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α-Substituted Boron Difluoride Acetylacetonates

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Abstract—By treatment of α-substituted acetylacetone derivatives with boron trifluoride etherate a series of earlier unknown boron difluoride complexes is obtained. The series includes binuclear complexes containing boron in the chelate fragment connected via sulfur or selenium atom. Gas chromatographic and spectral characteristics of the obtained compounds were investigated. By means of chromato-mass spectrometry their reaction with hydrazine in acidic and alkaline media was studied.

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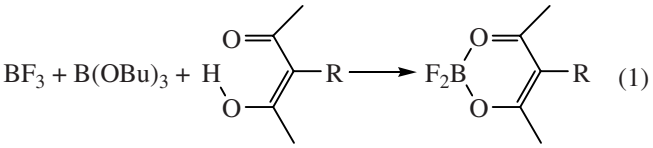
Boron difluoride acetylacetonates possessing a substituent at the central carbon atom of the chelate ring were poorly studied so far. The data were published on complexes containing α-substituent in the acetylacetone fragment: chlorine or bromine [1], alkyl or aryl groups [2]. This situation partly originated from the impossibility to employ the reactions of electrophilic substitution that are widely used for the synthesis of substituted metal diketonates [3] to the preparation of substituted boron difluoride complexes. The preparation of substituted boron difluoride acetylacetonates by template synthesis from acetic anhydride, α-substituted ketone, and boron trifluoride seems hardly feasible due to the possibility of various side processes [2]. Therefore we applied to the preparation of new boron difluoride acetylacetonates chelating with the acetylacetone α-substituted derivatives.



(1)

I–XV **XVI–XXX**

R = Cl (**I, XVI**); Br (**II, XVII**); I (**III, XVIII**); NO_2 (**IV, XIX**); OMe (**V, XX**); $OC(O)CH_3$ (**VI, XXI**); OC(O)H (**VII, XXII**); $OS(O)_2Ph$ (**VIII, XXIII**); SCN (**IX, XXIV**); SEt (**X, XXV**); SPh (**XI, XXVI**); SCH_2Ph (**XII, XXVII**); –S– (**XIII, XXVIII**); –SS– (**XIV, XXIX**); –SeSe– (**XV, XXX**).

By treatment of diketones **I–XV** with the mixture of boron trifluoride etherate and butyl borate we prepared in good yield complexes **XVI–XXX**.

It is opportune to carry out reaction (1) in ether, although with liquid diketones it can be performed without a solvent. In most cases this reaction proceeds with heat evolution. With large amounts of reagents a self-heating can lead to tarring of the reaction mixture. Yields of the formed complexes little depend on the presence of solvent (Table 1). The only exclusion is the synthesis of complex **XXII** that contains formyloxy group. This compound we obtained in a low yield and only in a process without solvent. The nearest analog of the formyloxyacetylacetone, the acetoxyacetone, forms borofluoride chelate in high yield in any conditions applied. Earlier we have noted that formyloxy-substituted metal acetylacetonates could not be obtained in reaction of diketone **X** with copper(II), aluminum(III), and chromium(III) ions [4]. One of the reasons probably preventing formation of formyloxy-substituted acetylacetonates was their low stability, as we demonstrated by an example of complex **XXII** that differed from the other boron difluoride complexes we synthesized by its extremely low stability.

We succeeded in detection by means of gas chromatography of an intermediate compound formed in the reaction of boron trifluoride with disulfide

Table 1. Method of preparation, yield, physical and analytical characteristics of $F_2B(acacR)$, compounds **XVI–XXX**

