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β-Diketones derived from cyclopentadienyl rhenium tricarbonyl

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Abstract

The acetyl complex (η^5–$C_5H_4COCH_3$)Re(CO)$_3$ reacts with KO^{t}Bu and an excess of appropriate ester to provide cyrhetrenyl-β-diketones complexes (η^5–$C_5H_4COCH_2COR$)Re(CO)$_3$ (R = CF_3, **1a**; CH_3, **1b**; Ph, **1c**). These new 1,3-diketones exist predominantly as enol tautomer, although a enol/keto mixture of approx. 10:1 is present in complexes **1b**–**c**, in chloroform-d solution. The complexes have been characterized by spectroscopic techniques IR, ^{1}H and ^{13}C NMR and mass spectrometry. X-ray crystallography of complex **1b** shows that only the enol form occurs in the solid state. The O–C–C–C–O fragment of the molecule is planar with asymmetric enolisation in the direction furthest from the cyrhetrenyl group.

Keywords: Cyrhetrenyl-1,3-diketone; Rhenium; Organometallic ligand

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Ferrocene containing β-diketones were first prepared in 1958 [1]. More recently new synthetic routes have been developed to obtain these compounds in a much better yield [2]. Owing to the coordination capability of these ligands, several transition metal complexes of the type M(ferrocene-diketonate)$_n$ (M = VO, Mn, Co, Ni, Cu, Zn. $n = 2$; M = Al, Cr, Mn, Fe. $n = 3$) have been studied with regards to their structural, electrochemical and kinetic aspects [3].

As far as we know, no other cyclopentadienyl complexes containing β-diketones as a side arm have been reported in the literature. This encouraged us to find a method to synthesize cyrhetrenyl-β-diketones of the type (η^5–$C_5H_4COCH_2COR$)Re(CO)$_3$. These new compounds can be prepared, by following a similar procedure to that reported for the ferrocenyl-β-diketones, that is by using the known acetyl complex (η^5–$C_5H_4COCH_3$)Re(CO)$_3$ in reaction with KO^{t}Bu in THF solution, followed by the addition of an excess of the corresponding ester ($RCO_2CH_2CH_3$) and further acidification with aqueous HCl solution [4a] (Scheme 1).

The use of KO^{t}Bu, rather than other recommended bases ($NaNH_2$ or LiNPr$^i_2$), to deprotonate acetylcyrhetrene provides a much more reproducible synthesis of **1a**–**c**.

Cyrhetrenyl β-diketones complexes **1**, could be isolated as yellow pale microcrystals in moderate to low yields: 1-cyrhetrenyl-4,4,4-trifluorobutane-1,3-dione **1a** ($R = 48\%$) [4a], 1-cyrhetrenyl-butane-1,3-dione **1b** ($R = 42\%$) [4b], 1-cyrhetrenyl-3-phenylpropane-1,3-dione **1c** ($R = 26\%$) [4c].

The lower yield of **1c** probably is associated to the less electrophilic character of the carbonyl carbon of ethyl benzoate compared to ethyl acetate and ethyl trifluoroacetate. This can also explain the presence of acetylcyrhetrene after the reaction workup.

The presence of the β-diketone group in **1a**–**c**, was unequivocally established by IR, ^{1}H and ^{13}C NMR spectroscopies. For all cases the IR spectra, in addition to the absorption bands for the CO groups bound to rhenium, showed the presence of a new CO band at 1606 cm^{-1} (CH_2Cl_2 solution) which is shifted to lower wavenumber compared to their acetyl precursor ($\nu CO = 1688$ cm^{-1}) [5].

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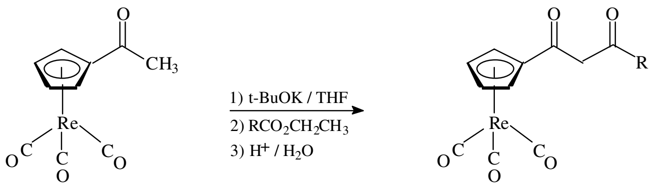

1a, R = CF_3
1b, R = CH_3
1c, R = Ph.

