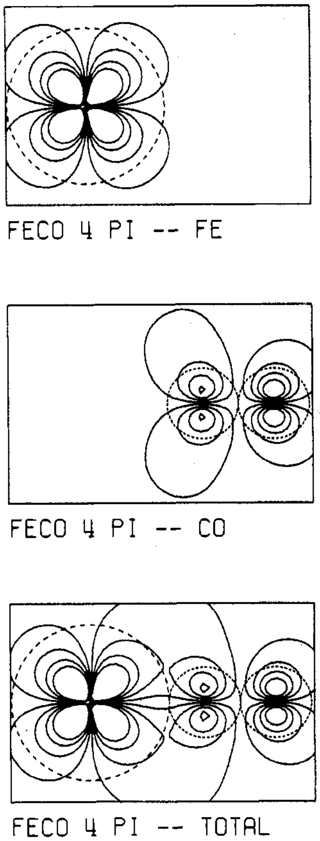


Figure 1. Contour diagrams of the 4π orbital of FeCO. The dashed circles represent the atomic sphere boundaries. Relative contour values, from outermost to innermost, are ±1, ±2, ±4, and ±8, where the contours change sign at the nodes: top diagram, the Fe contribution to the orbital only; middle diagram, the CO contribution to the orbital only; bottom diagram, the total orbital.

fact that there is more carbon than oxygen character in the orbital. This effect is noted in the $3t_{2g}$ orbital of $Cr(CO)_6$. The contour diagram of this orbital (Figure 4 of ref 2) clearly shows that the orbital is primarily CO 2π in character, yet the atomic spheres charge analysis attributes a greater fraction of the charge to the oxygen atoms. By using the PXα method we have circumvented these interpretative difficulties and have arrived at the chemically more reasonable conclusion that metal–ligand back-bonding is an important factor in metal–carbonyl bonding.

Acknowledgment. This research was supported by the National Science Foundation. B.E.B. was the recipient of a Procter and Gamble Fellowship for 1977–1978.

Registry No. $Cr(CO)_6$, 13007-92-6; $Ni(CO)_4$, 13463-39-3.

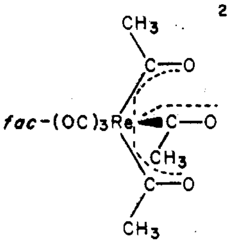
Contribution from the Department of Chemistry,
Vanderbilt University, Nashville, Tennessee 37235

Reactions of Coordinated Molecules. 24. Reaction of the Triacetyltricarbonylrhenate Dianion with the Boron Trihalides

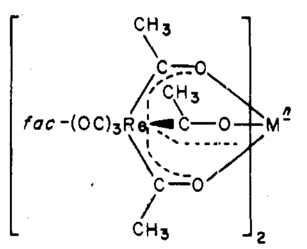
David T. Hobbs and C. M. Lukehart*[1]

Received October 12, 1979

In an earlier communication we reported the preparation of the triacetyltricarbonylrhenate dianion, $[fac\text{-}(OC)_3Re(CH_3CO)_3]^{2-}$ (**1**), and its coordination to Al(III) and Hf(IV) metal ions.[2] This dianion coordinates to metal ions presumably as a symmetrical, tridentate chelating ligand as shown in **2**. Subsequently, we reported a general preparative route for the synthesis of these metalla ligands and their coordination complexes and confirmed their solution structure by demonstrating the existence of geometrical isomerism when one of the alkyl substituents of each ligand is not a methyl group.[3]



1



2

We wish to report that the dianion, **1**, reacts with the boron trihalides at −50 °C, affording the neutral (*fac*-triacetyltricarbonylrhenato)B(X) compounds, **3–6**, where X is F, Cl, Br, or I, in low to moderate yields, and that the boron bromide complex reacts with excess silver tetrafluoroborate in primary alcohol solutions, affording the neutral (*fac*-triacetyltricarbonylrhenato)B(OR) compounds, **9–11**, where R is methyl, ethyl, or *n*-propyl. These boron complexes are related to the (rhena-β-diketonato)BX_2 complexes,[4] and they represent an interesting class of neutral, four-coordinate boron compounds. To our knowledge these are the only known boron complexes having trioxygen, vicinal, bifurcated chelating ligands.[5,6] The tripodal ligand **1** formally contains two anionic oxygen donor atoms and one neutral oxygen donor atom; however, electronic delocalization within the boron complexes of **1** should alter the electronic environment of the boron atom quite considerably from that observed in the classical neutral boron adduct complexes.