Comp. no.	R	Preparation method	Yield, %	mp, °C[a]	Color	Found C, %	Formula	Calculated C, %
XVI	Cl	*a*	25	73.5–75 (hexane)	colorless	32.80	$C_5H_6BClF_2O_2$	32.93
XVI	Cl	*b*	78	73.5–75 (hexane)	colorless			
XVII	Br	*b*	95	109–110[b] (hexane)	colorless	26.55	$C_5H_6BBrF_2O_2$	26.48
XVIII	I	*a*	28	151–153 (ether)	yellow	22.21	$C_5H_6BF_2IO_2$	21.93
XVIII	I	*b*	26	151–153 (ether)	yellow			
XIX	NO_2	*a*	60	62–65 (ether–hexane)	colorless	31.27	$C_5H_6BF_2NO_4$	31.13
XIX	NO_2	*b*	45	59–63.5 (ether–hexane)	colorless			
XX	OMe	*a*	60	64.5–65.5 (ether–hexane)	colorless	40.56	$C_6H_9BF_2O_3$	40.50
XXI	OAc	*a*	89	113–115 (ether)	colorless	40.94	$C_7H_9BF_2O_4$	40.82
XXI	OAc	*b*	61	112.5–114 (ether)	colorless			
XXII	OFr	*a*	–	–	–			
XXII	OFr	*b*	4	–	colorless			
XXIII	$OS(O)_2Ph$	*a*	64	125–127 (benzene–hexane)	colorless	43.55	$C_{11}H_{11}BF_2O_5S$	43.45
XXIV	SCN	*a*	78	133–142, decomp. (3×ether)	yellow-brown	35.28	$C_6H_6BF_2NO_2S$	35.16
XXV	SEt	*a*	80	12–13 (hexane)	colorless	40.33	$C_7H_{11}BF_2O_2S$	40.42
XXVI	SPh	*a*	74	72–73 (hexane)	light yellow	51.71	$C_{11}H_{11}BF_2O_2S$	51.59
XXVII	SBz	*a*	75	92–93.5 (hexane)	colorless	53.52	$C_{12}H_{13}BF_2O_2S$	53.36
XXVIII	S	*a*	92	174–176 (benzene)	colorless	37.21	$C_{10}H_{12}B_2F_4O_4S$	36.86
XXIX	S_2	*a*	93	198–210 (benzene)	colorless	33.62	$C_{10}H_{12}B_2F_4O_4S_2$	33.56
XXX	Se_2	*a*	71	198–205, decomp. (benzene)	grey-green	27.02	$C_{10}H_{12}B_2F_4O_4Se_2$	26.59

[a] Solvent in recrystallization. [b] Published 108°C [1].

tetraketone **XIV**. In the reaction mixture appeared and later disappeared a volatile compound whose mass spectrum corresponded to a formula $F_2B(acacSSacacH)$.

Complexes **XVI–XXVII** are low-melting crystalline substances well soluble in chloroform, benzene, THF and moderately soluble in hexane. The binuclear complxes **XXVIII–XXX** demonstrated a lower solubility. In contrast to mononuclear complexes, they are sparingly soluble in benzene and ether and possess higher melting points. The ethylthio-substituted complex **XXV** under normal conditions is colorless liquid readily crystallizing at cooling.

Principal analytical characteristics of compounds **XVI–XXX** are listed in Table 1.

Among the compounds we obtained the formyloxy-substituted complex **XXII** is the less stable and substantially decomposes at low temperature (0°C) in 2-3 days. Nitro-substituted chelate **XIX** can be kept at cooling for 2–3 weeks. Acetoxy-substituted complex **XXI** decomposes partially within one year storage. Other chelates do not decompose noticeably at prolonged keeping.

Mononuclear chelates (compounds **XVI–XXII** and **XXIV–XXVII**) are volatile enough for studying them by gas chromatography. Chromatograms of these compounds besides the peak of main substance contain one-two peaks of diketone forming the complex. Hence, in the evaporator of the chromatograph the complexes suffer partial decomposition. The relative intensity of the diketone peak depends on the solvent used, the injector temperature, and the purity of the complex. Under the conditions that we commonly used (solution in chloroform, injector temperature 280°C) the intensity of the diketone peak is 5–7% of that of the main peak. With solutions in alcohol the chromatograms contain only the diketone peaks while those of chelates are totally absent.

The chromatograms of diketones **II**, **V–VII** obtained on a non-polar phase in capillary column contain two separate peaks. Mass spectra of these peaks are similar and correspond to the respective diketone empirical formula. In the mass spectra of components with large retention time the peaks of molecular ions are stronger. It may be assumed that appearance of two separate peaks reflects separation of ketone and enol tautomers.

