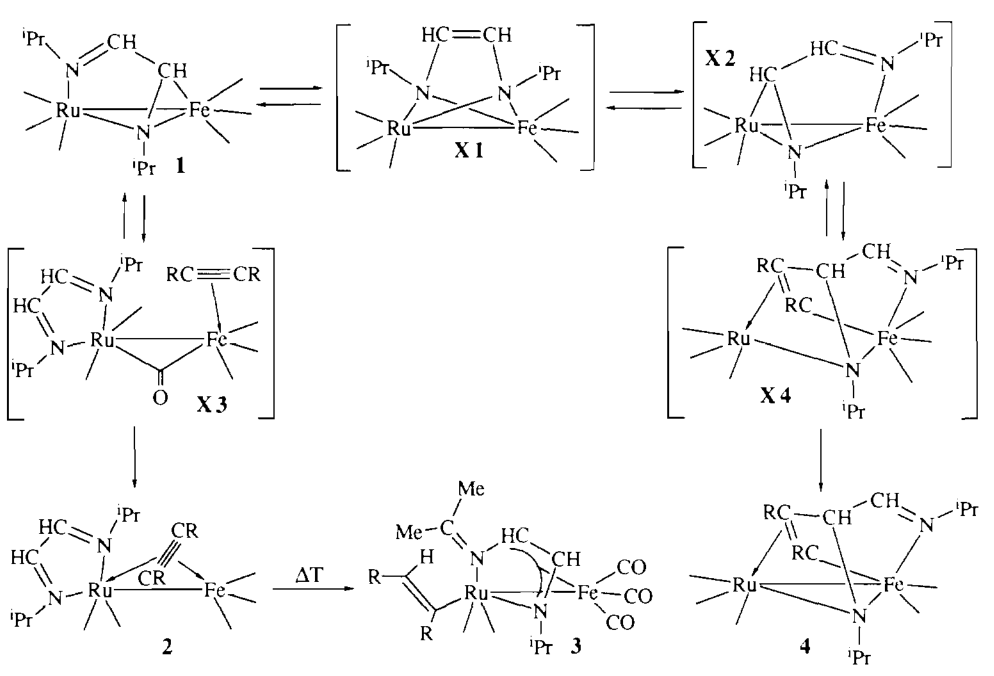


Scheme 1. Proposed mechanism for the reactions of FeRu(CO)$_6$(^{i}Pr-DAB) (1) with DMADC (taken from ref. 9).

For these reasons we were prompted to investigate the reactions of FeRu(CO)$_6$(^{i}Pr-Pyca) with DMADC and MP and compare the results with those found for FeRu(CO)$_6$(^{i}Pr-DAB) [9]. In this article we present the results of the reactivity of FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) towards the alkynes DMADC and MP, in relation to the results reported for FeRu(CO)$_6$(^{i}Pr-DAB) [9].

Experimental

Materials and apparatus

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-100 and AMX-300 spectrometers. IR spectra (ν(CO); 2200–1600 cm^{-1}) were measured on a Perkin-Elmer 283 spectrometer. Mass spectra were obtained on a Varian MAT 711 double focussing mass spectrometer with a combined EI/FI/FD ion source and coupled to a spectro system MAT 100 data acquisition unit [12]. Elemental analyses were carried out by the section elemental analyses of the Institute of Applied Chemistry TNO, Zeist, The Netherlands. All preparations were carried out under an atmosphere of purified nitrogen, using carefully dried solvents. Column chromatography was performed using silica gel (Kieselgel 60, Merck, 70–230 Mesh ASTM, dried and activated before use) as the stationary phase. Dimethyl acetylene dicarboxylate and methyl propionate were obtained from Aldrich and used as received. FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) was prepared according literature procedures [11].

*Synthesis of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-C(R)=C(R)−C(O)) (R=C(O)OMe (**6a**)) by reaction of FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) with DMADC*

FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) (250 mg, 0.53 mmol) was dissolved in 75 ml hexane and 150 mg DMADC (1.06 mmol) was added. The mixture was stirred at room temperature until IR spectroscopy indicated that the conversion was completed (about 22 h). The precipitated product FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-(R)C=C(R)-C(O)) (R=C(O)OMe (**6a**)) was filtered off, washed with hexane and extracted from the filter with CH$_2$Cl$_2$. Evaporation to dryness afforded **6a** in 80–90% yield. Crystallization from hexane/THF resulted in red crystals that were suitable for an X-ray single crystal structure determination.

*Synthesis of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-C(R)=C(H)−C(O)) (R=C(O)OMe (**6b**)) by reaction of FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) with MP*

FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) (470 mg, 1.0 mmol) was dissolved in 100 ml hexane and 3 equiv. of MP (0.25 g) were added. The mixture was stirred at 35 °C until IR spectroscopy indicated that complex **5** had disappeared (about 30 h). The precipitated product was filtered off and extracted from the filter with CH$_2$Cl$_2$. The extract was concentrated to 5 ml and purified by column chromatography. Elution with ligroin/CH$_2$Cl$_2$ (1/1) afforded a yellow–brown fraction containing a small amount of an unidentified product. Elution with CH$_2$Cl$_2$ afforded a red–purple fraction that was evaporated to dryness and yielded FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-

η^1,η^3-C(R)=C(H)−C(O)) (R=C(O)OMe (**6b**)) in about 50% yield.

Thermal conversion of $FeRu(CO)_5)(^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}(R)C{=}C(R){-}C(O))$ (R=C(O)OMe) (6a) to $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}RC{=}CHR')$ (R=R'=C(O)OMe) (7a)

$FeRu(CO)_5(^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}(R)C{=}C(R){-}C(O))$ (R = C(O)OMe (**6a**)) (250 mg, 0.43 mmol) was dissolved in 40 ml toluene and stirred at 100 °C until IR spectroscopy indicated that the absorptions of complex **6a** were replaced by those of complex **7a** (about 90 min). During this reaction the color changed from purple to brown. Subsequently the reaction mixture was evaporated to dryness, dissolved in 5 ml CH_2Cl_2 and purified by column chromatography. Elution with ligroin/CH_2Cl_2 (1/1) afforded a small yellow–brown fraction containing a small amount of unidentified product. Elution with CH_2Cl_2 gave a brown fraction which after evaporation yielded $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2(\mu,\eta^2\text{-}RC{=}CHR')$ (R=R'=C(O)OMe (**7a**)) in about 50% yield. Further elution with CH_2Cl_2 yielded in some cases a small red fraction of unreacted **6a**.

Thermal conversion of $FeRu(CO)_5(^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}CR{=}CH{-}CO)$ (R=C(O)OMe) (6b) to a mixture of $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}HC{=}C(H)(COOMe))$ (7b) and $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}C(COOMe){=}CH_2)$ (7b')

$FeRu(CO)_5(^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}CR{=}CH{-}CO)$ (R= C(O)OMe (**6b**)) (250 mg, 0.45 mmol) was dissolved in 40 ml toluene and stirred at 110 °C until IR spectroscopy showed that all absorptions of **6b** were replaced by those of the product(s) (about 30 min). During the reaction the color of the reaction mixture changed from purple to brown. After evaporating the reaction mixture to dryness the residue was dissolved in 5 ml CH_2Cl_2 and purified by column chromatography. Elution with hexane/CH_2Cl_2 (1/1) gave a small unidentified yellow fraction. Elution with CH_2Cl_2 yielded two fractions. The first brown fraction contained a mixture of the two isomeric complexes $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}HC{=}C(H)(COOMe))$ (**7b**) and $FeRu(CO)_5(C_5H_4N\text{-}2\text{-}CHN{=}C(Me)_2)(\mu,\eta^2\text{-}(COOMe)\text{-}C{=}CH_2)$ (**7b'**). The small second red fraction contained a very small amount of unreacted **6b**. The combined yield of **7b** and **7b'** was about 50% (based on the amount of **6b** consumed).

