Metallation of the methyl group in *o*-nitrosotoluene: synthesis and the molecular structure of the binuclear complex $[o\text{-}(NO)(CH_2)C_6H_4)]_2Pd_2(\mu\text{-}OOCCF_3)_2$

T. A. Stromnova, S. T. Orlova, D. N. Kazyul'kin, I. P. Stolyarov, and I. L. Eremenko*

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117907 Moscow, Russian Federation. Fax: +7 (095) 954 1279. E-mail: strom@ionchran.rinet.ru

The reaction of the tetranuclear cluster $Pd_4(CO)_4(OOCCF_3)_4$ with *o*-nitrosotoluene afforded the Pd^{II}-containing complex $[o\text{-}(NO)(CH_2)C_6H_4]_2Pd_2(\mu\text{-}OOCCF_3)_2$. The elimination of CO_2 and the formation of organic products of transformation of tolylnitrene species (azotoluene, ditolylamine, and tolylisocyanate) were observed in the course of the reaction. The title complex was characterized by IR and ^1H NMR spectroscopy. Its structure was established by X-ray diffraction analysis. It was suggested that the reaction proceeds through intermediate formation of nitrene complexes.

Key words: palladium, carbonyl complexes, clusters, metallation, nitrosotoluene.

Palladium and its compounds are widely used in catalysis of reductive carbonylation of aromatic nitro compounds.[1] Palladium complexes containing nitrosoaromatic and arylnitrene ligands are generally postulated as key intermediates in these reactions.[2] However, data on such complexes are scarce[3–5] and data on their reactivities are virtually absent. Previously,[4] we have demonstrated that the reaction of the tetranuclear cluster $Pd_4(CO)_4(OAc)_4$ with nitrosobenzene affords organic products of conversions of NO-containing compounds (azoxybenzene, azobenzene, and aniline) as well as the binuclear complex $Pd_2(\mu\text{-}OAc)_2(PhNC_6H_4NO)_2$ and is accompanied by elimination of CO_2. In the present work, we studied the reaction of the $Pd_4(CO)_4(OOCCF_3)_4$ cluster (**1**) with *o*-nitrosotoluene.

Results and Discussion

We found that the reaction of complex **1** with $o\text{-}(NO)(Me)C_6H_4$ in toluene (50 °C, 4–5 h) affords CO_2 and palladium black (30–35% of the initial Pd) as well as organic nitrogen-containing products and the unusual binuclear complex $[o\text{-}(NO)(CH_2)C_6H_4]_2Pd_2(\mu\text{-}OOCCF_3)_2$ (**2**) in 35–38% yield with respect to palladium. The structure of complex **2** was established by X-ray diffraction analysis (Fig. 1, Table 1). Molecule **2** was found to consist of two binuclear fragments with two trifluoroacetate bridges (Pd—Pd, 2.871(1) Å; Pd—O, 2.031(17)–2.208(13) Å). The metal—metal distance in the complex is smaller than the sum of the covalent radii of the Pd atoms and the direct metal—metal interaction is not ruled out. The chelating $1,2\text{-}(NO)(CH_2)C_6H_4$ ligands are coordinated to the Pd atoms through the N atoms of the NO groups (Pd—N, 1.930(19) and 1.964(13) Å) and the C atoms of the methylene groups (Pd—C, 1.966(13) and 2.024(16) Å). Each Pd atom has a 16-electron configuration and a planar-square coordination environment (if the possible metal—metal bond is ignored). The binuclear