Complex **XXIII** that contains phenylsulfonate group decomposes considerably when subjected to chromatography. The chromatogram of this compound contains a strong "hump" corresponding to the decomposition products. The diketone and boron chelate peaks are of low intensity and partially are overlapped by the peaks of the decomposition products. The unambiguous identification of the latter can be achieved only by application of mass spectrometry.

Binuclear complexes cannot be studied by GLC, probably due to low volatility.

IR spectra of the obtained compounds are typical of boron difluoride acetylacetonates (Table 2). It is commonly suggested that boron fluoride chelates exhibit two strong bands in the region of 1600–1450 cm^{-1} due to vibration of C=O and C=C bonds in the chelate ring [5]. For sulfur-containing complexes **XXVI-XXVIII** we observed in the region of 1600–1450 cm^{-1} three bands: In spectra of these compounds additionally appears a high-frequency band of low intensity. In the spectra of other complexes it can be seen as a bend. Hence, the spectra of boron difluoride substituted acetylacetonates contain three bands in the region of 1600–1450 cm^{-1} belonging to vibrations of the bonds C=O (chelate) and C=C. Intensity of these bands decreases when frequency increases. In the most of studied spectra two main bands are 70–80 cm^{-1} distant. One exclusion is nitro-substituted chelate displaying the bands of C=O and C=C vibrations almost as close as in the unsubstituted acetylacetonate.

Alongside the adsorption bands due to vibrations of F_2B(*acac*) fragment the spectra contain characteristic bands of respective substituents (Table 2).

^{1}H NMR spectra of compounds **XVI-XXX** are consistent with the expected structures (Table 2). The complex formation with boron fluoride group shifts signals of β-methyl groups of the parent acetylacetones by 0.2–0.3 ppm downfield, in agreement with the data of [6]. In all the complexes including dimeric chelates **XXVIII–XXX** the methyl groups are equivalent and resonate as one peak.

Mass spectra of complexes **XVI–XXVII** contain peaks of molecular ions with isotopic composition corresponding to calculated ones. The most common direction of their fragmentation is ejecting fluorine atom and methyl group. Spectra of halo-substituted acetylacetonates **XVI–XVIII** show that this route of fragmentation for these compounds predominates. For the complexes with more complicated substituents these reactions become less significant, and fragmentation route depends on the substituent nature (Table 2).

The main band in UV spectra of boron difluoride substituted acetylacetonates is that corresponding to π_3–π_4 transition (Table 3). The introduction of oxygen-

Table 2. Data on IR, ^{1}H NMR, and mass spectra of boron difluoride β-diketonates F_2B(*acac*-R)

R	ν, cm^{-1}			δ, ppm		*m*/*z* (intensity, %, $[ion]^+$)
	C=O C=C	B–F B–O	other bands	CH_3 (chelate)	R	
H	(1574) 1556	1150 1088	812 – $C_α$-H	2.21[a] s (6H)		
Cl	1568 1495	1175 1109		2.51[b] s (6H)		184, 183, 182 (22%, 10%, 65%, $[M]^+$), 169, 168, 167 (22%, 14%, 100%, $[M–CH_3]^+$), 165, 164, 163 (24%, 21%, 53%, $[M–F]^+$), 55 (87%)
Br	1560 1491	1172 1081		2.56[c] s (6H)		228, 227, 226 (71%, 25%, 74%, $[M]^+$), 213, 212, 211 (89%, 30%, 95%, $[M–CH_3]^+$), 209, 208, 207 (38%, 34%, 44%, $[M–F]^+$), 79 (20%), 55 (100%)

Table 2. (Contd.)

