

σ -CUMULENIC TRANSITION METAL COMPOUNDS. REMARKABLY STABLE COBALOXIME COMPLEXES; $(R)_2C=C=C=CHCo(dmga)_2py$

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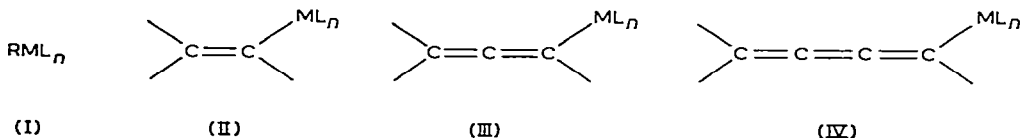
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Summary

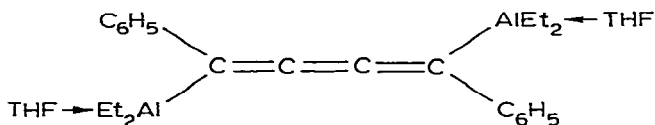
Interaction of $NaCo(dmga)_2py$ with $(R)_2C=C(OSO_2CF_3)C\equiv CH$ in methanol provides a simple route to novel, stable cumulenylyl complexes $(R)_2C=C=C=CHCo(dmga)_2py$, where $R = CH_3$ or C_6H_5 . In the case of $R = H$ the stable ene-yne complex $H_2C=C(C\equiv CH)Co(dmga)_2py$ was isolated. The formation and properties of these complexes are discussed.

Introduction

A large and diverse number of alkyl-transition metal complexes (I) have been investigated. Considerably fewer vinyl-transition metal derivative of type II are known [1] and only a handful of stable σ -bonded metalloallenes (III) have been reported [2]. The next homologous member of the family of unsaturated σ -



bonded organometallic compounds, namely cumulenylyl-transition metal complexes (IV) is, to our knowledge, unknown to date. The only known tetratriene complex is the dialuminum compound V recently reported by Hoberg and



(V)

TABLE I
SUMMARY OF PHYSICAL AND SPECTRAL DATA FOR COMPOUNDS VII AND X

Compound	Yield (%)	M.p. (°C)	IR (cm ⁻¹) ^a	¹ H NMR ^b (δ, ppm)	¹³ C NMR ^c (δ, ppm)	Elemental analysis (Found (calcd.)) (%)	
						C	H
VIIb	11	149-151 (dec.)	2028 (w, C≡C=C=C)	8.6 (m, 2 H) α-pv, 7.7 (m, 1 H) γ-py 7.3 (m, 2 H) β-py, 5.9 (s, 1 H) 2.2 (s, 12 H), 1.9 (s, 3H) 1.8 (s, 3 H)	150.2, 149.5, 137.9 125.3, 164.4, 156.4 109.7, 24.0, 22.6 12.3	12.5 (13.2)	50.72 (51.01)
VIIc	13	157-159 (dec.)	1990 (w, C≡C=C=C)	8.8 (m, 2 H) α-pv 7.3-8.0 (m, 13 H), β + γ-py, ph 6.9 (s, 1 H) 2.1 (s, 12 H)	170.9, 156.7, 150.1 150.0, 138.8, 138.4 138.0, 129.6, 128.3 128.0, 127.0, 126.7 125.4, 118.3, 12.2	9.76 (10.3)	60.89 (60.95)
X	25	183-185 (dec.)	3220 (s, C≡C-H) 2063 (w, C≡C)	8.6 (m, 2 H) α-pv, 7.7 (m, 1 H) γ-py 7.3 (m, 2 H) β-py, 5.1 (s, 1 H) 5.2 (s, 1 H), 3.4 (s, 1 H) 2.1 (s, 12 H)	150.3, 149.5, 139.1 126.0, 128.0, 88.2 82.6, 12.3	13.3 (14.0)	48.94 (48.69)

^a KBr pellets, ^b CDCl₃ int. TMS, ^c VIIIb and VIIc in CDCl₃, X in DMSO-d₆. ^d By atomic absorption spectroscopy.

coworkers [3]. Therefore, in this paper we wish to report a general and simple method of preparation of a class of remarkably stable σ -bonded cumulenyl complexes (IV).