Crystal structure determination of $FeRu(CO)_5(^iPr\text{-}Pyca)(\mu,\eta^1,\eta^3\text{-}(R)C{=}C(R){-}C(O))$ (R=C(O)OMe) (6a)

A red, block-shaped crystal suitable for X-ray structure determination was glued to the tip of a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Crystal data and details of the structure determination are given in Table 1.

Lattice parameters were refined by least-squares fitting of the SET4 setting angles of 25 reflections with $10.9 < 2\theta < 16.3°$. The unit cell parameters were checked for the presence of higher lattice symmetry [13]. Data were corrected for Lp and for a small linear decay (6%) of the intensities of the reference reflections during 134 h of X-ray exposure time; no absorption correction was applied. The space group $P2_1/n$ was established from observed systematic absences: $h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$. The structure was solved by automatic Patterson methods followed by tangent expansion [14] and subsequent difference Fourier syntheses. At this stage of the refinement ($R=0.067$) a difference Fourier showed various peaks (≈ 1.9 e Å^{-3}) located around $x=0.283$, $y=0.346$ and $z=0.130$. No discrete solvent model could be fitted in this density. The BYPASS procedure [15] was used to take the electron density in this hole into account in the re-

TABLE 1. Crystallographic data for $FeRu(CO)_5(^iPr\text{-}Pyca)(DMADC{-}CO)$ (**6a**)

Crystal data	
Formula	$FeRuC_{21}H_{18}N_2O_{10}\cdot C_4H_8O$
Molecular weight	687.4
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å)	9.277(2)
b (Å)	20.112(4)
c (Å)	15.964(2)
β (°)	97.267(15)
V (Å^3)	2939.7(9)
D_{calc} (g/cm^3)	1.553
Z	4
$F(000)$	1392
μ (cm^{-1})	10.4
Crystal size (mm)	0.1×0.2×0.4
Data collection	
Temperature (K)	295
Radiation	Mo Kα, Zr-filtered (0.71073 Å)
$\theta_{min}/\theta_{max}$ (°)	1.0, 27.5
Scan type	$\omega/2\theta$
$\Delta\omega$ (°)	$0.89+0.35\tan(\theta)$
Aperture: horizontal, vertical (mm)	3.00, 6.00
Reference reflections	$\bar{2}\,2\,5$; $3\,2\,1$; $\bar{1}\,6\,2$
Data set	h 0:12; k −20:20; l −26:0
Total data	9767
Unique data	6742 ($R_{int}=0.035$)
Observed data ($I>2.5\sigma(I)$)	4123
Refinement	
Refined parameters	327
R, R_w, S	0.040, 0.029, 1.59
Weighting scheme	$1/\sigma^2(F)$
Absorption correction	no
$(\Delta/\sigma)_{av}$ in final cycle	0.010
Max./min. residual density (e Å^{-3})	0.37, −0.51

finement. An electron count of 40.8 was found in a volume of 151 Å^3, which is indicative of the presence of one THF molecule in the asymmetric unit. The volume occupied by a THF molecule in the liquid phase amounts to 135 Å^3.

In the final cycles of full-matrix least-squares refinement, using SHELX76 [16], 327 parameters were refined, including an overall scale factor, positional and anisotropic thermal parameters for all non-H atoms. H atoms were included in the refinement on calculated positions riding on their bonded atoms (C–H = 0.98 Å) with separate overall isotropic thermal parameters for the H atoms in the methyl and isopropyl groups (0.129(6) Å^2) and the other H atoms (0.068(6) Å^2).

Scattering factors were taken from Cromer and Mann [17]; anomalous-dispersion corrections for all atoms from Cromer and Liberman [18]. Geometric calculations were performed with the EUCLID package [19].

Results and discussion

Formation of complexes 6a, b and 7a, b

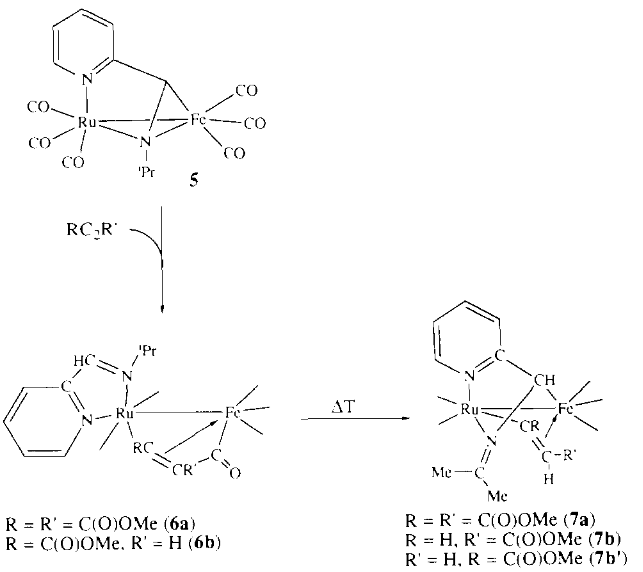
Reaction of FeRu(CO)$_6$(^{i}Pr-Pyca) (**5**) with the alkynes RC≡CC(O)OMe (R = C(O)OMe (**a**); R = H (**b**)) gave formation of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-MeOC(O)C=C(R)–C(O)) (R = C(O)OMe (**6a**); R = H (**6b**)). Thermal conversion of the complexes **6a**, **b** afforded FeRu(CO)$_5$(C$_5$H$_4$N-2-CHN=C(Me)$_2$)(μ,η^2-RC=CHR') (R = R' = C(O)OMe (**7a**); R = H, R' = C(O)OMe (**7b**); R = C(O)OMe, R' = H (**7b'**)).

The observed reactions and the structures of the new complexes are schematically presented in Scheme 2. In the following we will first discuss the spectroscopic and structural data of the relevant complexes and subsequently deal with aspects of their formation and their properties.

Molecular structure of 6a

A view of the molecular structure of **6a** is shown in Fig. 1 while in Tables 2, 3 and 4 the fractional coordinates, the bond distances and bond angles of the non-hydrogen atoms of **6a** are listed, respectively.

The molecular structure of **6a** possesses a Fe(CO)$_3$ fragment which is bonded to a Ru(CO)$_2$ fragment via a single Fe–Ru bond (Fe–Ru = 2.7733(10) Å). The ^{i}Pr-Pyca ligand is σ-N,σ-N' coordinated to the Ru centre with a C=N distance of 1.280(5) Å for the imine bond and 1.350(5) Å for the C=N bond within the pyridine ring; these values are comparable to those reported for Fe$_2$Ru(CO)$_{10}$(^{i}Pr-Pyca) [11] in which the ^{i}Pr-Pyca ligand is also σ-N,σ-N' coordinated to the metal centre (values of 1.271(4) and 1.354(4) Å, respectively, were found for Fe$_2$Ru(CO)$_{10}$(^{i}Pr-Pyca)) [11].



Scheme 2. Observed reaction sequence for the preparation of complexes **6a**, **b** and **7a**, **b**.

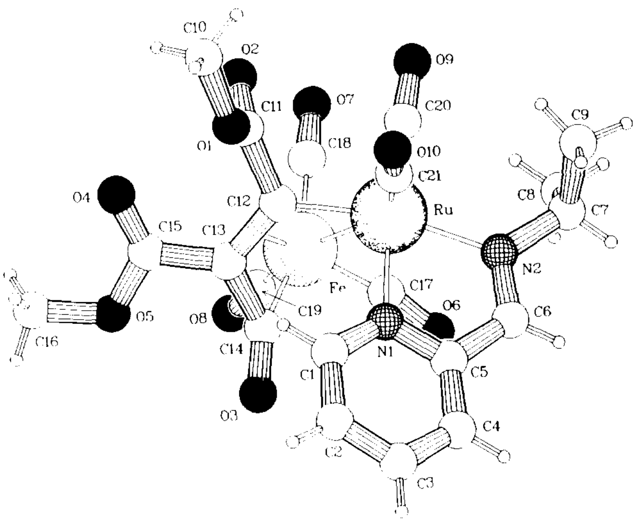


Fig. 1. Pluto drawing of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-(R)C=C(R)–C(O)) (R = C(O)OMe) (**6a**).