R	ν, cm^{-1}			δ, ppm		*m/z* (intensity, %, $[ion]^+$)
	C=O C=C	B–F B–O	other bands	CH_3 (chelate)	R	
I	1555 1481	1161 1083		2.67 s (6H)		274 (100%, $[M]^+$), 259 (59%, $[M–CH_3]^+$), 255 (18%, $[M–F]^+$), 208 (14%), 127 (26%, $[I]^+$)
NO_2	1581 1545	1183 1065	1450, 1481 – N–O (NO_2), 841 – $C_α$–N (NO_2)	2.71 s (6H)		193 (38%, $[M]^+$), 176 (31%), 174 (46%, $[M–F]^+$), 127 (100%, $[M–COCH_3–H]^+$), 117 (22%), 53 (55%)
OMe	1595 1511	1184 1060	1236 – $C_α$–O–Me	2.38 s (6H)		178 (100%, $[M]^+$), 163 (21%, $[M–CH_3]^+$), 159 (53%, $[M–F]^+$), 135 (49%, $[M–COCH_3]^+$), 133 (100%), 120 (31%), 92 (33%)
OAc	1598 1529	1189 1067	1786, 1766 – C=O ($OOCCH_3$), 891	2.29 s (6H)	2.34 s (3H, $OOCCH_3$)	206 (17%, $[M]^+$), 187 (31%, $[M–F]^+$), 164 (35%, $[M–OCCH_2]^+$), 149 (148, $[M–OCCH_2–CH_3]^+$), 145 (94%, $[M–OCCH_2–F]^+$), 144 (100%, $[M–OCCH_2–HF]^+$), 115 (36%), 101 (36%), 77 (35%)
OFr	1597 1519	1191	1740 – C=O (OOCH)	2.40 s (6H)	8.02 s (1H, OOCH)	192 (11%, $[M]^+$), 173 (31%, $[M–F]^+$), 164 (67%, $[M–CO]^+$), 149 (97%, $[M–CO–CH_3]^+$), 145 (65%, $[M–CO–F]^+$), 144 (100%, $[M–CO–HF]^+$), 129 (40%), 101 (32%), 93 (33%), 55 (97%)
$OS(O)_2Ph$	1593 1516	1200 1072	824, 781, 760, 651, 620, 599 – SO_3Ph	2.11 s (6H)	7.66–7.96 m (5H, Ph)	304 (7%, $[M]^+$), 285 (9%, $[M–F]^+$), 163 (41%, $[M–SO_2Ph]^+$), 144 (53%, $[M–SO_2Ph–HF]^+$), 141 (48%, $[SO_2Ph]^+$), 125 (56%, $[SOPh]^+$), 77 (100%, $[Ph]^+$)
SCN	1560 1478	1176 1116	2164 – SCN	2.74 s (6H)		205 (81%, $[M]^+$), 190 (7%, $[M–CH_3]^+$), 186 (33%, $[M–F]^+$), 114 (26%), 114 (69%)
SEt	1560 1470	1186 1119		2.63 s (6H)	2.60 q (2H, SCH_2, 7.5), 1.24 t (3H, CH_3, 7.5)	208 (62%, $[M]^+$), 193 (1%, $[M–CH_3]^+$), 189 (20%, $[M–F]^+$), 165 (31%, $[M–COCH_3]^+$), 160 (10%, $[M–Et]^+$), 137 (26%), 133 (41%), 99 (100%)
SPh	1581 1559 1469	1190 1125	749 – $C_α$–S	2.56 s (6H)	7.08–7.35 m (5H, Ph)	256 (84%, $[M]^+$), 237 (10%, $[M–F]^+$), 221 (13%), 194 (24%), 169 (20%), 165 (20%), 147 (100%, $[M–SPh]^+$), 121 (23%), 103 (37%), 103 (37%)
SBz			1496 – $C_α$–SBz, 773, 709	2.22 s (6H)	3.67 s (2H, CH_2), 7.08–7.33 m (5H, Ph)	270 (2%, $[M]^+$), 251 (1%, $[M–F]^+$) 91 (100%, $[CH_2Ph]^+$), 65 (17%)
S	1574 1554 1477	1178 1132		2.57 s (12H)		
S_2	1553 1467	1206 1117		2.60 s (12H)		
Se_2	1545 1467	1190 1092		2.64 s (12H)		

[a] Published in [6]. [b] Published 2.50 ppm [7]. [c] Published 2.57 ppm [6].

containing groups to the central carbon atom (compounds **XX**, **XXI** and **XXIII**) and halo-substitution leads to a red shift of this band and to decrease in intensity. Therewith the band intensity falls more when shift to red region is larger. Thus, in the spectrum of iodo-substituted complex whose π_3-π_4 transition band is the most shifted (by 43 nm) the band intensity is approximately a half of that in the spectrum of F_2B(*acac*H).