Experimental

General data. All reactions were carried out under argon and solvents were used without purification. Infrared spectra were recorded on a Nicolet FT-IR or a Beckman Acculab 3. Proton NMR spectra were recorded on a Varian EM-390 spectrometer with chemical shifts reported in δ (ppm) vs. TMS. Carbon-13 NMR spectra were recorded on a Varian FT-80 or a Varian XL-100 using CDCl_3 or $\text{DMSO}-d_6$ as the solvent and internal standard. Chemical shifts are reported in δ (ppm) assigning the CDCl_3 to be at 77.20 ppm. All carbon-13 spectra were run with ^1H decoupling. The carbon atoms α to cobalt were not observed due to carbon-cobalt coupling, an effect which has been observed earlier for alkyl-cobaloxime complexes [4]. The starting triflates (VI) were prepared according to literature procedure [5]. The silica gel used for chromatography was dried for 5 h at 0.01 mmHg and then stored under argon.

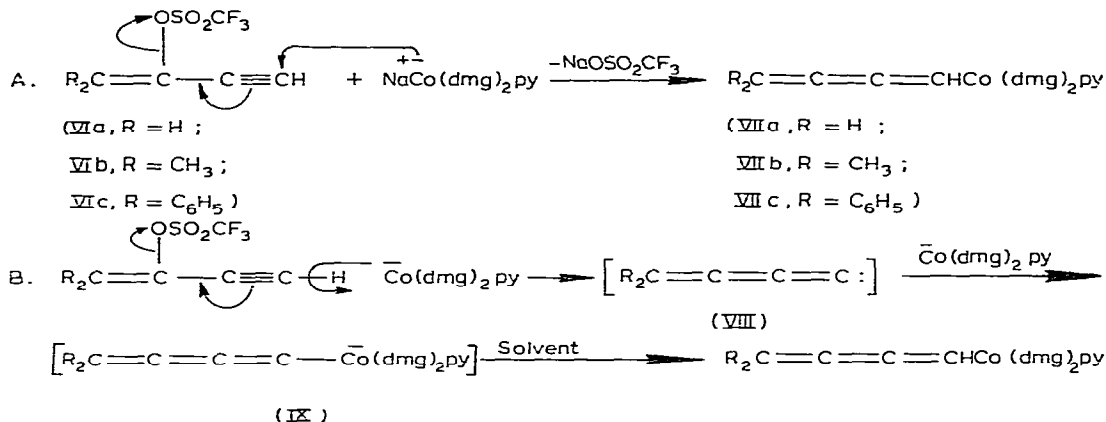
General procedure. A mixture of dimethylglyoxime (2.32 g, 20 mmol) and $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (2.36 g, 10 mmol) was stirred in MeOH (40 ml) for 30 minutes. Aqueous NaOH (0.80 g, 20 mmol in 4 ml H_2O) was added, followed by pyridine (0.79 g, 10 mmol). The solution stirred for 20 minutes and cooled to 0°C . Aqueous NaOH (0.40 g, 10 mmol in 2 ml water) was added, followed by aqueous NaBH_4 (0.10 g, 2.6 mmol in 0.5 ml H_2O) [6]. After stirring the dark blue solution for 5 minutes, 11 mmol of the appropriate triflate was added and the resulting brown solution stirred for another 5 minutes at 0°C . After a quick filtration, 40 ml H_2O was added and the solution cooled to -15°C . The orange precipitate was filtered after 1 h, dried and subjected to column chromatography on silica gel/dry ether using a 30×1 cm column. The solvent from the yellow fraction was evaporated and the residue, a yellow orange solid, was pure by proton NMR but may be recrystallized from a 60/40 mixture of ethanol/water. The yields and the physical and spectral properties of the complexes are summarized in Table 1.