The molecule is bridged by a μ-η^1,η^3-(R)C=C(R)–C(O) fragment resulting from coupling of the DMADC molecule with a carbonyl ligand. In addition to the analogous Fe$_2$ complex Fe$_2$(μ-η^1,η^3-MeOC(O)C=CH–C(O))(CO)$_5$(^{i}Pr-Pyca) [20] there are several other complexes known containing a bridging μ-η^1,η^3-(R)C=C(R)–C(O) fragment [21–27] or the related μ-η^1,η^3-(R)C=C(R)–CR$_2$ moiety [28]. Some discussion has been going on in the literature about the best way to describe the bonding between a μ-η^1,η^3-(R)C=C(R)–C(O) bonded fragment and a bimetallic core for which three structures have been proposed (Fig. 2).

TABLE 2. Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-(R)C=C(R)–C(O)) (R=C(O)OMe) (**6a**) with e.s.d.s in parentheses

	x	y	z	U_{eq} (Å^2)^a
Ru	0.79364(4)	0.05495(2)	0.23675(2)	0.0375(1)
Fe	0.51795(7)	0.11180(3)	0.20405(4)	0.0448(2)
O1	0.9146(4)	0.20854(16)	0.3346(2)	0.0761(16)
O2	0.7940(4)	0.24015(15)	0.2085(2)	0.0761(14)
O3	0.4433(3)	0.05925(15)	0.36551(17)	0.0605(11)
O4	0.6304(4)	0.26390(15)	0.3598(2)	0.0925(16)
O5	0.4504(3)	0.20737(14)	0.40307(19)	0.0669(14)
O6	0.4756(4)	−0.02781(17)	0.1618(2)	0.0899(16)
O7	0.5525(4)	0.1871(2)	0.0490(2)	0.1054(19)
O8	0.2063(4)	0.1397(2)	0.1714(3)	0.1080(19)
O9	0.8693(4)	0.12454(14)	0.08280(18)	0.0701(14)
O10	1.1027(4)	0.0721(2)	0.3246(2)	0.0986(18)
N1	0.7558(4)	−0.00343(15)	0.34251(18)	0.0412(11)
N2	0.8065(4)	−0.04463(16)	0.19289(19)	0.0506(14)
C1	0.7503(5)	0.0168(2)	0.4214(2)	0.0502(16)
C2	0.7317(6)	−0.0262(2)	0.4855(3)	0.0614(18)
C3	0.7191(6)	−0.0926(2)	0.4702(3)	0.0683(19)
C4	0.7291(5)	−0.1148(2)	0.3901(3)	0.0626(18)
C5	0.7487(5)	−0.06958(19)	0.3279(2)	0.0479(16)
C6	0.7760(5)	−0.0895(2)	0.2441(3)	0.0559(18)
C7	0.8500(7)	−0.0691(2)	0.1115(3)	0.075(2)
C8	0.7403(6)	−0.0461(3)	0.0369(3)	0.104(3)
C9	1.0058(6)	−0.0464(3)	0.1072(3)	0.094(3)
C10	1.0158(7)	0.2624(3)	0.3335(5)	0.124(3)
C11	0.8066(5)	0.2038(2)	0.2678(3)	0.0510(19)
C12	0.7175(5)	0.14288(18)	0.2776(2)	0.0402(14)
C13	0.6041(4)	0.14932(18)	0.3259(2)	0.0399(14)
C14	0.5057(5)	0.0916(2)	0.3194(3)	0.0452(17)
C15	0.5642(5)	0.2134(2)	0.3630(3)	0.0521(19)
C16	0.4124(6)	0.2665(3)	0.4462(3)	0.091(3)
C17	0.5089(5)	0.0272(2)	0.1768(3)	0.0596(19)
C18	0.5441(5)	0.1590(2)	0.1096(3)	0.064(2)
C19	0.3295(6)	0.1292(3)	0.1853(3)	0.066(2)
C20	0.8371(5)	0.0980(2)	0.1411(2)	0.0486(16)
C21	0.9880(5)	0.0638(2)	0.2900(3)	0.0562(17)

$^a U_{eq}$=1/3 trace of the orthogonalized U tensor.

TABLE 3. Bond distances (Å) of the non-hydrogen atoms of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-(R)C=C(R)–C(O)) (R=C(O)-OMe) (**6a**) with e.s.d.s in parentheses

Ru–Fe	2.7733(10)	O1–C11	1.344(6)	N2–C6	1.280(5)
Ru–C20	1.855(4)	O5–C15	1.325(6)	C3–C4	1.372(7)
Fe–C14	1.907(5)	O8–C19	1.148(7)	C7–C9	1.528(9)
O1–C10	1.435(7)	N1–C5	1.350(5)	C13–C15	1.490(6)
O4–C15	1.192(5)	C2–C3	1.359(6)	Ru–C12	2.049(4)
O7–C18	1.134(6)	C7–C8	1.509(7)	Fe–C13	2.119(3)
N1–C1	1.332(4)	C13–C14	1.470(6)	Fe–C19	1.761(6)
C1–C2	1.372(6)	Ru–N2	2.131(3)	O3–C14	1.199(5)
C5–C6	1.457(6)	Fe–C12	2.120(4)	O6–C17	1.163(5)
C12–C13	1.407(6)	Fe–C18	1.831(5)	O10–C21	1.130(6)
Ru–N1	2.131(3)	O2–C11	1.187(5)	N2–C7	1.504(6)
Ru–C21	1.874(5)	O5–C16	1.446(6)	C4–C5	1.380(6)
Fe–C17	1.755(4)	O9–C20	1.153(5)	C11–C12	1.500(6)

TABLE 4. Bond angles (°) of the non-hydrogen atoms of FeRu(CO)$_5$(^{i}Pr-Pyca)(μ-η^1,η^3-(R)C=C(R)–C(O)) (R=C(O)-OMe) (**6a**) with e.s.d.s in parentheses

Fe–Ru–N1	96.41(10)	Ru–N2–C6	115.0(3)
Fe–Ru–N2	115.11(10)	Ru–N2–C7	128.9(2)
Fe–Ru–C12	49.42(12)	C6–N2–C7	116.0(3)
Fe–Ru–C20	88.21(14)	N1–C1–C2	122.8(4)
Fe–Ru–C21	146.83(13)	C1–C2–C3	120.2(4)
N1–Ru–N2	76.57(12)	C2–C3–C4	118.1(4)
N1–Ru–C12	96.55(13)	C3–C4–C5	119.5(4)
N1–Ru–C20	173.90(16)	N1–C5–C4	122.2(3)
N1–Ru–C21	87.83(17)	N1–C5–C6	114.7(3)
N2–Ru–C12	162.90(16)	C4–C5–C6	122.8(4)
N2–Ru–C20	97.88(15)	N2–C6–C5	118.8(4)
N2–Ru–C21	97.91(16)	N2–C7–C8	109.9(4)
C12–Ru–C20	89.48(16)	N2–C7–C9	109.2(4)
C12–Ru–C21	97.44(18)	C8–C7–C9	113.3(4)
C20–Ru–C21	90.48(20)	O1–C11–O2	123.7(4)
Ru–Fe–C12	47.22(11)	O1–C11–C12	109.2(4)
Ru–Fe–C13	76.94(10)	O2–C11–C12	126.9(4)
Ru–Fe–C14	85.81(14)	Ru–C12–Fe	83.36(13)
Ru–Fe–C17	69.68(16)	Ru–C12–C11	116.6(3)
Ru–Fe–C18	97.37(15)	Ru–C12–C13	125.5(3)
Ru–Fe–C19	166.99(20)	Fe–C12–C11	129.0(3)
C12–Fe–C13	38.76(14)	Fe–C12–C13	70.6(2)
C12–Fe–C14	73.18(17)	C11–C12–C13	117.1(3)
C12–Fe–C17	115.20(19)	Fe–C13–C12	70.7(2)
C12–Fe–C18	94.79(18)	Fe–C13–C14	61.0(2)
C12–Fe–C19	142.2(2)	Fe–C13–C15	126.3(3)
C13–Fe–C14	42.42(16)	C12–C13–C14	113.5(3)
C13–Fe–C17	124.66(18)	C12–C13–C15	123.6(3)
C13–Fe–C18	119.40(19)	C14–C13–C15	121.3(4)
C13–Fe–C19	107.62(19)	Fe–C14–O3	144.9(4)
C14–Fe–C17	91.43(20)	Fe–C14–C13	76.5(2)
C14–Fe–C18	160.43(19)	O3–C14–C13	137.8(4)
C14–Fe–C19	89.7(2)	O4–C15–O5	123.7(4)
C17–Fe–C18	107.8(2)	O4–C15–C13	123.9(4)
C17–Fe–C19	98.3(2)	O5–C15–C13	112.4(3)
C18–Fe–C19	90.9(2)	Fe–C17–O6	166.8(4)
C10–O1–C11	116.7(4)	Fe–C18–O7	176.1(4)
C15–O5–C16	115.4(3)	Fe–C19–O8	178.4(5)
Ru–N1–C1	128.1(3)	Ru–C20–O9	177.6(4)
Ru–N1–C5	114.6(2)	Ru–C21–O10	176.1(4)
C1–N1–C5	117.1(3)		

