The action of lithium perchlorate in ether on (allyl propargyl ether) hexacarbonyldicobalt complexes

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Received 10 June 1997

Abstract

Lithium perchlorate in dry ether can promote cyclopentenone formation from (alkyne)dicobalt hexacarbonyls plus alkenes (Khand reaction), but in lower yield than other promoters. However, in the case of allyl propargyl ether derivatives, these metal-free products are accompanied by three types of trinuclear cobalt carbonyl complexes, whose structures have been established by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Cobalt; Alkyne complexes; Allyl propargylic ethers; Lithium perchlorate; Rearrangements

1. Introduction

The ability of lithium perchlorate, as a saturated solution in dry ether, to promote reactions which require a highly polar medium is well recognised, chiefly as a result of studies by Grieco et al. [1–3]. At the same time, the use of highly polar solvents has been recognised as one of several modifications of the Khand reaction [4], which allow lower temperatures and shorter reaction times to be used, while also giving much better yields [5]. This communication describes the results of our attempt to establish whether lithium perchlorate/ether would also be a useful promoter of Khand reactions.

2. Results and discussion

Under the conditions chosen, lithium perchlorate/ether did indeed promote the reaction of hexacarbonyl(phenylethyne) dicobalt and allyl alcohol (Scheme 1). But the low yield of the expected cyclopentenone gave little hope that this procedure could be

optimised to the point where it would be adopted in preference to established methods. However, when an intramolecular example, the previously well-studied bi-cyclisation of the allyl propargyl ether complex (2a) [4,6,7] (Scheme 2) was tried, the results proved to be unexpected.

On chromatography of the reaction mixture (after all the starting complex (2a) had disappeared and lithium perchlorate had been extracted into water), a number of highly coloured organocobalt complexes were eluted with less polar solvents than required to elute the expected bicyclic enone. Several of these complexes were unstable under the isolation conditions and/or present in trace amounts. But three fractions yielded stable black crystalline complexes. Their colour and character-istic infrared peaks in the carbonyl stretching region readily placed them in the group of trinuclear complexes of the general structure (3) [8] and this was fully confirmed by mass spectrometry of the most abundant complex.

This class of compounds was extensively studied 25 years ago, chiefly by Seyferth et al. at MIT [9] and by Robinson et al. in New Zealand [10]. Whereas they are usually most conveniently prepared from the trihalides, RCX_3, the first identified examples of this type were obtained from terminal alkyne–dicobalt complexes (1) on treatment with sulfuric acid in methanol [11]. When the propargyl–ether complex (2a) was treated in this

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Scheme 1.

(2a-d)

(a) R = R' = H
(b) R = H, R' = Me
(c) R = R' = Me
(d) R,R' = (CH₂)₅
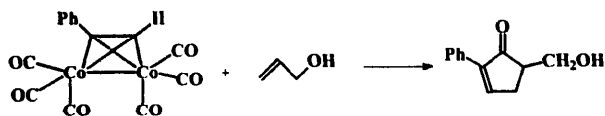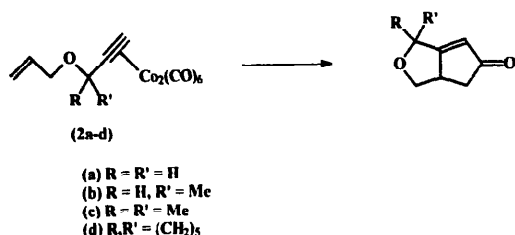
Scheme 2.

way, it gave the known and readily identifiable C–ethyl complex (4) [8–10], which was not a product of the LiClO₄ reaction. It must have arisen from reductive cleavage of the ether moiety. None of our new complexes were found and they were also absent when, as choice of a typical Lewis acid, we selected BF₃-etherate to react with complex (2a).

The mass spectrum of our most abundant trinuclear complex showed that it had a pendent group ($R = C_5H_7O$) and its proton NMR spectrum consisted of three (somewhat broadened) peaks in the ratio 2:2:3. These facts lead uniquely to structure (5a) and crystallography provided elegant confirmation of this assignment. The X-ray structure [2] is shown in Fig. 1. All structural parameters for the (μ^3-C)Co₃(CO)₉ fragment are as expected [8–10] and the C(11)–C(14) distance, 1.337(8) Å, shows unequivocally that the position of the double bond in the organic fragment is as deduced from the ¹H NMR spectrum. The five-membered ring is planar.

Repetition of the reaction focused our attention on a second, slightly less polar complex which was only just

eluted ahead of complex (5a) (using a flash silica column). Its ms identified it as an isomer of (5a) and its proton NMR spectrum was much more complex. We have not as yet been able to obtain high quality crystals, but the best available, while unsuitable to give the highest precision data, revealed the structure unambiguously to be (6a) [3] and is shown in Fig. 2. The bicyclic nature of the product is consistent with the available spectroscopic data. The fused cyclopropyl group induces puckering in the five-membered ring (in contrast to (5a)) and all structural parameters are typical of such a species.