Scheme 1.

The ^{1}H NMR spectrum for **1a**, showed only one of two possible tautomers, since the expected resonance at about δ 4.0 for the keto form was not detected even in a saturated deuterobenzene solution, whereas for **1b**–**c** a mixture of enol (major) and keto (minor) forms were established in about 10:1 ratio. Similar tautomeric mixtures have been observed in β-diketones containing a ferrocenyl group: $(\eta^5\text{–}C_5H_5)Fe(\eta^5\text{–}C_5H_4COCH_2COR)$, $R = CF_3$ [2,6], CH_3 [7] and C_6H_5 [2,6].

The enol tautomers were easily identified by a broad low field resonance ($\delta \sim 15$) characteristic for a β-diketones hydrogen-bond and a singlet at about 6 ppm assigned to the olefinic hydrogen (CH). The latter occurs at similar δ to those reported for ferrocene derivatives mentioned above. On the other hand, the ^{1}H NMR spectra of **1b** and **1c** but no **1a,** showed a singlet at about 4 ppm, assigned to the CH_2 group of the keto form, as well as two triplets for the cyrhetrenyl group. The two observed signals for the methyl groups found in the ^{1}H NMR spectrum of **1b** (δ 2.10 and δ 2.29) are also indicative of the presence of the tautomers in solution.

The presence of a single resonance at δ −69.2 in the ^{19}F NMR spectrum of **1a** (assigned to the fluorine atoms of the CF_3 group) is a further evidence for the existence of the enol tautomer for this compound. This value is very similar to the corresponding shift found for trifluoroacetylacetone (δ: −70.1) and trifluorophenylbutane-1,3-dione (δ: −69.8) in $CDCl_3$ [8]. It is important to note that Swart et al. on the basis of ^{1}H NMR determined over 99% enolisation in several β-diketones containing a CF_3 group [6].

The ^{13}C NMR spectrum, also in $CDCl_3$ solution, showed only the expected resonances for the enol tautomer. For **1a**, the resonances at δ 117.3 ($^1J_{FC} = 281.0$ Hz) and δ 172.2 ($^2J_{FC} = 36.7$ Hz) are almost identical to those reported for the complex $(\eta^5\text{–}C_5H_5)Fe(\eta^5\text{–}C_5H_4COCH_2\text{-}COCF_3)$ [2,6] (assigned to CF_3 and $COCF_3$ groups, respectively).

In all cases, the ^{13}C shift of the side-chain (CH) and cyclopentadienyl C_{ipso} occurring in the range 92–96 ppm, were unequivocally assigned by using DEPT 135 and ^{1}H–^{13}C-HSQC. The two CO shifts of the diketone fragment of **1b** and **1c** (δ 181–189) are close to the CO shift reported for pentane-2,4-dione and the analogous ferrocenyl-diketone [2,7]. It is not possible to determine from the chemical shift data alone the sense in which the enolization of these compounds occur. The resonances for the terminal CO groups (Re–CO) occurred at almost the same δ to that reported for the acetylcyrhetrene [5].

Each of **1a**–**c** shows a strong molecular ion in the mass spectrum. In addition, the successive loss of three CO are the most relevant fragments observed in the spectra of the compounds.

Despite the considerable number of β-diketones described in the literature, crystallographic information for those containing one or two metal fragments as substituents is still scarce [7b]. With the aim to provide typical metrical data for this type of compound the X-ray structure analysis of **1b** was conducted [9].