Experimental Section

All reactions and other manipulations were performed under prepurified nitrogen at 25 °C unless otherwise stated. Tetrahydrofuran and hexane were dried over Na/K alloy, methylene chloride was dried over phosphorus pentoxide under a nitrogen atmosphere, and all solvents were distilled before use. Methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol were stored over 4A molecular sieves and were purged with nitrogen before use. Boron trifluoride and boron trichloride were purchased from K and K Laboratories (Plainview, NY) and Matheson Gas Products, respectively, while boron tribromide and boron triiodide were purchased from Alfa-Ventron. Silver tetrafluoroborate was purchased from Ozark-Mahoning Co. (Tulsa, OK). Acetylpentacarbonylrhenium was prepared according to an established procedure.[7]

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a JEOL MH-100 NMR spectrometer with Me_4Si as an internal reference. Mass spectra were obtained on a LKB 9000 spectrometer in the direct ionization mode. Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

General Preparation of the Complexes $[fac\text{-}(OC)_3Re(CH_3CO)_3]B(X)$ Complexes, 3–6. A solution of 0.20–0.41 g of acetylpentacarbonylrhenium in 30 mL of methylene chloride was cooled to 0 °C. To this solution was added 2.3 molar equiv of low halide methyllithium (as an ether solution), and the reaction mixture was stirred at 0 °C for 30 min. The solvent was removed at 0 °C under reduced pressure, and the reaction residue was dried at 0 °C under high vacuum for

---

(1) Research Fellow of the Alfred P. Sloan Foundation.
(2) Hobbs, D. T.; Lukehart, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 8357.
(3) Hobbs, D. T.; Lukehart, C. M. *Inorg. Chem.* **1979**, *18*, 1297.
(4) Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1978**, *17*, 201.
(5) Block, D. St. C.; Hartshorm, A. J. *Coord. Chem. Rev.* **1973**, *9*, 219.
(6) Goodwin, H. A. "Chelating Agents and Metal Chelates"; Dwyer, F. P., Mellor, D. P., Eds.; Academic Press: New York, 1964; p 143.
(7) Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, *93*, 901.