Three homologues of the starting complex, the methyl (2b), dimethyl (2c) and pentamethylene complex (2d) gave similar product mixtures, albeit in different proportions. The yield of each complex was typically in the range 5–15%. The least polar trinuclear complex obtained from the precursor (2a) was initially disregarded because of its low abundance. But its analogue was a prominent and readily crystallisable product when the methyl substituted propargyl ether complex (2b) was subjected to the lithium perchlorate reaction. X-ray crystallography allowed its identification as the compound (7b) with the methyl group (R') in the E configuration about the olefinic group X (X = CH=CHMe). Its formation must involve the cleavage of the allyloxy grouping. We have also determined the crystal structure of the monocyclic product (5b) in this series and details of these compounds and their structures will be reported at a later date.

A very recent communication on the reaction of allyl propargyl ether with methyl(pentacarbonyl)manganese [12] reports cyclisation to curiously similar methylene tetrahydrofurans (cf. (5)) and a cyclopropa-tetrahydro-

² Crystal data for (5a): C₁₅H₇Co₃O₁₀, M_r = 524.01, orthorhombic, space group Pna2₁ (No. 33), a = 15.830(1), b = 12.750(2), c = 9.393(2) Å, U = 1895.8(9) Å³, Z = 4, ρ_{calc} = 1.836 g cm⁻³. Black prismatic crystals were grown by slow evaporation of a methanol solution of the complex. A crystal (0.8×0.25×0.25 mm) was mounted on a glass fibre on a Rigaku AFC7S diffractometer and the unit cell determined from 23 accurately centred reflections (35.7 ≤ 2θ ≤ 43.7°). 3131 Data were collected at room temperature using graphite monochromated Mo K_α radiation (λ = 0.71069 Å) in ω-2θ mode. 2θ_max = 59.9°. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Data were reduced and Lorentz, polarisation and absorption (empirical psi-scans; trans. factors 0.91–1.00) corrections were applied. The structure was solved by direct methods and expanded using Fourier techniques. Full matrix least-squares refinement (on F) with all non-H atoms anisotropic led to R = 0.033, R_w = 0.038, GOF = 1.16, for 1942 reflections with I > 2σ(I) and 253 parameters. Residual electron density was in the range 0.33 to −0.28 eÅ⁻³.