Single crystals of **1b** were obtained by slow diffusion of hexane into an ether solution of **1b**. Fig. 1 shows an ORTEP view of the structure of **1b**, together with some selected bond distances and angles. All the heavy atoms in the side-chain C(6), C(8), O(1) and O(2) are coplanar, with the two oxygen atoms on the same side of the chains, and separated by 2.482 Å. This is the same overall conformation as adopted in ferrocenyl-butane-1,3-dione [7b] and in other enolized 1,3-diketones [10]. The bond length C(6)–C(7) of 1.399(10) Å and C(7)–C(8) of 1.355(10) Å are slightly shorter than those measured for the distinct C–C bonds in asymmetric enolized 1,3-diones [7b,10]. Similarly the C(6)–O(1) and C(8)–O(2) distances 1.261(8) Å and 1.307(7) Å, lie in the low limit of the ranges observed in such enols for the two types of C–O distances (1.269–1.283 Å and 1.306–1.337 Å, respectively). It is important to mention at this point that C–C and C═O bond distances measured in non-enolized 1,3-diketones lie in the ranges 1.507–1.537 Å and 1.212–1.221 Å, respectively [11], wholly different from the values found in **1b**. By considering the above results and the co-planarity of the 1,3-butanedione fragment, we conclude that **1b**, in the solid state, possesses an asymmetric enolisation in the direction away from the cyrethrenyl side group. Further more, the dihedral angle of 4.20° (0.25) between the pseudo-aromatic β-diketone

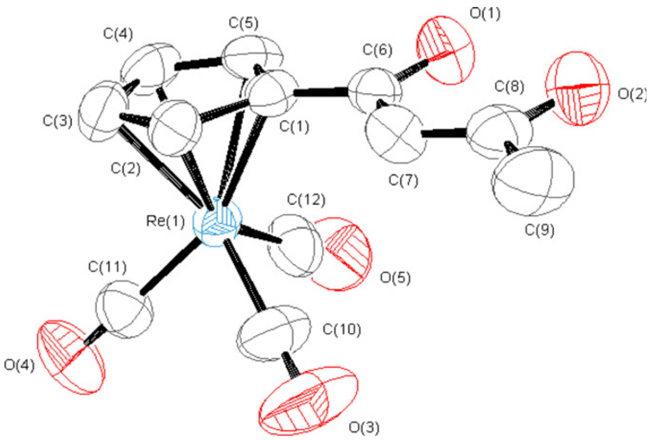

Fig. 1. Molecular structure of **1b**. Selected bond lengths (Å) and bond angles (°): C(1)–C(6) 1.469(9), C(6)–C(7) 1.399(10), C(7)–C(8) 1.355(10), $Cp_{(centroid)}$–Re 1.945(4), Re–(CO) 1.912, O(1)–C(6)–C(7) 120.2(7), C(6)–C(7)–C(8) 121.1(7), C(7)–C(8)–O(2) 122.4(8). Dihedral angle 4.20°(0.25), C(O)–Re–C(O) 89.13.

plane and the planar cyclopentadienyl ring attached to the β-diketone skeleton indicates appreciable conjugation between the two groups. On the other hand, within the cyrhetrenyl group, the average Re–C(O) distance and the Re–C–O angle are concordant with related tricarbonyl cyclopentadienyl rhenium (I) complexes [12].