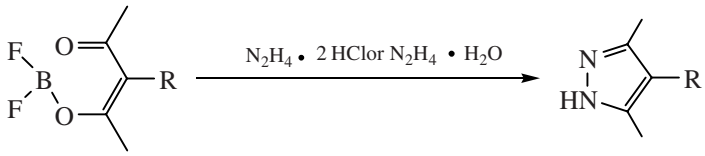
In the spectra of NO_2- and SCN-substituted complexes the band underwent a red shift only by 1-2 nm, but its intensity falls considerably. This behavior fits to the same trend already noted for the substituted acetylacetonates of metals [7]. It is suggested that the presence of two methyl groups retards conjugation of unsymmetrical NO_2 and SCN groups with electronic system of acetylacetonate ring leading in the case of metal acetylacetonates to blue shift of π_3–π_4 transition.

In the spectra of thio-substituted complexes **XXV**, **XXVI,** and **XXVII** the band of π_3–π_4 transition is shifted by 3–9 nm to red region and its intensity falls. Besides, in the spectra of these compounds a band of low intensity is present in the region of 320–400 nm that probably originates from the electron transitions on the sulfur atom (S–S* transition). This band occurs also in the spectra of the corresponding ligands.

The most problematic is the interpretation of the spectra of binuclear complexes **XXVIII** and **XXIX**. Each spectrum of these compounds contains two basic bands approximally equal in intensity. Assuming that spectra of complexes **XXVIII** and **XXIX** are analogous to those of other S-substituted chelates (**XXV**, **XXVI**, and **XXVII**), it is presumable that the long-wave band (338 nm for complex **XXVIII** and 296 nm for complex **XXIX**) is induced by S–S* transition and the short-wave one, by π_3–π_4 transition. This means that the binuclear complexes are the only boron difluoride chelates where introducing of an α-substituent leads to a blue shift of spectral bands.

Electronic spectra of the ethanol solution of the majority of studied compounds differ considerably from the spectra of solutions in hexane and chloroform, and coincide with the spectra of parent diketones. Consequently, the chelates decomposed at dissolution in ethanol. An exclusion were S-substituted acetylacetonates **XXV**, **XXVI**, **XXVII** and F_2B (*acac*H) whose spectra in ethanol were the same as in chloroform and hexane.

Using the obtained compounds we continued a study of the reaction of substituted acetylacetonates with hydrazine by chromato-mass spectrometry [8]. We were interested in a possibility of judging from the structure of the formed pyrazoles on the structure of the parent complexes. Reactions were carried out in ethanol with hydrazine hydrochloride (acidic conditions) or hydrazine hydrate (alkaline conditions) as the reagents. In most cases we observed formation of the respective 4-R-3,5-dimethylpyrazoles.



(2)

Table 3. Electronic spectra of substituted acetylacetone derivatives and boron difluoride acetylacetonates

R	Solvent	H(*acac*-R), λ_{max}, nm (log ε)			F_2B(*acac*-R), λ_{max}, nm (log ε)		
		Ph–Ph*	π_3–π_4	S–S*	Ph–Ph*	π_3–π_4	S–S*
H	chloroform					288 (4.22)	
	hexane					288 (–)	
	ethanol		275 (3.92)			286 (4.15)	
Cl	chloroform		295 (3.80)			317 (4.09)	
	hexane		291 (3.79)			315 (–)	
	ethanol		295 (3.79)			294 (3.84)	
Br	chloroform					320 (4.05)	
	hexane					317 (–)	
	ethanol					296 (3.55)	

Table 3. (Contd.)