0020-1669/80/1319-1811$01.00/0 © 1980 American Chemical Society

2 h to remove all traces of diethyl ether. The reaction residue was then suspended in 30 mL of methylene chloride, cooled to −50 °C, and treated with 1 molar equiv of the appropriate boron trihalide as a gas (BF_3 or BCl_3), liquid (BBr_3), or solid (BI_3). The reaction mixture was stirred at −50 °C for 15 min, followed by warming to 0 °C, and the solvent was removed under reduced pressure. The reaction residue was extracted with 3 × 20 mL of hexane, and following filtration the filtrate was concentrated to ca. 10 mL. The filtrate was placed at −20 °C for 20 h, affording the product complexes as crystalline solids. The detailed characterization of each complex is provided below.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B(F) (3). Yellow crystals (21%), dec pt 151–156 °C. IR ($CHCl_3$): ν(CO) 2036 (s), 1965; $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1447 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.36 (s, CH_3). Mass spectrum: molecular ion at *m/e* 430 with correct isotopic pattern. Anal. Calcd for $C_9H_9O_6BFRe$: C, 25.19; H, 2.11; F, 4.43. Found: C, 25.02; H, 2.04; F, 4.63.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B(Cl) (4). Yellow crystals (23%), dec pt 115 °C. IR ($CHCl_3$): ν(CO) 2035 (s), 1962 (vs); ν(C—O) 1446 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.34 (s, CH_3). Mass spectrum: molecular ion at *m/e* 446 with correct isotopic pattern. Anal. Calcd for $C_9H_9O_6BClRe$: C, 24.25; H, 2.05; Cl, 7.96. Found: C, 24.40; H, 2.24; Cl, 8.14.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B(Br) (5). Yellow crystals (20%), dec pt 105 °C. IR ($CHCl_3$): ν(CO) 2039 (s), 1964 (vs); $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1450 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.34 (s, CH_3). Mass spectrum: molecular ion at *m/e* 490 with correct isotopic pattern. Anal. Calcd for $C_9H_9O_6BBrRe$: C, 22.06; H, 1.85; Br, 16.31. Found: C, 22.13; H, 2.00; Br, 16.74.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B(I) (6). Yellow crystals (13%), dec pt 87 °C. IR ($CHCl_3$): ν(CO) 2034 (s), 1957 (vs); $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1457 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.32 (s, CH_3). Mass spectrum: molecular ion at *m/e* 538 with correct isotopic pattern. Satisfactory elemental analyses could not be obtained for this compound due to the apparent elimination of molecular iodine.

General Preparation of the [*fac*-$(OC)_3Re(CH_3CO)_3$]B(OR) Complexes, 9–11. To a solution of 0.050–0.100 g of [*fac*-$(OC)_3Re(CH_3CO)_3$]B(Br) (5) in 10 mL of the appropriate primary alcohol (methanol, ethanol, or 1-propanol) was added a solution of 4 molar equiv of $AgBF_4$ in 3 mL of the appropriate alcohol. A cream-colored precipitate formed immediately. The reaction mixture was stirred for 30 min, and the solvent was removed at reduced pressure. The reaction residue was extracted with 4 × 10 mL of hexane, and following filtration the filtrate was concentrated to a volume of ca. 1 mL. The filtrate was placed at −20 °C for 20 h, affording the product complexes as yellow solids. The detailed characterization of each complex is provided below.

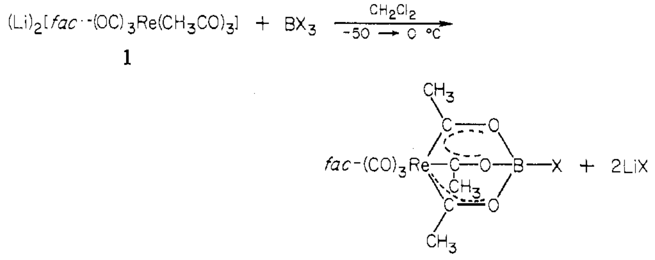
[*fac*-$(OC)_3Re(CH_3CO)_3$]B(OCH_3) (9). Yellow crystals (45%), dec pt 139.5–141.5 °C; IR ($CHCl_3$): ν(CO) 2035 (s), 1960(vs); $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1450 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 6.00 (s, 3, OCH_3), 7.40 (s, 9, CCH_3). Mass spectrum: molecular ion at *m/e* 441 with correct isotopic pattern. Anal. Calcd for $C_{10}H_{12}O_7BRe$: C, 27.22; H, 2.74. Found: C, 27.13; H, 2.76.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B(OCH_2CH_3) (10). IR ($CHCl_3$): ν(CO) 2032 (s), 1957 (vs); $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1457 (w). ^1H NMR ($CDCl_3$): τ 5.70 (q, 2, CH_2), 7.37 (s, 9, CH_3CO), 8.46 (t, 3, CH_3). Mass spectrum: molecular ion at *m/e* 455 with correct isotopic pattern.