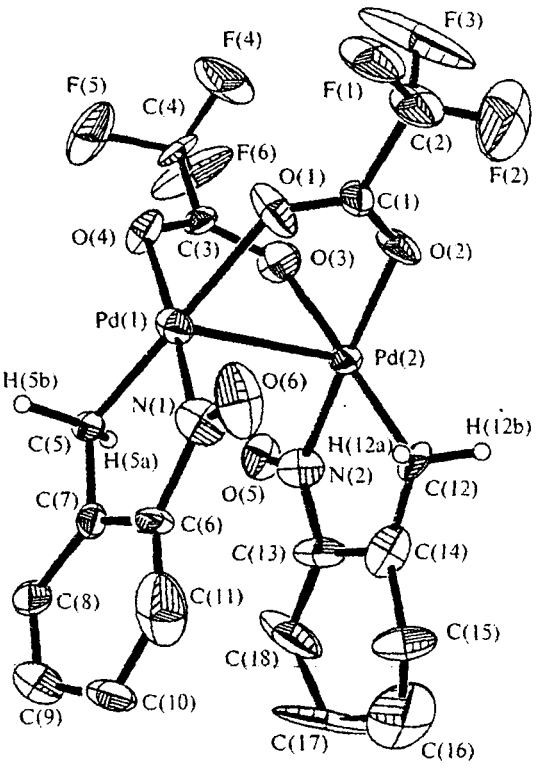


Fig. 1. Molecular structure of the complex $[o\text{-}(NO)(CH_2)C_6H_4]_2Pd_2(\mu\text{-}OOCCF_3)_2$.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 147–150, January, 2000.

1066-5285/00/4901-0150 $25.00

Table 1. Principal bond lengths (d) and bond angles (ω) in the $[o\text{-}(NO)(CH_2)C_6H_4]_2Pd_2(\mu\text{-}OOCCF_3)_2$ complex (**2**)

Bond	d/Å	Angle	ω/deg
Pd(1)—Pd(2)	2.871(1)	O(1)—Pd(1)—O(4)	89.8(6)
Pd(1)—Pd(2a)	3.165(1)	O(1)—Pd(1)—N(1)	94.0(7)
Pd(1)—O(1)	2.208(13)	O(4)—Pd(1)—C(5)	92.3(6)
Pd(1)—O(4)	2.170(11)	N(1)—Pd(1)—C(5)	83.8(7)
Pd(1)—N(1)	1.930(19)	O(1)—C(1)—O(2)	130.2(12)
Pd(1)—C(5)	1.966(17)	O(2)—Pd(2)—O(3)	85.4(6)
Pd(2)—O(2)	2.041(14)	O(3)—Pd(2)—N(2)	98.8(6)
Pd(2)—O(3)	2.031(17)	O(2)—Pd(2)—C(12)	93.7(7)
Pd(2)—N(2)	1.964(13)	N(2)—Pd(2)—C(12)	82.1(7)
Pd(2)—C(12)	2.024(16)	O(2)—C(3)—O(3)	127.8(11)
N(1)—O(6)	1.085(22)		
N(2)—O(5)	1.191(37)		

molecules are linked in chains through weak intermolecular Pd...Pd interactions (Pd...Pd, 3.165(1) Å) (Fig. 2). An analogous mode of packing of Pd_2 species has recently been found in the $Pd_2(\mu\text{-}OAc)_2(PhN{=}C_6H_4{=}NO)_2$ complex (**3**) (Pd—Pd, 2.84 Å).[4] However, the intermolecular Pd...Pd contacts in **3** are substantially longer.

The monodentate coordination of the nitrosoarene ligand is typical of all known (few in number) palladium complexes with nitrosoarenes. Previously, this coordination has been found[3] in the mononuclear complex $PdCl_2(ONPh)_2$ (**4**; the Pd atom has a planar-square coordination formed by two N atoms, which are located in *trans* positions in the PhNO molecules, and two Cl atoms), in binuclear complex **3** (the Pd atom is coordinated by the ligands through the N atom of the nitroso group and the N atom of the amide group), and in mononuclear bis(4,6-dimethyl-2-nitrosophenylamido)palladium (**5**; the coordination sphere about the Pd atoms is analogous to the ligand environment about the Pd atoms in complex **3**). The geometry of the coordination environment about the N atom of the nitroso group is virtually identical in all complexes (Table 2) in spite of the fact that the nitrosoarene ligand in mononuclear chlorine-containing complex **4** is coordinated only through the N atom, whereas this ligand in binuclear complexes **2** and **3** and in mononuclear complex **5** is involved in the formation of chelate metallocycles.