³ Crystal Data for (6a): C₁₅H₇Co₃O₁₀, M_r = 524.01, monoclinic, space group P2₁/c (No. 14), a = 7.980(2), b = 30.087(9), c = 15.884(3) Å, β = 100.04(2)°, U = 3754(1) Å³, Z = 8, two independent molecules in the unit cell. ρ_{calc} = 1.854 g cm⁻³. Black plates were grown by slow evaporation of a solution of the complex in methanol. A crystal was mounted on a glass fibre and 4490 data collected as described above for (5a). 4126 unique reflections were subject to the usual L_p correction. Due to the crystal size, diffraction was weak and reflections could only be measured to 2θ_max = 42°. As a result, there were insufficient reflections for a fully anisotropic refinement. Nevertheless, isotropic refinement (on F) led to a chemically reasonable model. At this stage an absorption correction was calculated (DIFABS, trans. factors: 0.79–1.00) and further refinement with only the Co atoms anisotropic resulted in a model with R = 0.070, R_w = 0.075, GOF = 1.64 for 1813 unique reflections with I > 1.5σ(I) and 256 parameters. Residual electron density was in the range 0.86 to −0.58 eÅ⁻³. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-100312. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: Int Code+-1223-336033; email: deposit@chemcrys.cam.ac.uk).
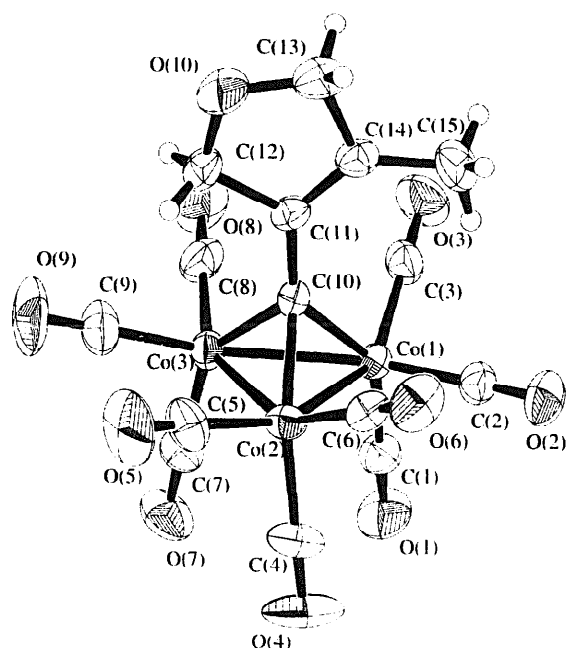
Fig. 1. X-ray crystal structure of (5a) showing the atom numbering scheme and with thermal ellipsoids drawn at the 40% level. Selected bond lengths (Å) and angles (°): Co–Co (av) = 2.466, Co–C$_{CO}$ (av) = 1.804, C–O$_{CO}$ (av) = 1.126, Co(1)–C(10) = 1.906(5), Co(2)–C(10) = 1.952(6), Co(3)–C(10) = 1.905(5), C(10)–C(11) = 1.436(7), C(11)–C(12) = 1.499(8), C(12)–O(10) = 1.380(7), O(10)–C(13) = 1.436(8), C(13)–C(14) = 1.485(8), C(14)–C(15) = 1.482(9), C(11)–C(14) = 1.337(8), Co(1)–C(10)–C(11) = 137.1(4), Co(2)–C(10)–C(11) = 129.0(4), Co(3)–C(10)–C(11) = 130.1(4), C(10)–C(11)–C(12) = 121.6(5), C(10)–C(11)–C(14) = 131.4(5), C(12)–C(11)–C(14) = 107.0(5), C(11)–C(12)–O(10) = 108.0(5), C(12)–O(10)–C(13) = 109.2(5), O(10)–C(13)–C(14) = 105.1(5), C(13)–C(14)–C(15) = 118.5(6), C(11)–C(14)–C(13) = 110.4(6), C(11)–C(14)–C(15) = 131.1(6).
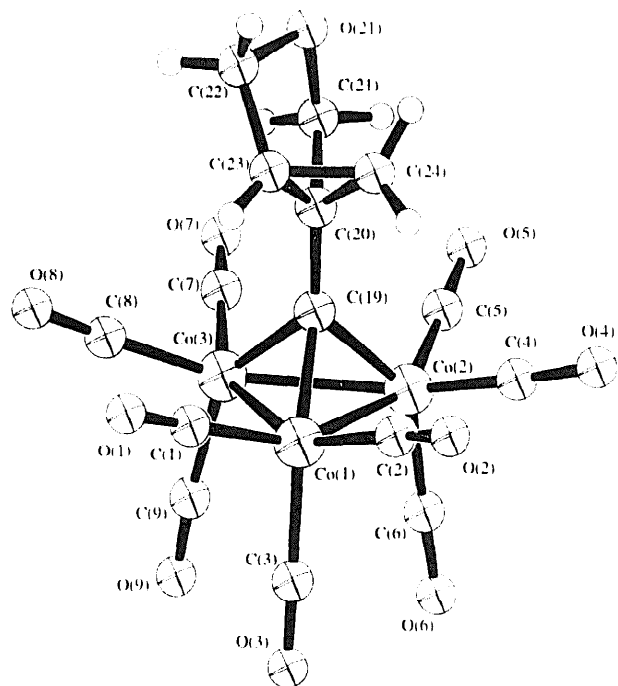

Fig. 2. X-ray crystal structure of one molecule of (6a) showing the atom numbering scheme and the atoms as ideal spheres.

furan (cf. (6)) albeit almost certainly by a quite different mechanism.

With no evidence to suggest how the transformations of di- to trinuclear cobalt complexes occur [8–10], it seems difficult to suggest an overall mechanism. If we consider only the organic portion, we can see that the change from complex (2a) to complex (6a) formally requires cleavage of two cobalt–carbon bonds and formation of two carbon–carbon bonds, e.g., as suggested in the partial structure (8).

Despite the uncertainty regarding its mechanism, the LiClO$_4$/Et$_2$O promoted Khand reaction has shown quite an unexpected rearrangement of the cobalt cluster framework coupled with a truly remarkable intra-molecular cyclisation. Our continuing work on these systems will, therefore, include tests to find whether complex (6a) might be a precursor of its isomer (5a); we will also study the effects of substituting the allyl moiety and replacing the oxygen atom by other atoms or groups.
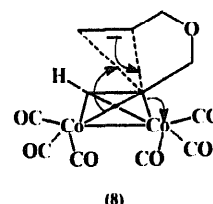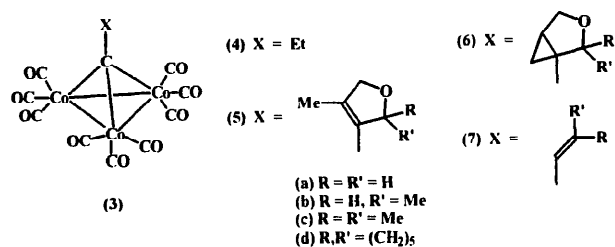
(3)

(4) X = Et

(5) X =

(6) X =

(7) X =

(a) R = R' = H
(b) R = H, R' = Me
(c) R = R' = Me
(d) R,R' = (CH$_2$)$_5$

(8)

Acknowledgements

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