In the case of A one might consider the presence of a bimetallacyclopentenone ring with the C(12)=C(13) bond η^2-bonded to Fe. One may also view the structure as a μ_2-carbene with the ketene moiety η^2-bonded to Fe through C(13)=C(14) (case B). Finally one might, as has been found for similar compounds, imagine an η^3-allylic type of bonding (description C) which lies between the two extremes A and B. In general it was concluded, on basis of the C(12)–C(13) and C(13)–C(14) distances, the angles around C(14) and the various M–C distances, that structure A is probably the best description but, due to a substantial contribution of structure B, there are good arguments to present the bonding situation by structure C in several cases [21, 23, 25, 27].

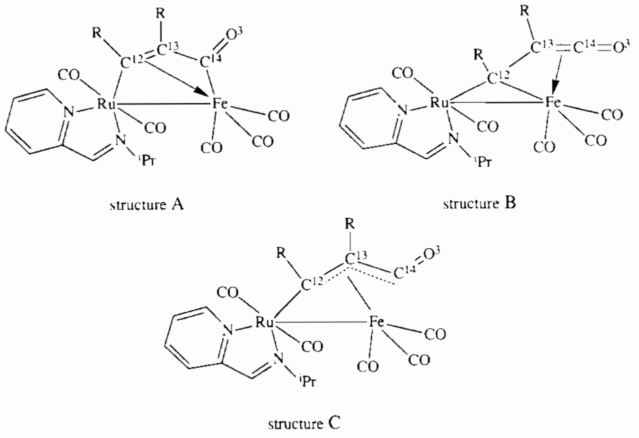

structure A structure B structure C

Fig. 2. Possible descriptions for coordination of a C(R)=C(R)–C(O) fragment to a bimetallic core.

When we consider the structure of **6a** we may note the following details: firstly, the C(13)–C(14) distance in **6a** (1.470(6) Å) is among the longest found for a μ-η^1,η^3-(R)C=C(R)–C(O) fragment bonded to a bimetallic core compared to literature values of for instance 1.442(5) [20], 1.451(12) [24], 1.469(8) [23], 1.461(5) [25] or 1.450(4) Å [22]. Secondly, the Fe–C(14) distance (1.907(5) Å) is significantly shorter than the Fe–C(12) and Fe–C(13) distances (2.120(4) and 2.119(3) Å). Thirdly, it should be noted that the C(13)C(14)O(3) angle is substantially larger (137.8(4)°) than 120° which would be expected for a sp^2 hybridized carbon atom. This angle is comparable to the values found for some complexes reported in the literature (138.1(4)° [25, 27], 138.3(4)° [21], 138.9(7)° [21], 139.8(3)° [20]). The first two observations agree with description A, but the third observation indicates that description B contributes to the actual bonding situation. We therefore suggest that the actual bonding situation lies somewhere between A and B, i.e. with the allylic description of structure C.

IR spectroscopy, mass spectroscopy and elemental analyses

The IR spectroscopic data are listed in Table 5 together with the mass spectroscopic data and the results of the elemental analyses.

The absorptions of the terminally bonded carbonyl ligands are observed as expected within the range of 1900–2070 cm^{-1}. The stretching frequencies of the ester carbonyl group of the complexes **6** and **7** are observed between 1700 and 1740 cm^{-1}. Finally, the ketonic carbonyl groups of the μ-η^1,η^3-(R)C=C(R)–C(O) moieties of the complexes **6** have been observed in the same region as the ester carbonyl group which is as expected [20].

Complexes **7** were not analyzed since they could only be isolated as oily substances, which, as shown by NMR spectroscopy, contained traces of solvents.

NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR data are listed in Tables 6 and 7, respectively. Both the ^{1}H NMR and the ^{13}C NMR of complexes **6** show the characteristic features of an α-diimine ligand in a 4e donating σ-N,σ-N′ coordination mode (imine proton around 8.65 ppm and imine carbon around 159 ppm). The carbonyl region of the ^{13}C NMR spectrum shows only one signal, both for the carbonyls coordinated to ruthenium and the carbonyls coordinated to iron, indicating that these ligands are involved in a scrambling process which is rapid on the NMR timescale. The ketonic carbonyl groups of the μ-η^1,η^3-(R)C=C(R)–C(O) moieties of the complexes **6** are observed at very low field (230–235 ppm region) which agrees with reported values [20, 23].

Both ^{1}H NMR (CR=C*H*–CO at 4.53 ppm) and ^{13}C NMR (APT pulse sequence, *C*(R)=C(H)–C(O) at 147 ppm and C(R)=*C*(H)–C(O) at 47.6 ppm) unambiguously showed that the product **6b** resulted from the coupling of a carbonyl ligand to the unsubstituted alkyne C atom [20]. No evidence was found for the formation of the other isomer in which a carbonyl ligand would be coupled to the substituted alkyne C atom.

From the absorptions of the imine group of complexes **7**, which are observed around 3.85 ppm in the ^{1}H NMR spectrum and around 72 ppm in the ^{13}C NMR spectrum, it can be concluded that the coordination of the Pyca ligand has changed from a 4e donating σ-N,σ-N′ coordination mode to a 6e donating σ-N,μ_2-N′,η^2-C=N′ coordination mode. The former ^{i}Pr-CH_3 groups are observed as two singlets in the ^{1}H NMR spectrum whereas the septet of the former ^{i}Pr-CH proton is no longer present. In the case of **7a** a singlet is observed at 6.02 ppm belonging to the olefinic –CR=CRH proton as a result of the H abstraction from the ^{i}Pr-Pyca ligand. In the case of **7b**/**7b′** both a –CH=CRH and a –CR=CH_2 fragment were observed indicating that the proton transfer reaction did not proceed regioselectively. The ^{13}C NMR of the mixture of **7b**/**7b′** enabled us to determine only the signals belonging to the major component (i.e. **7b**) unambiguously.