R	Раство-ритель	H(*acac*-R), λ_{max}, нм (lgε)			F_2B(*acac*-R), λ_{max}, нм (lgε)		
		Ph–Ph*	π_3–π_4	S–S*	Ph–Ph*	π_3–π_4	S–S*
I	chloroform					331 (3.20)	
	hexane					328 (–)	
	ethanol					285 (–)	
NO_2	chloroform					289 (3.93)	
	hexane				211 (–)[a]; 248 (–)[a]	290 (–)	
	ethanol					276 (3.82)	333 (3.23)
OMe	chloroform					314 (4.11)	
	hexane					313 (–)	
	ethanol					295 (3.93)	
$OOCCH_3$	chloroform		285 (3.41)			304 (4.14)	
	hexane		281 (3.48)			303 (–)	
	ethanol		286 (3.43)			282 (3.81)	
$OS(O)_2Ph$	chloroform	275 (3.82)	281 (3.81)			300 (4.16)	
	hexane	219 (3.94); 274 (3.84)	279 (3.82)			300 (–)	
	ethanol	220 (3.97); 275 (3.76)	283 (3.75)		221 (–); 275 (–)	[280 (–)]	
SCN	chloroform					290 (3.94)	
	hexane					291 (–)	
	ethanol				236 (3.56)[a]	280 (3.78)	
SEt	chloroform		290 (3.91)	[320 (3.15)]		295 (4.01)	335 (3.26)
	hexane		288 (3.85)	[315 (3.06)]	235 (–)[a]	293 (–)	[325 (–)]
	ethanol		290 (3.88)	[318 (3.16)]	235 (3.05)[a]	293 (3.96)	[329 (3.18)]
SPh	chloroform	253 (4.11)	281 (3.90)	330 (3.06)		291 (4.04)	356 (3.09)
	hexane	250 (4.07)	279 (3.81)	329 (3.00)	238 (–); [244 (–)]	290 (–)	349 (–)
	ethanol	249 (4.10)	281 (3.90)	328 (3.10)	238 (4.03); 246 (4.04)	288 (3.97)	339 (3.02)
SBz	chloroform		291 (3.83)	[320 (3.05)]		297 (3.93)	[329 (3.20)]
	hexane		291 (3.92)	[310 (–)]		297 (–)	
	ethanol		291 (3.88)	[310 (–)]	216 (4.06)	296 (3.90)	[325 (–)]
S	chloroform		292 (3.86)	338 (3.70)		269 (4.04)	338 (3.88)
	hexane			331 (3.69)	218 (–)[a]	269 (–)	338 (–)
	ethanol		278 (4.06)			–	
S_2	chloroform			290 (4.08)			296 (4.09)
	hexane		[254 (–)]	288 (4.10)		246 (–)	295 (–)
	ethanol		[254 (–)]	289 (4.14)		260 (–)	287 (4.07)
Se_2	chloroform		289 (4.09)			279 (4.19)	
	hexane		290 (4.03)			279 (–)	
	ethanol		–			285 (–)	

[a] Not identified.

The pyrazoles are more volatile than the parent boron difluorides complexes. Therefore it was possible to transform non-volatile chelates into the volatile pyrazoles for studying the latter by gas chromatography. We used this technique to confirm the structure of dimeric chelates. At the treatment of compound **XXVIII** with hydrazine hydrochloride we obtained bis-(3,5-dimethylpyrazolyl-4)sulfide, and from compound **XXIX,** bis-(3,5-dimethylpyrazolyl-4) disulfide.

However, in some cases we observed side processes.

At performing the process under acidic conditions, chlorine substitution for R group occurs in some cases. Actually, at the treatment with hydrazine hydrochloride of Br-substituted complex **XVII**, in the reaction mixture were detected 4-chloro- and 4-bromo-3,5-dimethylpyrazoles in ca. 2:1 ratio. Formation in small amount of 4-chloro-3,5-dimethylpyrazole was also detected in the case of the phenylsulfo-substituted coomplex **XXIII**. The reactions with complexes **XVIII** and **XXX** were unsuccessful: the liberation of iodine and red selenium ocurred, and the reaction mixture contained in minor amount a volatile substance while 4-iodo-3,5-dimethylpyrazole and bis-(3,5-dimethylpyrazolyl-4)diselenide were not found (similar result was obtained in the reaction under alkaline conditions). From complex **XIX**, 4-nitro-3,5-dimethylpyrazole was formed, but in a very small amount. Reaction of hydrazine hydrochloride with SCN-substituted complex **XXIV** was extremely complex. Depending on the reagents ratio and reaction duration the formation of 3 to 6 substances occurred, among which bis-(3,5-dimethylpyrazole-4)disulfide was identified by mass-spectrometry. We failed to establish the structure of remaining substances. 4-Thiocyano-3,5-dimethylpyrazole was not found among the products.