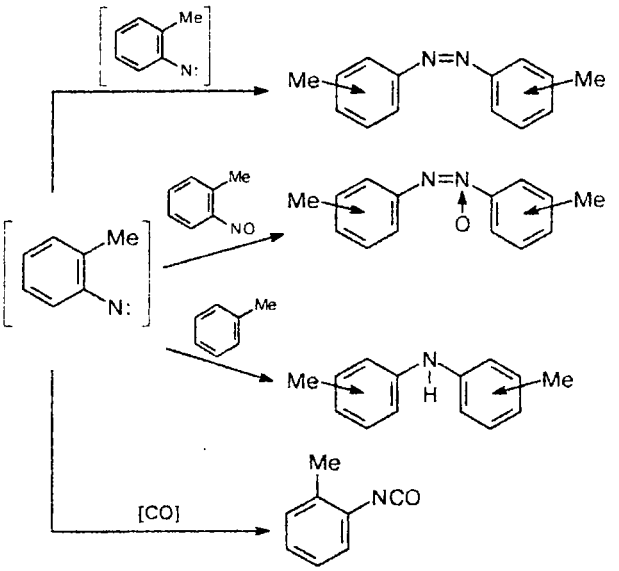
The formation of complex **2** in the reaction under consideration is somewhat unexpected. Previously, it has been demonstrated that the reactions of coordinated carbonyl groups with nitrosoarenes lead to oxidation of the CO group by the nitroso group to form complexes containing arylnitrene ligands:

$$M{-}CO + ONR \rightarrow CO_2 + M{-}NR. \qquad (1)$$

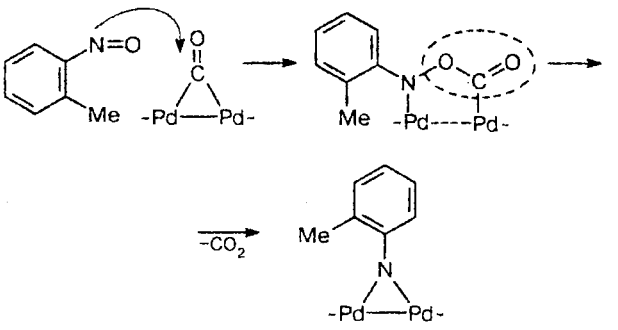
It is this procedure, *i.e.*, the oxidation of CO groups in carbonyl clusters of Fe, Ru, and Os by nitrosobenzene, that was used for preparing the cluster complexes $Fe_3(\mu^3\text{-}NPh)_2(CO)_9$,[6] $Ru_3(\mu^3\text{-}NPh)(CO)_{10}$,[7] and $Os_3(\mu^3\text{-}NPh)(CO)_{10}$.[8]

It is believed that the reaction of cluster **1** with *o*-nitrosotoluene also proceeds through intermediate formation of tolylnitrene species. This suggestion is confirmed by the fact that not only CO_2 but also a number of nitrogen-containing organic products are formed in the course of the reaction. For example, azotoluene appears, apparently, as a result of dimerization of two tolylnitrene species. Azoxytoluene is a product of the reaction of a tolylnitrene species with a nitrosotoluene molecule. The insertion of a tolylnitrene species at the C—H bond of the phenyl ring of the toluene molecule affords bitolylamine, and the reaction of tolylnitrene with the coordinated carbonyl group yields tolylisocyanate (Scheme 1).

Scheme 1



It can be assumed that the first stage of the reaction involves coordination of the nitrosotoluene molecule followed by elimination of CO_2 to give an unstable intermediate:



This intermediate, which is, apparently, a tetranuclear complex containing $Pd_2(\mu\text{-}OOCCF_3)_2$ groups linked through bridging tolylnitrene ligands, undergoes disproportionation to form Pd^0 and Pd^{2+}, which is accompanied by elimination of tolylnitrene species. The