Reaction of 5 with DMADC

Reactions of **5** with alkynes were carried out with the aim to compare the reactivity of **5** with that of FeRu$(CO)_6$(^{i}Pr-DAB) (**1**) [9, 10]. FeRu$(CO)_6$(^{i}Pr-DAB) reacted with DMADC to give two products, i.e. FeRu$(CO)_5$(^{i}Pr-DAB)(μ_2,η^2-DMADC) (**2**) and FeRu$(CO)_5$(AIB) (**4**). The proposed mechanism (Scheme 1) contains **X1** as a key intermediate. It should

TABLE 5. Mass spectroscopic and IR data and elemental analyses of the complexes **6a**, **b** and **7a**, **b**/**b**′

Complex	FD-mass obs. (calc.)	IR[a] (cm^{-1}) ν(C=O)	Elemental analysis (%): obs. (calc.)		
			C	H	N
6a	616 (615.32)	2045(s), 2015(vs), 1980(m), 1967(sh), 1915(w), 1737(m), 1713(w)	41.24 (40.90)	3.09 (3.09)	4.37 (4.57)
6b	558 (557.28)	2038(s), 2005(vs), 1968(s), 1953(sh), 1900(w), 1725(sh), 1712(m)	40.66 (40.95)	2.96 (2.90)	4.91 (5.03)
7a	588 (587.31)	2045(s), 2010(s), 1980(s), 1970(sh), 1715(m), 1710(sh)	not analyzed		
7b/**7b**′	539 (529.27)	2045(s), 2005(s), 1968(s), 1953(sh), 1700(m)	not analyzed		

[a] CH_2Cl_2 solution.

TABLE 6. ^{1}H NMR[a] data of the complexes **6a**, **b** and **7a**, **b**/**b**′

6a	8.67 (1H, s, N=CH); 8.11 (1H, d, 5 Hz, py-H6); 7.79 (2H, m, py-H3/H4); 7.31 (1H, dd, 7 Hz/5 Hz, py-H5); 4.34 (1H, sept, 6 Hz, ^{i}Pr-CH); 3.86/3.67 (3H/3H, s, C(O)OCH_3); 1.48 (6H, d, 6 Hz, ^{i}Pr-CH_3)
6b	8.64 (1H, s, N=CH); 8.17 (1H, d, 5 Hz, py-H6); 7.79 (2H, m, py-H3/H4); 7.25 (1H, dd, 7 Hz/5 Hz, py-H5); 4.53 (1H, s, C(R)=CH); 4.37 (1H, sept, 6 Hz, ^{i}Pr-CH); 3.89 (3H, s, C(O)OCH_3); 1.48 (6H, d, 6 Hz, ^{i}Pr-CH_3)
7a	8.52 (1H, d, 6 Hz, py-H6); 7.86 (2H, m, py-H3/H4); 7.25 (1H, dd, 6 Hz/7.5 Hz, py-H5); 6.02 (1H, s, C=C(R)H); 3.80 (1H, s, N–CH); 3.72/3.64 (3H/3H, s, C(O)OCH_3); 2.18/1.75 (3H/3H, s, N=C$(CH_3)_2$)
7b	9.40 (1H, d, 16 Hz, Ru–CH=C); 8.43 (1H, d, 6 Hz, py-H6); 7.69 (2H, m, py-H3/H4); 7.10 (1H, dd, 7 Hz/6 Hz, py-H5); 6.41 (1H, d, 16 Hz, C=C(R)H); 3.85 (1H, s, N–CH); 3.69 (3H, s, C(O)OCH_3); 2.05/1.71 (3H/3H, s, N=C$(CH_3)_2$
7b′	8.47 (1H, d, 6 Hz, py-H6); 7.64 (2H, m, py-H3/H4); 7.12 (1H, dd, 7 Hz/6 Hz, py-H5); 6.30/5.41 (1H/1H, s, C=CH_2); 3.92 (1H, s, N–CH); 3.66 (3H, s, C(O)OCH_3); 2.15/1.71 (3H/3H, s, N=C$(CH_3)_2$)

[a] $CDCl_3$, 100 MHz, 293 K.

TABLE 7. ^{13}C NMR[a] data of the complexes **6a**, **b** and **7a**, **b**/**b**′

6a	23.8/24.2 (^{i}Pr-CH_3); 52.8/53.0 (OCH_3); 53.4 (CR=*C*R–CO); 66.2 (^{i}Pr-CH); 126.7 (py-C^5); 128.2 (py-C^3); 138.5 (py-C^4); 152.0 (py-C^6); 153.2 (py-C^2); 158.1 (*C*R=CR–CO); 159.4 (N=CH); 166.0/176.4 (*C*OOMe); 191.0 (Ru–CO); 197.5 (Fe–CO); 230.4 (CR=CR–*C*O)
6b	23.6/24.2 (^{i}Pr-CH_3); 47.6 (CR=*C*H–CO); 53.1 (OCH_3); 65.9 (^{i}Pr-CH); 126.1 (py-C^5); 128.1 (py-C^3); 138.2 (py-C^4); 147.0 (*C*R=CH–CO); 151.9 (py-C^6); 153.5 (py-C^2); 159.1 (N=CH); 176.7 (*C*OOMe); 191.0 (Ru–CO); 198.4 (Fe–CO); 236.6 (CR=CH–*C*O)
7a	26.9/32.9 (N=C$(CH_3)_2$); 51.8 (OCH_3); 72.6 (N=C$(Me)_2$); 102.5 (*C*R=CHR); 121.8 (py-C^5); 122.0 (py-C^3); 124.7 (CR=*C*HR); 138.2 (py-C^4); 151.5 (py-C^6); 153.5 (py-C^2); 163.4 (N=*C*Me_2); 170.8/177.2 (*C*OOMe); 197.7/202.4 (Ru–CO); 215.6 (Fe–CO)
7b	27.1/33.7 (N=C$(CH_3)_2$); 53.3 (OCH_3); 71.7 (N=C$(Me)_2$); 113.8 (*C*H=CHR); 121.8 (py-C^5); 122.2 (py-C^3); 131.6 (CH=*C*HR); 138.3 (py-C^4); 151.5 (py-C^6); 154.2 (py-C^2); 165.6 (N=*C*Me_2); 173.8 (*C*OOMe); 199.3/203.4 (Ru–CO); 213.4 (Fe–CO)

[a] $CDCl_3$, 25 MHz, 263 K.

be emphasized that **X1**, which has been proposed several times [3, 9, 29], has never been isolated or detected. In our case it is obvious that **5** would not be able to give a product like **4**, since intermediate **X1** is not accessible due to the presence of the aromatic pyridine ring in the ^{i}Pr-Pyca ligand.

Complex **5** reacted with DMADC to give **6a** (Scheme 2) in which both nitrogens are still coordinated to the Ru centre and which contains a μ-η^1,η^3-C(R)=C(R)–C(O) fragment resulting from a coupling of the alkyne to a carbonyl ligand. In this reaction the ^{i}Pr-Pyca ligand changed from a 6e donating σ-N,μ_2-N′,η^2-C=N′ coordination mode to a 4e donating σ-N,σ-N′ coordination mode. Although $FeRu(CO)_6$(^{i}Pr-DAB) (**1**) (Scheme 1) and $FeRu(CO)_6$(^{i}Pr-Pyca) (**5**) (Scheme 2) react differently with DMADC, i.e. producing **2** and **6a**, respectively, the formation of **6a** does not change the arguments favouring the proposed mechanism for the reaction of **1** with DMAC (Scheme 1). Since both **6a** and **2** contain an α-diimine ligand coordinated to the Ru centre, while no product like **4** was observed starting from **5**, the formation of **6a** as a single product is in agreement with the mechanisms shown in Schemes 1 and 2, and with the proposed structure of the key intermediate **X1**.