In this reaction under alkaline conditions replacement of R by hydrogen atom can occur due to reducing action of hydrazine. At the treatment of chloro-, bromo- and sulfo-substituted complexes was registered the formation, besides 4-R-3,5-dimethylpyrazols, of dimethylpyrazole in a substantial amount.

EXPERIMENTAL

IR spectra in the region of 4000–400 cm^{-1} were registered on a Spectrum 100 BX-II instrument from KBr pellets. The ^1H NMR spectra were obtained on a Bruker WH 250 instrument with operating frequency 250 MHz from solutions in deuterochloroform with TMS as a reference. Mass spectra were obtained on a gas chromatograph with mass-selective detector. The gas chromatographic study was carried out on the instruments HP 5890 (series II) with flame ionization detector and HP 5890 (series II) with mass-selective detector HP 5971. The chromatographic analysis conditions were as follows: column HP-5MS (HP-5) 30 m × 0.250 mm × 0.25 μ; carrier gas helium (for GS–MS) or argon (for GS-FID); regime of continuous flow; flow rate in the column 0.7 ml min^{-1}. Injector: temperature 280°C; flow distribution 1:20. Temperature program: 1 min at 50°C, temperature raised at a rate 10 deg min^{-1} to 280°C, 20 min at 280°C. Regime of flame ionization detector: temperature 290°C, hydrogen 40 ml min^{-1}, air 300 ml min^{-1}, blowing gas argon, 30 ml min^{-1}. Regime of mass-selective detector: temperature of the conjugation node 280°C, ionization energy 70 eV, total scan in the *m/z* range from 50 to 450, detection delay 2 min.

The diketones used in the work were obtained along the following methods: H*acac*OMe [9], H*acac*$OOCCH_3$ [10], H*acac*SEt, H*acac*EPh [11], $(Hacac)_2S$, $(HacacS)_2$ [12], $(HacacSe)_2$ [13].

H*acac*Cl is obtained by passing chlorine to the stirred mixture of H*acac*H with water (1:3 by volume) at 0°C to achieve the calculated weight gain. The organic layer was many times washed with water, dried over Na_2SO_4 and several times distilled monitoring the product purity by gas chromatography. Yield 50–58%, bp 57–60°C (28–30 mm Hg) (published data: mp 41-44.5°C at14 mm Hg [14]).

H*acac*Br is obtained similarly by adding bromine in 10% excess. The product was used without additional purification. Yield 65–70%. The product contained *acac*Br_2 (8–10%, by GLC).

H*acac*I. To a solution of 15 g of H*acac*H in 100 ml of CCl_4 (anhydrous) at stirring and cooling to –20°C was added dropwise a solution of 13.67 g of ICl in 20 ml of CCl_4. After 10 min stirring, the reaction mixture was washed with water and dried over $MgSO_4$. Solvent was then removed in a vacuum and the residue was kept at 40–50°C and under a vacuum 1–2 mm Hg to remove completely H*acac*H and H*acac*Cl (GLC monitoring), and the product was used without further purification.

H*acac*NO_2. A mixture of 3.52 g of Cu(*acac*$NO_2)_2$, 50 ml of chloroform and 50 ml of 1N sulfuric acid was

shaken to complete dissolution of the chelate. Organic layer was then washed with a fresh portion of acid and afterwards several times with water. After drying the mixture over $MgSO_4$ the solvent was removed in a vacuum at 30–40°C. Residual viscous oil was used without further purification.