[*fac*-$(OC)_3Re(CH_3CO)_3$]B($OCH_2CH_2CH_3$) (11). IR ($CHCl_3$): ν(CO) 2030 (s), 1958 (vs); $\nu(\mathrm{C}\overset{--}{-}\mathrm{O})$ 1455 (w) cm^{-1}. ^1H NMR ($CDCl_3$): τ 5.79 (t, 2, OCH_2), 7.38 (s, 9, CH_3CO), 8.20 (h, 2, CH_2), 8.99 (t, 3, CH_3).

Results and Discussion

The dilithium salt of the *fac*-triacetyltricarbonylrhenate dianion, **1**, reacts with 1 molar equiv of a boron trihalide to afford the boron halide complexes **3**–**6**. These complexes are isolated in ca. 20% yield as yellow solids which decompose thermally from 87 to 151 °C. The thermal stability decreases in going from the fluoride complex to the iodide complex, and the iodide complex, **6**, decomposes in solution and the solid state with the formation of a purple solid which is presumably molecular iodine.



1

3, X = F
4, X = Cl
5, X = Br
6, X = I

The solution-phase infrared spectra for all four boron halide complexes, **3**–**6**, are nearly identical. The terminal carbonyl stretching vibrations are consistent with a *fac*-$(OC)_3Re$ moiety. The A_1 and E modes of these complexes appear at ca. 16 and 37 cm^{-1}, respectively, to higher frequency than the same vibrational modes of the neutral bis(triacetyltricarbonylrhenato)hafnium(IV) complex, **7**. Also, the intraligand acyl $\mathrm{C}\overset{--}{-}\mathrm{O}$ stretching band of the boron halide complexes appears at ca. 15 cm^{-1} to lower frequency than does the same band of the hafnium complex, **7**. These shifts are consistent with the greater Lewis acidity of the B(X) group relative to the Hf(IV) ion in complex **7**. The proton NMR spectra for the boron halide complexes show a singlet at δ 2.66 ± 0.02 in $CDCl_3$ solution for the three equivalent methyl groups indicating idealized C_{3v} symmetry for these complexes in solution. The corresponding resonance in the hafnium complex, **7**, occurs at δ 2.46 (acetone-d_6). This observed shift of the methyl resonance to lower field is also indicative of the greater electronegativity of the B(X) group relative to the Hf(IV) ion in complex **7**.

Mass spectral data were obtained for all four of the boron halide complexes, **3**–**6**. Molecular ion peaks with the correct isotopic pattern were observed for all the complexes, and a comparison of the relative intensities of the $[P-X]^{+\cdot}$ peaks, which were normalized to the base peak of each spectrum, indicates that the B–X bond strength in the parent ion decreases in the order F > Cl ~ Br > I.

Several difficulties that were encountered in the synthesis of the boron bromide and iodide complexes, **5** and **6**, are worth mentioning. If the addition of either BBr_3 or BI_3 is carried out above −30 °C, then a significant amount of the boron chloride complex, **4**, was formed, presumably due to the reaction of these strong Lewis acids with the CH_2Cl_2 solvent affording mixed boron halides, such as BX_2Cl or $BXCl_2$.[8] Also, the presence of LiBr or diethyl ether obtained from the commercial methyllithium solution complicated the synthesis of the boron iodide complex, **6**. The byproducts formed were the boron bromide compound, **5**, and the boron ethoxy complex, [*fac*-$(OC)_3Re(CH_3CO)_3$]B(OEt). Complex **5** was obtained presumably via a halide-exchange reaction with BI_3, while the boron ethoxy complex was probably formed by an ether-cleavage reaction initiated by BI_3. Compound **6** does not react with either LiBr or ether under these reaction conditions, and it can be prepared by excluding these impurities.