However, an interesting question is why in the case of **5** a coupling reaction between the alkyne and a carbonyl ligand takes place (Scheme 2), while in the case of **1** it does not (Scheme 1). For $Fe_2(CO)_6$(L) (L=R-DAB, R-Pyca, Bipy) a similar behaviour was observed since $Fe_2(CO)_6$(R-DAB) reacts with DMADC to form $Fe_2(CO)_5$(R-DAB)(μ_2-DMADC) [30] while

$Fe_2(CO)_6$(R-Pyca) and $Fe_2(CO)_6$(Bipy) react with DMADC to give $Fe_2(\mu\text{-}\eta^1,\eta^3\text{-}(R)C{=}C(R){-}C(O))(CO)_5(L)$ (L = R-Pyca, Bipy; R = C(O)OMe) in 50% and 75% yield, respectively [20]. Moreover MP reacts with $Fe_2(CO)_6(L)$ to give $Fe_2(\mu\text{-}\eta^1,\eta^3\text{-}(R)C{=}C(R'){-}C(O))(CO)_5(L)$ for L = R-DAB (yield about 5%) and for L = R-Pyca (yield about 50%).

These results indicate that the alkyne–carbonyl coupling is favoured when weaker π-accepting R-Pyca or Bipy ligands are used instead of R-DAB. The electronic properties of the α-diimine as described above influence the amount of π-backdonation to the carbonyl ligands thus making them more or less susceptible to nucleophilic attack by the alkyne*. Alternatively one may employ an alkyne which is sufficiently nucleophilic to attack a carbonyl ligand, i.e. an alkyne which does not have two electron withdrawing substituents.

An analogous coupling of an alkyne and a carbonyl ligand resulting in complexes containing a $\mu\text{-}\eta^1,\eta^3\text{-}C(R){=}C(R){-}C(O)$ fragment has been observed for reactions of $M_2(CO)_4(C_p)_2$ with various alkynes [25, 27]. Often mixtures of CR−CR′−CO and CR′−CR−CO coupled products were obtained. It was concluded that steric effects are important in determining the product distribution, especially when alkynes of the type HC≡CR were used [27]. However, since steric differences of the alkyne substituents cannot explain the differences in reactivity between the R-DAB, R-Pyca and Bipy systems as described above, we think that in our case electronic effects are dominant. These results again clearly indicate that our systems differ substantially from the photochemically induced reactions reported by Knox and co-workers [27] for which a plausible mechanism via a CO-loss photoproduct has been reported by Bursten *et al.* [32]. Support for the idea that the photochemical induction is one of the main causes for the observed differences can be found in the work of Shaw and co-workers who reported a comparable alkyne–carbonyl coupling on a FePt system [24]. For this non-photochemical system coupling of the carbonyl ligand to the unsubstituted alkyne C atom proved to be the favoured product which is in agreement with the non-photochemical systems presented here**.

In Scheme 3 two possible routes for the formation of complexes **6** are presented. The first one involves a direct attack of the coordinated alkyne at the Fe centre on one of the carbonyl ligands to give **6**. The second one, which is comparable to the mechanism proposed by Knox and co-workers [27], proceeds via intermediate **X5** and involves an initial C–C coupling of the alkyne to a carbonyl ligand at the Fe centre. The ferracyclobutenone fragment produced this way, after a rearrangement, leads to the formation of a complex containing a $\mu\text{-}\eta^1,\eta^3\text{-}C(R){=}C(R){-}C(O)$ fragment. For reasons outlined above we suggest a direct nucleophilic attack of the alkyne on the carbonyl ligand to be the most likely possibility in our case.

Reaction of 5 with MP

The reactions of $FeRu(CO)_6(^iPr\text{-}DAB)$ (**1**) with MP gave the complex $FeRu(CO)_4(^iPr\text{-}DAB)(HC{=}CC(O)OMe)$ in which the alkyne is μ_2-bridging and the DAB ligand acts as an 8e donating $\sigma\text{-}N,\sigma\text{-}N',\eta^2\text{-}C{=}N,\eta^2\text{-}C{=}N'$ ligand [9]. It was therefore of interest to try the corresponding reaction with **5**, since its ^{i}Pr-Pyca ligand can at most donate 6 electrons.

The reaction of **5** with MP resulted in the formation of **6b** (Schemes 2 and 3), containing five terminal carbonyl ligands and a $\mu\text{-}\eta^1,\eta^3\text{-}C(R){=}C(H){-}C(O)$ fragment. Although in principle two regioisomers might be expected for **6a** spectroscopic data indicated that only that product is formed in which a carbonyl ligand is coupled to the unsubstituted alkyne C atom. Since the unsubstituted C atom is more nucleophilic than the alkyne C atom carrying the electron withdrawing substituent the coupling to the unsubstituted C atom therefore again supports the suggestion that the alkyne–carbonyl coupling is a result of a nucleophilic attack of the alkyne on a carbonyl ligand (*vide supra*).

When comparing the reactivity of MP with $Fe_2(CO)_6$(Pyca) and **5**, respectively, we find an enhanced regioselectivity for **5**, since in the case of $Fe_2(CO)_6$(Pyca) both coupling to the substituted and the unsubstituted alkyne C atom is observed [20] whereas the reaction of **5** with MP gives rise to the CR−CH−CO coupled product exclusively. This is in accord with the findings by Knox and co-workers who concluded that the FeRu compound appeared to be far more selective in coupling reactions of carbonyl ligands and alkynes than the homonuclear complexes [27, 33]. It is however important to note that for the systems reported by Knox and co-workers coupling to the substituted alkyne C atom proved to be the favoured, whereas in the case of the $M_2(CO)_6$(R-Pyca) systems coupling to the unsubstituted alkyne C atom is the favoured one. In the system presented here electronic effects appear to favour

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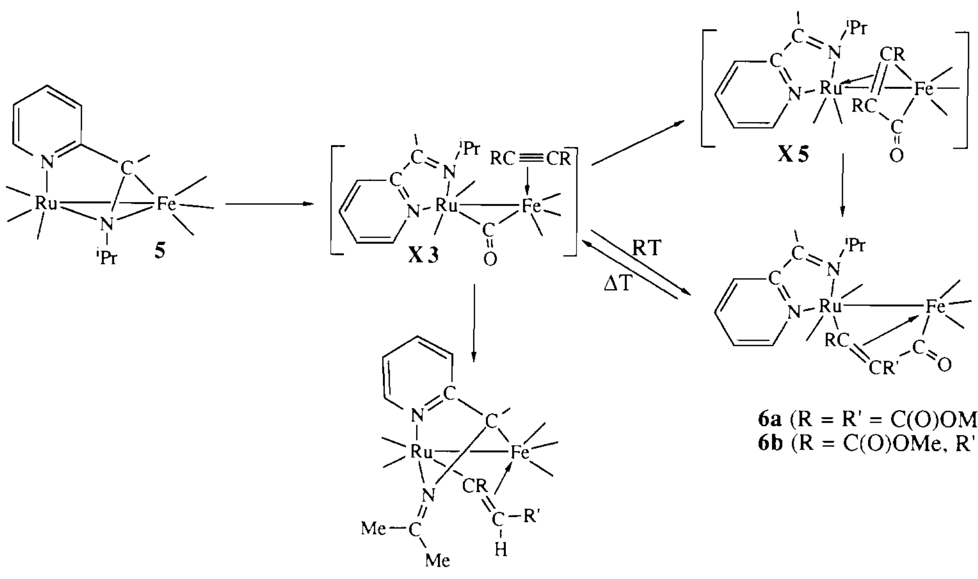
*It is known that more π-backdonation leads to more positive polarization of the carbonyl C atom thus making the carbonyl ligand more susceptible for nucleophilic attack. At first sight this seems counterintuitive, but it has been found [31] that the calculated positive charges of the carbonyl C atoms decrease in the order $V(CO)_6^-$ (+0.25), $Cr(CO)_6$ (+0.20) and $Mn(CO)_6^+$ (+0.18).

**Unlike Shaw and co-workers we found no evidence for the occurrence of isomerization of the Ru−C(R)=C(H)−C(O)−Fe complex to the comparable Ru−C(H)=C(R)−C(O)−Fe complex. However, this does not rule out the possibility that the formation of a C(R)=C(H)−C(O) coupled product is kinetically controlled while a C(H)=C(R)−C(O) coupled product would thermodynamically have been more favourable, since the R group would then occupy the sterically least demanding site.