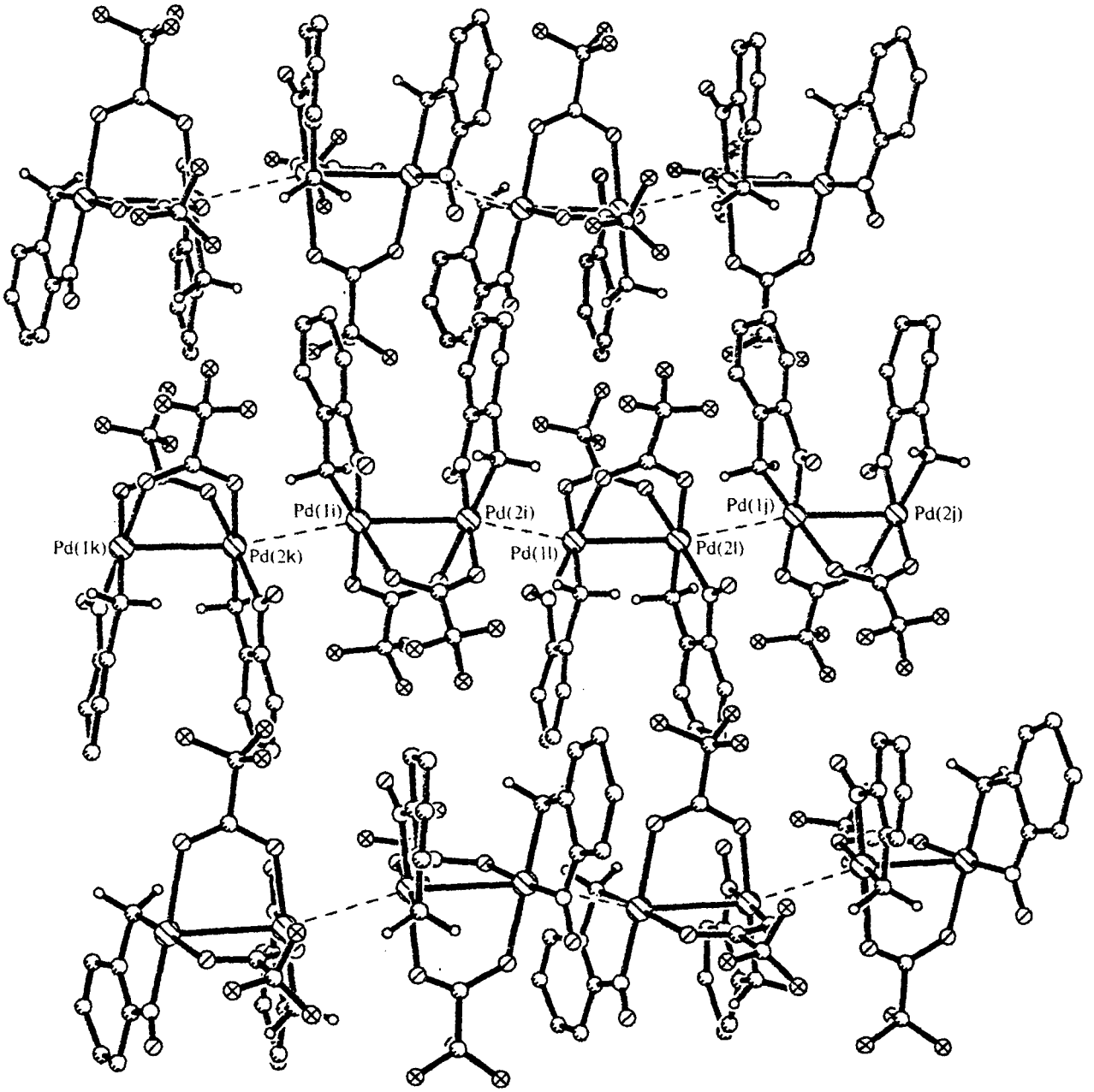


Fig. 2. Molecular packing in the crystal of the $[o\text{-}(NO)(CH_2)C_6H_4]_2Pd_2(\mu\text{-}OOCCF_3)_2$ complex.

Table 2. Principal geometric parameters of the coordinated nitroso groups in the palladium complexes with nitrosoaromatic ligands

Complex	Distance/Å		φ_Σ/deg[a]	Reference
	Pd—N	N—O		
$Pd_2(\mu\text{-}OOCCF_3)_2(CH_2C_6H_4NO)_2$ (**2**)	1.93	1.08, 1.19	359.8	[b]
$Pd_2(\mu\text{-}OAc)_2(PhNC_6H_4NO)_2$ (**3**)	1.98	1.24	359.5	4
$PdCl_2(ONPh)_2$ (**4**)	1.99	1.209	359.8	3
$Pd(4,6\text{-}Me_2\text{-}2\text{-}NOC_6H_2NH)_2$ (**5**)	2.02	1.24	359.6	5