Supplementary material

CCDC 644403 contains the supplementary crystallographic data for **1b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[4] (a) Synthesis of (η^5-C_5 $H_4COCH_2COCF_3$)Re(CO)$_3$ (**1a**). To a solution of complex (η^5–$C_5H_4COCH_3$)Re(CO)$_3$ (100 mg, 0.26 mmol) in THF (10 mL) was added *t*-BuOK (32 mg, 0.29 mmol). After 30 min of stirring at room temperature, an excess of $CF_3CO_2CH_2CH_3$ (2.62 mL, 26.0 mmol, $d = 1.273$ g/mL) was used to ensure complete reaction, and the resulting suspension was stirred overnight. After this time, the diketonate salt was converted to the diketone by shaking it with 50% aqueous HCl solution (20 mL) and the product was extracted from the mixture with ether (2 × 20 mL). The combined ether extracts were dried over sodium sulfate, filtered through Celite and the solvent evaporated under reduced pressure, affording a pale yellow solid. Extraction with hexanes (2 × 10 mL) yielded a white–yellow solid, 59 mg, 48% yield. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2033 (s), 1942 (vs), 1606 (w). ^{1}H NMR ($CDCl_3$) δ: (enol tautomer $\geqslant$ 99): 5.47 (t, 2H, $J = 4.4$ Hz, C_5H_4); 6.01 (s, H, CH); 6.06 (t, 2H, $J = 4.4$ Hz, C_5H_4); 14.30 (s, br., 1H, OH). ^{1}H RMN (C_6D_6) δ: 4.15 (t, 2H, $J = 2.0$ Hz; C_5H_4); 4.88 (t, 2H, $J = 2.0$ Hz; C_5H_4); 5.59 (s, H, CH). ^{13}C {^{1}H}RMN ($CDCl_3$)δ: 85.8 (s, C_5H_4); 87.6 (s, C_5H_4); 92.1 (s, C_{ipso} C_5H_4); 92.9 (s, CH), 117.3 (q, $J = 281.0$ Hz; CF_3); 172.2 (q, $J = 36.7$ Hz; $COCF_3$); 184.6 (s, CO); 191.1 (s, Re–CO). ^{13}C {^{1}H}RMN (C_6D_6) δ: 85.3 (s, C_5H_4); 87.4 (s, C_5H_4); 92.1 (s, C_{ipso} C_5H_4); 93.1 (s, CH); 118.1 (q, $J = 281.0$ Hz; CF_3); 171.8 (q, $J = 36.6$ Hz; $COCF_3$); 184.9 (s, CO); 191.7 (s, Re–CO). ^{19}F NMR (C_2D_6CO) δ: −69.2 (s, CF_3). Mass spectrum (based on ^{187}Re) *m*/*z*: 474 [M$^+$]; 455 [M$^+$–F]; 446 [M$^+$–CO]; 418 [M$^+$–2CO]; 405 [M$^+$–CF_3]; 390 [M$^+$–3CO]. Anal. Calc. for $C_{12}H_6O_5F_3Re$: C 30.45, H 1.28%; Found: C 30.76, H 1.32%;
(b) Synthesis of (η^5–$C_5H_4COCH_2COCH_3$)Re(CO)$_3$ (**1b**): Complex **1b** was obtained following the same procedure for **1a**, but using $CH_3CO_2CH_2CH_3$. It was isolated as a pale yellow solid 47 mg (42%). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2030 (s), 1937 (vs), 1606 (w). ^{1}H NMR ($CDCl_3$), enol/keto ratio ~10:1. Enol tautomer; δ: 2.10 (s, 3H, CH_3); 5.44 (t, 2H, $J = 2.4$ Hz; C_5H_4); 5.69 (s, H, CH); 6,03 (t, 2H, $J = 2.4$ Hz; C_5H_4); 15.39 (s, an, H, OH). Keto tautomer; δ: 2.29 (s, 3H, CH_3); 3.71 (s, 2H, CH_2); 5.43 (t, 2H, $J = 2.4$ Hz; C_5H_4); 6.00 (t, 2H, $J = 2.4$ Hz; C_5H_4). ^{13}C {^{1}H}RMN ($CDCl_3$) δ: 24.1 (s, CH_3); 85.0 (s, C_5H_4); 86.7 (s, C_5H_4), 95.7 (s, C_{ipso} C_5H_4); 96.2 (s, CH); 182.8 (s, $COCH_3$); 188.5 (s, CO); 192.0 (s, Re–CO). Mass spectrum (IE, based on ^{187}Re) *m*/*z* : 420 [M$^+$]; 392 [M$^+$–CO]; 364 [M$^+$–2CO]; 336 [M$^+$–3CO]. Anal. Calc. for $C_{12}H_9O_5Re$: C 34.37, H 2.16%; Found: C 34.69, H 2.07%;