6a (R = R' = C(O)OMe)
6b (R = C(O)OMe, R' = H)

7a (R = R' = C(O)OMe)
7b (R = H, R' = C(O)OMe)
7b' (R' = H, R = C(O)OMe)

Scheme 3. Proposed mechanism for the reactivity of $FeRu(CO)_6(^iPr\text{-}Pyca)$ (5) towards alkynes.

the coupling of the carbonyl ligand to the more nucleophilic unsubstituted alkyne C atom, whereas in the case of the $M_2(CO)_4(C_p)_2$ system formation of a $\mu\text{-}\eta^1,\eta^3\text{-}C(H)=C(R)-C(O)$ fragment is dominated by steric factors [25, 27, 33].

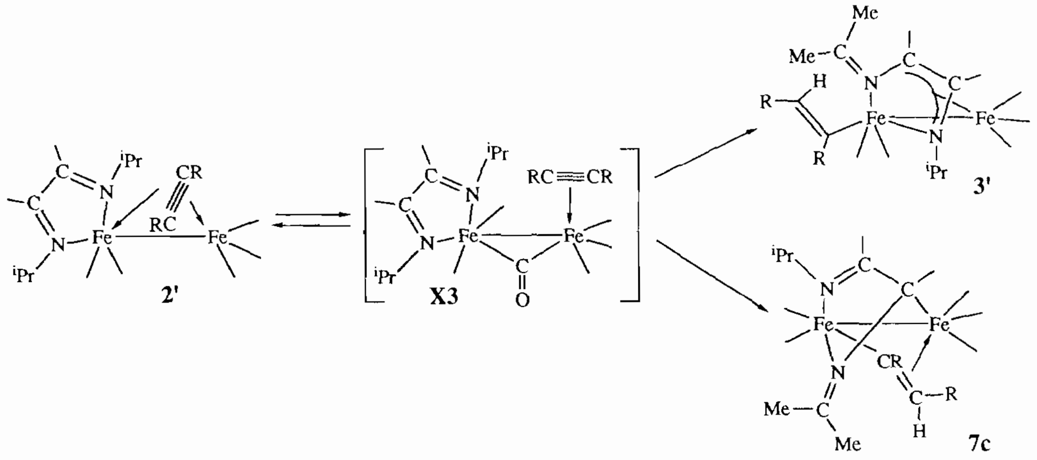
Thermal conversion of 6a and 6b to complexes 7a, b

Complexes containing a $\mu\text{-}\eta^1,\eta^3\text{-}C(R)=C(R)-C(O)$ fragment have proved to provide a convenient entry into diruthenium chemistry [32, 34, 35]. In these reactions a facile decoupling of the alkyne and the carbonyl ligand is often observed, which is very important in determining the reactivity of complexes containing a $\mu,\text{-}\eta^1,\eta^3\text{-}C(R)=C(R)-C(O)$ fragment. A similar decoupling of the alkyne and the carbonyl ligand within the $\mu\text{-}\eta^1,\eta^3\text{-}C(R)=C(R)-C(O)$ fragment did also occur during the thermal conversion of complexes **6**. Heating of **6a** yields **7a**, which has lost one CO and in which a H atom has been transferred from the N-bound isopropyl carbon atom to the terminal vinyl carbon (former alkyne).

The thermal conversion of $FeRu(CO)_5(^iPr\text{-}Pyca)(\mu\text{-}\eta^1,\eta^3\text{-}CR=CH-CO)$ (R = C(O)OMe (**6b**)) also leads to a proton abstraction reaction. Although **6b** occurs as one regioisomer, the thermal conversion produced a mixture of the regioisomers **7b** and **7b′** which differ in which alkyne carbon atom abstracts a proton from the Pyca ligand. This implies that after the decoupling of the carbonyl ligand and the alkyne in the $\mu\text{-}\eta^1,\eta^3\text{-}CR=CH-C(O)$ fragment an intermediate is formed in which the alkyne is coordinated in such a way that both alkyne carbon atoms are able to abstract the isopropyl H atom. In all cases however these seems to be a large preference for the formation of **7b** over the formation of **7b′** with ratios **7b**/**7b′** varying from 5 to 7.

Several examples have been found in which a complex containing a $\mu\text{-}\eta^1,\eta^3\text{-}C(R)=C(R)-C(O)$ fragment is converted to one containing a $\mu,\eta^2\text{-}RC=CHR$ bonded fragment [24, 33, 36–38]. However, it was not explained why in some cases the substituted alkyne C atom and in other cases the unsubstituted alkyne C atom is the one that is protonated. In this case it is again interesting to compare our heteronuclear FeRu system with the results of the FeRu system described elsewhere [33]. For the only HC≡CR-type alkyne used (propyne) exclusive protonation of the substituted alkyne C atom and the formation of a $\mu,\eta^2\text{-}(H)C=C(Me)(H)$ fragment was observed. Although the selectivity is not as large as reported by Knox and co-workers and small amounts of complexes containing a $\mu,\eta^2\text{-}(R)C=CH_2$ fragment were formed (**7b′**) the main product however proved to contain a $\mu,\eta^2\text{-}(H)C=C(R)(H)$ fragment (**7b**) in analogy to the $FeRu(CO)_4(C_p)_2$ system [33].

The formation of a $\mu,\eta^2\text{-}(R)C=C(R')(H)$ fragment has also been observed for other heteronuclear systems with FePt [24] and NiW [37] bonds or from homonuclear species [38], but in these cases again no obvious preference for protonation of the substituted alkyne C atom or the unsubstituted alkyne C atom could be observed and often mixtures of $\eta^2\text{-}CH=C(R)(H)$ and $\eta^2\text{-}CR=CH_2$ products were found, which in some cases could be converted into each other.



Scheme 4. Observed sequence for the thermal conversion of Fe$_2$(CO)$_5$(^{i}Pr-DAB)(μ_2,η^2-RC≡CR) (R = C(O)OMe)) [30].

We have as yet no clear idea about the intramolecular proton abstraction mechanism. Although there are several indications that the reaction proceeds via a metal hydride as intermediate [36, 37], this intermediate itself has never been observed. However, the reaction mechanism must involve a decoupling of the alkyne and the carbonyl ligand which is a phenomenon that is quite common for complexes containing a μ-η^1,η^3-C(R)=C(R)−C(O) fragment [32, 34, 35]. In this respect it is interesting to note that thermal conversion of Fe$_2$(CO)$_5$(^{i}Pr-DAB)(μ_2,η^2-C(R)≡C(R)) (**2'**) leads to a similar C−H activation reaction but the starting complex of this system contained a μ_2,η^2-coordinated alkyne [30] (Scheme 4). It is therefore reasonable to surmise that a common type of intermediate, like for instance intermediate **X3**, is formed during the proton abstraction reactions of **6a** and **2'**, producing **7a** and **7c**, respectively (Schemes 3 and 4).

It is interesting to note that in the case of Fe$_2$(CO)$_5$(^{i}Pr-DAB)(μ_2,η^2-DMADC) (**2'**) a complex analogous to **7c** was not the only product obtained, since the main product was the allylic complex Fe$_2$(CO)$_5$(Me$_2$C=N-CHCHN-^{i}Pr)(η^1-RC=CHR) (**3'**) [30] (Scheme 4). The same reactivity was observed for the heteronuclear FeRu(CO)$_5$(^{i}Pr-DAB)(μ_2,η^2-DMADC) (**2**) which upon heating yielded FeRu(CO)$_5$(Me$_2$C=N−CHCHN-^{i}Pr)(η^1-RC=CHR) (**3**) [9] (Scheme 1). Due to the presence of the aromatic pyridine ring in **6a** a complex such as **3** or **3'** cannot be formed starting from **6a**. This result once again shows the enormous influence of the type of α-diimine used on the outcome of the reactions.