Discussion

The intensity of compounds VII and X follows from their spectral data summarized in Table 1. In particular, cumulenyl complexes VIIb and VIIc show a weak IR absorption at 2028 and 1990 cm^{-1} , respectively, that is highly characteristic of cumulenes [7]. In contrast the parent complex X shows IR absorption at 3220 cm^{-1} for the acetylenic hydrogen and at 2063 cm^{-1} for a conjugated triple bond in accord with the proposed ene-yne nature of this compound. The proton NMR provide further confirmation of the proposed structure. The most characteristic feature of these complexes is their ^{13}C NMR spectra and in particular the signals due to the *sp*-hybridized cumulenenic carbons in the expected [8] 100–170 range for complexes VIIb and VIIc and at 82.6 and 88.2 ppm for the two acetylenic carbons of X. These spectral data are in complete harmony with expectations for these structures as well as with literature data [2,4] on known model compounds $\text{H}_2\text{C}=\text{C}=\text{CHCo}(\text{dmg})_2\text{py}$ and $\text{HC}=\text{CCH}_2\text{Co}(\text{dmg})_2\text{py}$.

It is interesting to note that in contrast to the considerable instability of most cumulenes [7] as well as many organometallic compounds these cumulenyl-cobaloxime complexes are remarkably oxygen insensitive.

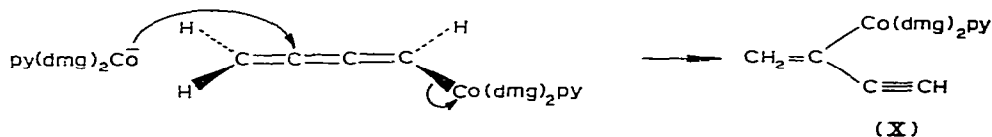
It is interesting to speculate on the mode of formation of these novel complexes. As summarized in Scheme 1 at least two mechanisms may be proposed.



SCHEME 1

Path A involves an S_N2' type displacement by the cobalt anion on the acetylenic carbon with concomittant loss of the triflate leaving group and direct formation of the cumulenyl complex. In mechanism B the cobalt anion acts as a base forming the known [9] extended unsaturated carbene VIII. Carbene VIII subsequently gets trapped by another anion and the resultant ylide IX is protonated by solvent to give the final product VII. Although we have no direct evidence, mechanism A involving an S_N2' type displacement, well preceded [2] in the preparation of the σ -allenyl complexes III from propargyl precursors, seems more likely than involvement of unsaturated carbene VIII as such carbenes may not survive the present reaction conditions [9].

Formation of ene-yne complex X in the case of the parent system VIa may occur by a number of pathways, including a possible direct displacement of the triflate anion by nucleophilic attack of the Co anion upon the starting vinyl triflate VIa. However, this seems unlikely as such S_N2 type vinylic displacements are extremely unfavorable and virtually unprecedented [10]. A much more likely possibility is a rapid attack of a second anion upon the initially formed cumulenyl complex VIIa [2,11]. Such an attack is precluded in the case of the dimethyl VIIb and diphenyl VIIc compounds by steric factors as the



approaching nucleophile and the β -substituents by necessity must lie in the same plane. Finally, some type of a direct intramolecular 1,3-cobalt shift in the initially formed parent cumulenyl adduct VIIa may also account for the formation of the ene-yne complex X in the case of the parent system.

In conclusion, anionic cobaloxime complexes readily interact with α -ethynylvinyl triflates (VI). The reaction is general for the parent, β -alkyl- or β -aryl-substituted ethynylvinyl triflates. In the case of alkyl- and aryl-substituted systems novel cumulenyl complexes VIIb and VIIc result most likely via an S_N2' type reaction between the cobalt anion and the corresponding triflate. The parent compound VIIa does not survive the reaction conditions but is rapidly converted to a new ene-yne complex X. Both cumulenyl complexes VIIb and VIIc as well as the ene-yne complex X are remarkably stable and oxygen insensitive. The generality of such cumulenyl σ -transition metal complex formation involving other metal anions as well as even more extended diynylvinyl systems together with the chemistry of these novel complexes is under active investigation and will be the subject of future reports.

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