The stoichiometric protonation of the dianion **1** using HCl/ether at low temperature to afford a neutral, dienolic tautomer similar to the rhena-β-diketone molecules was attempted.[9,10] Monitoring the reaction by IR showed the disappearance of the two-band pattern in the terminal carbonyl region of **1**, at 1957 and 1857 cm^{-1}, along with the concomitant appearance of a three-band ν(CO) pattern at 2020, 1940, and 1915 cm^{-1}. Also, the proton NMR spectrum showed the disappearance of the methyl resonance of **1** at δ 2.28 along

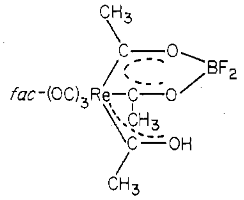
---

(8) A less likely source of chloride ion for generating the mixed halide boron compounds is from any LiCl produced by the reaction of methyllithium with the CH_2Cl_2 solvent. This source would require a significant solubility increase for LiCl in going from −50 to −30 °C.

(9) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365.

(10) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 4368.

with the appearance of two singlets at δ 2.71 and 2.69 of relative intensity of ca. 2:1, respectively. This species may be the expected dienolic tautomer, but the isolation of this compound was not possible due to its low thermal stability (the half-life of this species at 25 °C is ca. 5 min). When a solution of this protonated species is treated with BF_3, the boron fluoride complex **3** is formed along with a very small amount of another yellow product which has been tentatively assigned structure **8** on the basis of the proton NMR, IR and mass spectral data.[11] Complex **8** is a (methyl)(hydroxy)carbenoid analogue to the (rhenaacetylacetonato)BF_2 complex.[4]



8

The boron halide complexes, **3–6**, represent an unusual electronic structure for neutral, four-coordinate boron complexes. The boron atom is bonded formally to two anionic oxygen donor atoms and the anionic halide atom, while the fourth coordination site is occupied by a neutral, oxygen atom which is acting as an adduct molecule. However, the potential for electronic delocalization within the tripodal rhenium ligand apparently makes all three oxygen donor atoms equivalent to one another while maintaining a formal neutral charge on the boron atom. When the high thermodynamic stability of boron–oxygen bonds and the increased stability from the chelate effect of the vicinal, bifurcated rhenium ligand are considered, the boron halide complexes, **3–6**, may exhibit reaction chemistry more typical of a halo triorthoformate ester, $(RO)_3CX$. Since the tripodal rhenium ligand may not be displaced easily by an incoming nucelophile, we expect that these complexes should exhibit primarily S_N1 types of reaction chemistry.

As expected, the Finkelstein substitution reaction was unsuccessful when using complexes **4** and **5**. However, a silver ion assisted, ligand-exchange reaction did occur with complex **5** in alcoholic solution to afford the boron alkoxide complexes, **9–11**. The ligand-exchange reaction does not occur with secondary or tertiary alcohols.

$$\mathbf{5} + AgBF_4 \xrightarrow{ROH} [\mathit{fac}\text{-}(OC)_3Re(CH_3CO)_3]B(OR) + AgBr\downarrow + \{HBF_4\}$$

$$\mathbf{9},\ R = CH_3$$
$$\mathbf{10},\ R = CH_3CH_2$$
$$\mathbf{11},\ R = n\text{-}C_3H_7$$

These boron alkoxide complexes are yellow solids which are extremely difficult to separate from complex **5** by crystallization due to the high solubility of both types of complexes in organic solvents. Only the boron methoxide complex, **9**, could be isolated as an analytically pure solid. The proton NMR spectra of the reaction solutions indicate a bromide to alkoxide conversion of 90, 80, and 55% for **9**, **10**, and **11**, respectively. This variation in yield may be related to the decrease in the Brønsted acidities of the alcohols.

The carbonyl stretching vibrations of these complexes are essentially identical with those of the boron halide complexes, **3–6**. The proton resonances of the alkoxide ligand are shifted significantly to lower field from those resonances of either the free alcohol or the corresponding trialkylborate ester. This shift is a diagnositc indication of the formation of the rhenaboron alkoxide complexes and is probably due to the high electronegativity of the $(OC)_3Re$ moiety.

Acknowledgment. We thank the Tennessee Eastman Kodak Corp. for a fellowship to D.T.H. and acknowledge the support of the National Science Foundation, Grant No. 76-14304, and of the University Research Council of Vanderbilt University.