Supplementary material

Tables of anisotropic thermal parameters, all H atom parameters, bond lengths, bond angles and torsion angles for **6a** (6 pages), and listings of observed and calculated structure factor amplitudes for **6a** (28 pages) can be obtained from author A.L.S.

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References

1 (a) G. van Koten and K. Vrieze, *Adv. Organomet. Chem., 21* (1982) 151; (b) K. Vrieze, *J. Organomet. Chem., 300* (1986) 307; (c) G. van Koten and K. Vrieze, *Recl. Trav. Chim. Pays-Bas, 100* (1981) 129; (d) K. Vrieze and G. van Koten, *Inorg. Chim. Acta, 100* (1985) 79.

2 (a) J. Keijsper, L. H. Polm, G. van Koten, K. Vrieze, E. Nielsen and C. H. Stam, *Organometallics, 4* (1985) 2006; (b) J. Keijsper, L. H. Polm, G. van Koten, K. Vrieze, K. Goubitz and C. H. Stam, *Organometallics, 4* (1985) 1876; (c) L. H. Staal, G. van Koten, K. Vrieze, B. van Santen and C. H. Stam, *Inorg. Chem., 20* (1981) 3598; (d) J. Keijsper, L. H. Polm, G. van Koten, K. Vrieze, C. H. Stam and J.-D. Schagen, *Inorg. Chim. Acta, 103* (1985) 137; (e) L. H. Polm, G. van Koten, K. Vrieze, C. H. Stam and W. C. J. van Tunen, *J. Chem. Soc., Chem. Commun.,* (1983) 1177; (f) H.-W. Frühauf and F. Seils, *J. Organomet. Chem., 323* (1987) 67.

3 R. Zoet, K. Goubitz, C. J. G. van Halen, F. Muller, M. van Wijnkoop, C. H. Stam, G. van Koten and K. Vrieze, *Inorg. Chim. Acta, 149* (1988) 193.

4 L. H. Staal, L. H. Polm, R. W. Balk, G. van Koten, K. Vrieze and A. M. F. Brouwers, *Inorg. Chem., 19* (1980) 3343.

5 H.-W. Frühauf, A. Landers, R. Goddard and C. Krüger, *Angew. Chem., 90* (1978) 56.

6 L. H. Polm, G. van Koten, C. J. Elsevier, K. Vrieze, B. F. K. van Santen and C. H. Stam, *J. Organomet. Chem., 304* (1986) 353.

7 R. Zoet, C. A. A. Duineveld, C. J. Elsevier, K. Goubitz, D. Heijdenrijk, G. van Koten, C. H. Stam, P. Versloot, K. Vrieze and M. van Wijnkoop, *Organometallics, 8* (1989) 23.

8 (a) F. Muller and K. Vrieze, in J. J. Ziolkowski (ed.), *Coordination Chemistry and Catalysis,* World Scientific, Singapore, 1988; (b) C. J. Elsevier, F. Muller, K. Vrieze and R. Zoet, *New J. Chem., 12* (1988) 571.

9 F. Muller, K. A. A. Duineveld, D. Heijdenrijk, G. van Koten, M. J. A. Kraakman, C. H. Stam, K. Vrieze, R. Zoet and M. C. Zoutberg, *Organometallics, 8* (1989) 982.

10 F. Muller, D. Heijdenrijk, G. van Koten, M. J. A. Kraakman, K. Vrieze and M. C. Zoutberg, *Organometallics, 8* (1989) 1331.

11 M. J. A. Kraakman, C. J. Elsevier, J.-M. Ernsting, K. Goubitz and K. Vrieze, *Inorg. Chim. Acta, 203* (1993) 129.

12 L. H. Staal, G. van Koten, R. H. Fokkens and N. M. M. Nibbering, *Inorg. Chim. Acta, 50* (1981) 205.

13 A. L. Spek, *J. Appl. Crystallogr., 21* (1988) 578.

14 G. M. Sheldrick, *SHELXS86*, program for crystal structure determination, University of Göttingen, Germany, 1986.

15 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A, 46* (1990) 194.

16 G. M. Sheldrick, *SHELX76*, program for crystal structure determination, University of Cambridge, UK, 1976.

17 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 24* (1968) 321.

18 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53* (1970) 1891.

19 A. L. Spek, The EUCLID package, in D. Sayre (ed.), *Computional Crystallography,* Clarendon, Oxford, 1982, p. 528.

20 F. Muller, I. M. Han, G. van Koten, K. Vrieze, D. Heijdenrijk, J. van Mechelen and C. H. Stam, *Inorg. Chim. Acta, 158* (1989) 99.

21 F. A. Cotton, J. D. Jamerson and B. R. Stults, *Inorg. Chim. Acta, 17* (1976) 235.

22 W. F. Smith, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.,* (1976) 896.

23 H. Otto, F. J. G. Alonso and H. Werner, *J. Organomet. Chem., 306* (1986) C13.

24 X. L. R. Fontaine, G. B. Jacobsen, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.,* (1988) 741.

25 A. F. Dyke, S. A. R. Knox, P. J. Naish and G. E. Taylor, *J. Chem. Soc., Chem. Commun.,* (1980) 409.

26 (a) R. C. Pettersen, K. H. Pannell and A. J. Mayr, *Acta Crystallogr., Sect. B, 36* (1980) 2434; (b) R. S. Dickson, B. M. Gatehouse, M. C. Nesbit and G. N. Pain, *J. Organomet. Chem., 215* (1981) 97.

27 A. F. Dyke, S. A. R. Knox, P. J. Naish and G. E. Taylor, *J. Chem. Soc., Dalton Trans.,* (1982) 1297.

28 (a) A. F. Dyke, S. A. R. Knox, P. J. Naish and G. E. Taylor, *J. Chem. Soc., Chem. Commun.,* (1980) 803; (b) A. F. Dyke, J. E. Guerchais, S. A. R. Knox, J. Roué, R. L. Short, G. E. Taylor and P. Woodward, *J. Chem. Soc., Chem. Commun.,* (1981) 537.

29 H.-W. Frühauf, D. Meyer and J. Breuer, *J. Organomet. Chem., 297* (1985) 211.

30 F. Muller, G. van Koten, K. Vrieze, K. A. A. Duineveld, D. Heijendrijk, A. N. S. Mak and C. H. Stam, *Organometallics, 8* (1989) 1324.

31 K. G. Caulton and R. F. Fenske, *Inorg. Chem., 7* (1968) 1273.

32 B. E. Bursten, S. D. McKee and M. S. Platz, *J. Am. Chem. Soc., 111* (1989) 3428.

33 B. P. Gracey, S. A. R. Knox, K. A. Macpherson, A. G. Orpen and S. R. Stobart, *J. Chem. Soc., Dalton Trans.,* (1985) 1935.

34 (a) D. L. Davies, A. F. Dyke, S. A. R. Knox and M. J. Morris, *J. Organomet. Chem., 215* (1981) C30; (b) S. A. R. Knox, *Pure Appl. Chem., 56* (1984) 81; (c) M. O. Albers, D. J. Robindon and E. Singleton, *Coord. Chem. Rev., 79* (1987) 1; (d) G. S. Lewandos, S. A. R. Knox and A. G. Orpen, *J. Chem. Soc., Dalton Trans.,* (1987) 2703.

35 A.-J. DiMaio, T. E. Bitterwolf and A. L. Rheingold, *Organometallics, 9* (1990) 551.

36 A. F. Dyke, S. A. R. Knox, M. J. Morris and P. J. Naish, *J. Chem. Soc., Dalton Trans.,* (1983) 1417.

37 M. J. Chetcuti, J. C. Gordon, K. A. Green, P. E. Fanwick and D. Morgenstern, *Organometallics, 8* (1989) 1790.

38 R. Yáñez, J. Ros, I. Moldes, R. Mathieu, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.,* (1990) 3147.