H*acac*OOCH. To a mixture of 18 g of H*acac*Cl, 7.36 g of HOOCH and 75 ml of DMFA (anhydrous) at stirring was slowly added 17 g of NEt_3. After 1 h of stirring the reaction mixture was poured to water and then the product was extracted with chloroform. After drying over $MgSO_4$ and removing the solvent, the residue was several times distilled in a vacuum. Finally 5.0 g of colorless liquid with bp 75–77°C (3 mm Hg) was obtained, yield 26%. Chromatogram of the product contains two peaks with the same mass spectra: 144 $[M]^+$, 116 [H*acac*OH]$^+$, 102 $[CH_3C{=}CHO{\cdot}(O)CH]^+$, 74 $[CH_3COCH_2OH]^+$. ^{1}H NMR spectrum: 2.23 s (6H, CH_3); 5.80 s (1H, $CH(Ac)_2$); 8.42 s (1H, HCOO).

H*acac*OS(O)$_2$Ph is obtained similarly to H*acac*OS·$(O)_2$Me [9] (without chromatographic purification). PhI was removed by heating to 100°C under a vacuum of 1–2 mm Hg the residue obtained after distilling off the solvent (GLC monitoring). Mass spectrum: 256 $[M]^+$, 214 $[CH_3COCH_2OS(O)_2Ph]^+$, 143 $[(OH)_2SPh]^+$, 142 $[(HO)(O)SPh]^+$, 141 $[SO_2Ph]^+$, 125 $[SOPh]^+$, 77 $[Ph]^+$. ^{1}H NMR spectrum: 1.96 s (6H, CH_3); 4.53 (1H, $CH(Ac)_2$); 7.55–8.0 m (5H, Ph).

H*acac*SCN. To a solution of 12.5 g of H*acac*H in 100 ml of $CHCl_3$ (anhydrous) at cooling to –10°C and stirring was added 150 ml of a solution of $(SCN)_2$ in $CHCl_3$ (prepared from 38.6 g of $Pb(SCN)_2$ and 5.9 ml of Br_2). After stirring the reaction mixture for 1.5 h it was washed with water and dried over Na_2SO_4. After removing the solvent in a vacuum, the residue was washed with hexane and recrystallized from a benzene–hexane mixture. 11.56 g of beige crystals were obtained (yield 65%). Mass spectrum: 157 $[M]^+$, 142 $[COCH(SCN)COCH_3]^+$, 88 $[CH_3COCHS]^+$.

H*acac*SCH$_2$Ph.is obtained by analogy to H*acac*SPh [11]. Purified by recrystallization from hexane. Yield 70%, mp 52–54°C (published data: mp 55–56°C [15]). Mass spectrum: 222 $[M]^+$, 91 $[PhCH_2]^+$.

General procedure for the prepatation of boron difluoride acetylacetonates. *a*. A mixture of diketone (0.01 mol), boron trifluoride etherate (0.01 mol), tributyl borate (0.01 mol) and 20 ml of anhydrous ether was stirred at heating for 3 h and then the reaction mixture was left overnight at 0°C. The crystals settled were filtered off, washed with ether cooled to –20°C, and dried in air. The filtrate was evaporated by half and left standing again for crystallization. The crystals were combined and recrystallized from a solvent indicated in Table 1.

In the syntheses of compounds **XXVIII–XXX** 0.005 mol of respective diketone was used; repeated recrystallization was not applied.

General procedure for the prepatation of boron difluoride acetylacetonates. *b*. A mixture of diketone (0.01 mol), boron trifluoride etherate (0.01 mol), and tributyl borate (0.01 mol) was left for 24 h at room temperature and then was placed into a freezer (–10°C) for 5–6 days. The crystals formed were filtered off, washed with the ether cooled to –20°C, dried in air and then recrystallized from an appropriate solvent, as shown in Table 1.

General procedure of reaction with hydrazine. A mixture of 20 mg of a complex, 50 mg of $N_2H_4{\cdot}2HCl$, and 2 ml of ethanol was refluxed for 40 min and then poured to water, alkalinized with ammonia to pH = 11–12 and then extracted with 5 ml of chloroform. The chloroform extract was investigated using GLC–MS.

Reaction with hydrazine hydrate was carried out similarly.

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