Registry No. **1**, 69439-96-9; **3**, 73199-27-6; **4**, 73199-28-7; **5**, 73199-29-8; **6**, 73199-30-1; **8**, 73230-61-2; **9**, 73199-31-2; **10**, 73199-32-3; **11**, 73199-33-4; acetylpentacarbonylrhenium, 23319-44-0; BI_3, 13517-10-7; BBr_3, 10294-33-4; BCl_3, 10294-34-5; BF_3, 7637-07-2; 1-propanol, 71-23-8; ethanol, 64-17-5; methanol, 67-56-1.

---

[11] IR (C_6H_{14}): ν(CO) 2030 (s), 1958 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.34 (s, 3, CH_3), 7.36 (s, 6, 2 CH_3). Mass spectra: molecular ion peak at m/e 449 with the correct isotopic pattern.

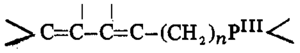
Contribution from Equipe IRCHA-CNRS,
94320 Thiais, France

1,3-Butadienylphosphines and Some of Their Complexes

F. Mathey,* F. Mercier, and C. Santini

Received September 25, 1979

The key roles of tervalent phosphorus derivatives and conjugated dienes as ligands in transition-metal chemistry are well-known. However only few complexes in which these two coordinating sites are linked within the same ligand have been described in the literature.[1-3] Such a paucity is partly due to the fact that free tervalent phosphorus derivatives of conjugated dienes are almost unknown.[4] In view of the various possibilities offered by such ligands in coordination chemistry (chelation, reversible exchange with free dienes, bridged complexes, etc.), we have launched a general study of (*Z*)- and (*E*)-1,3-butadienylalkylphosphines



$$>C{=}\overset{|}{C}{-}\overset{|}{C}{=}C{-}(CH_2)_nP^{III}<$$

A first paper was devoted to the synthesis of the (*Z*) compounds for $n = 2$.[7] The work reported hereafter describes the synthesis of (*E*)-1,3-butadienylphosphines ($n = 0$) and includes a preliminary study of their complexes with molybdenum and iron carbonyls.

Results and Discussion

Synthesis of (*E*)-1,3-Butadienylphosphines. One member of that family has been superficially described,[6] but its synthesis lacked generality. Since numerous syntheses of (*Z*)- and (*E*)-1,3-butadienylphosphoryl compounds were available,[8-20] a logical approach was to reduce the P=O bond of

---

[1] M. A. Bennett, R. N. Johnson, and I. B. Tomkins, *J. Am. Chem. Soc.*, **96**, 61 (1974).

[2] W. Winter, *Angew. Chem., Int. Ed. Engl.*, **15**, 241 (1976).

[3] M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **101**, 2627 (1979).

[4] As far as we know only two compounds in which a phosphino group is directly bonded to a conjugated diene are described in the literature, namely, 2-(diphenylphosphino)-1,3-butadiene[5] and 1-(diphenylphosphino)-4-phenyl-1,3-butadiene.[6] In both cases their characterization was minimal.

[5] C. A. Aufdermarsh, Jr., *J. Org. Chem.*, **29**, 1994 (1964).

[6] D. Gloyna and H. G. Henning, *Angew. Chem., Int. Ed. Engl.*, **5**, 847 (1966).

[7] F. Mathey and C. Santini, *Can. J. Chem.*, **57**, 723 (1979).

[8] E. Bergmann and A. Bondi, *Chem. Ber.*, **64**, 1455 (1931); *Chem. Abstr.*, **25**, 4238 (1931).

[9] G. M. Kosolapoff, Monsanto Chemical Co., U.S. Patents 2 389 576 (1945) and 2 486 657 (1949); *Chem. Abstr.* **40**, P 1536[4] (1946); **44**, P 2009*a* (1950).

[10] K. N. Anisimov and E. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 923 (1956).

0020-1669/80/1319-1813$01.00/0