(c) Synthesis of (η^5–$C_5H_4COCH_2COC_6H_5$)Re(CO)$_3$ (**1c**): The complex **1c** was prepared by a similar procedure to that described for **1a**, but using $C_6H_5CO_2CH_2CH_3$. However, an additional purification was needed to separate **1c** from the starting acetylcyrhetrene and the excess of ethylbenzoate. The reaction mixture was stirred with a saturated solution of $CuAc_2$ in ethanol. After 1 h, water 10 mL was added and then the copper complex of **1c** was extracted with CH_2Cl_2 (2 × 30 mL). The solvent of the organic layer was pumped off and the green solid formed was washed with hexane and redissolved in CH_2Cl_2, and treated with an aqueous HCl solution 6 M (20 mL) under stirring for 1 h. The organic layer was dried over sodium sulfate, filtered through Celite and the solvent removed under reduced pressure, affording a yellow pale solid. Crystallization from hexane at −18 °C gave **1c** as white microcrystals. 13 mg, 26% yield. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2030 (s), 1937 (vs), 1606 (w). ^{1}H NMR ($CDCl_3$) enol/keto ratio ~10:1. Enol form; δ: 5.44 (t, 2H, $J = 2.5$ Hz; C_5H_4); 6.09 (t, 2H, $J = 2.5$ Hz; C_5H_4); 6.29 (s, CH); 7.48 (t, 2H, $J = 7.3$ Hz; C_6H_5); 7.55 (t, H, $J = 7.3$ Hz; C_6H_5); 7.88 (d, 2H, $J = 7.8$ Hz; C_6H_5) 16.03 (s, br, H, OH). Keto form; δ: 4.25 (s, 2H, CH_2); 5.41 (t, 2H, $J = 2.5$ Hz; C_5H_4); 6.07 (t, 2H, $J = 2.5$ Hz; C_5H_4). ^{13}C {^{1}H}RMN ($CDCl_3$)δ: 85.0 (s, C_5H_4); 86.9 (s, C_5H_4); 92.8 (s, C_{ipso} C_5H_4); 96.1 (s, CH), 126.9 (s, C_6H_5); 128.7 (s, C_6H_5); 132.6 (s, C_6H_5); 134.2 (s, C_{ipso} C_6H_5); 181.8 (s, COC_6H_5); 184.2 (s, CO); 192.1 (s, Re–CO). Mass spectrum (IE, based on ^{187}Re): *m*/*z* 482 [M$^+$]; 454 [M$^+$–CO]; 398 [M$^+$–3CO]. Anal. Calc. for $C_{17}H_{11}O_5Re$: C 42.41, H 2.30%; Found: C 42.67, H 2.40%.

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[9] *Crystal data for* **1b** $C_{12}H_9O_5Re$, $M =$ 419.39, tetragonal, space group $P4_32_12$, $T =$ 298 K, $a = 10.0029(7)$ Å, $b = 10.0029(7)$ Å, $c = 24.966(2)$ Å, $V = 2498.1(3)$ Å^3, $Z = 8$, $F_{000} = 1568$, GOF = 1.077, $D_{calcd} =$ 2.230 g cm^{-3}, crystal size 0.24 × 0.19 × 0.18 mm. Data were collected on a Bruker Smart Apex diffractometer equipped with a CCD area detector, using graphite monochromated Mo Kα radiation ($\lambda =$ 0.71073 Å). A total of 21106 reflections were collected, of which 2908 reflections are independent [R(int) = 0.0491]. Absorption correction was performed using the multi-scan method. The structures were solved by Patterson method and refined by full-matrix least squares on F^2. The final $R_1(wR_2)$ factors were 0.0330(0.0735) for reflections $I > 2\sigma(I)$ and 0.0418(0.0766) for all the reflections.

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