[a] The sum of the angles about the N atom.
[b] Data of the present work.

coordinatively unsaturated $[Pd_2(\mu\text{-}OOCCF_3)_2]^{2+}$ cation reacts with the second nitrosotoluene molecule to yield the cationic complex $[(MeC_6H_4NO)_2Pd_2(\mu\text{-}OOCCF_3)_2]^{2+}$. In this complex, the nitrosobenzene molecule is coordinated to the Pd atom through the N atom of the nitroso group, and the agostic Pd...H—C bond with the methyl group can be formed. The cleavage of the C—H bond in the methyl group leads to elimination of the proton, yielding a complex with a stable metallocycle.

Experimental

Elemental analysis of the reaction products was carried out on a C,H,N-analyzer (Carlo Erba, Italy) using the micromethod. The IR spectra of the complexes in the 400—4000 cm^{-1} region were recorded on a Specord M-80 spectrometer (as Nujol mulls). The ^1H NMR spectra of the complexes in CD_2Cl_2 or $CDCl_3$ were measured on a Varian-200 instrument. The GLC analysis of gaseous products was carried out on an LKhM-80 instrument. The organic products were analyzed by GLC-mass spectrometry on an Automass instrument (Delsi Nermag, France). Columns with PEG-20M and silicon SE-30 phases were used. The DTA/TGA analysis was performed on an OD-102 derivatograph (MOM, Hungary).

Palladium carbonyl carboxylates $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OCOR)_4$ (R = CF_3 (**1**), Me, or Ph) were prepared according to procedures reported previously.[9—11] *o*-Nitrosotoluene *o*-MeC_6H_4NO was synthesized according to a known procedure[12] from *o*-nitrosoaniline and was isolated by azeotropic distillation with water vapor under atmospheric pressure. The purity of the *o*-nitrosotoluene obtained was checked by TLC on Silufol plates as well as by the melting point. The organic solvents were purified according to standard procedures.[13]

Reaction of cluster 1 with *o*-nitrosotoluene. A suspension of complex **1** (1.3 g, 4 mmol of Pd) in toluene (16 mL) was placed into a two-neck temperature-controlled reactor joined to a gas burette. The system was evacuated and filled with argon. Then a solution of *o*-nitrosotoluene (480 mg, 4 mmol) in toluene (24 mL) was added. The reaction mixture was kept at 50 °C until elimination of CO_2 completely ceased (4—5 h, volumetric control). Then the mixture was filtered and the filtrate was concentrated under reduced pressure to 1/4 of the initial volume. Complex **2** was precipitated with hexane, filtered, and dried *in vacuo*. The yield was 450—480 mg (1.4 mmol, 35% with respect to Pd). M.p. 177—180 °C (with decomp.). Found (%): C, 31.63; H, 1.65; N, 4.20; Pd, 32.5. $C_{18}H_{12}F_6N_2O_6Pd_2$. Calculated (%): C, 31.63; H, 1.65; N, 4.20; Pd, 32.5. ^1H NMR (200 MHz, $CDCl_3$), δ: 2.4 (s, 2 H, CH_2); 7.1 (m, 4 H, C_6H_4). IR (Nujol), ν/cm^{-1}: 1790, 1664, 1448.

X-ray diffraction study of complex 2. Single crystals suitable for X-ray diffraction study were prepared by recrystallization from a 1 : 2 dichloromethane—hexane mixture. X-ray diffraction data were collected on an automated four-circle CAD-4 diffractometer (T = 20 °C, λ(Mo-Kα) = 0.71073 Å). Crystals of **2** belong to the orthorhombic system, a = 12.513(3) Å, b = 15.084(3) Å, c = 11.870(3) Å, V = 2240.4(9) $Å^3$, d_{calcd} = 2.013 g cm^{-3}, μ = 16.92 cm^{-1}, space group $Pna2_1$. The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms of the Ph rings were generated geometrically. The positions of the H atoms of the methylene fragment were located from difference electron density syntheses and refined isotropically; R = 0.049, R_w = 0.071 (for 2005 observed reflections); the weighting scheme $w^{-1} = \sigma^2(F) + 0.0036F^2$ was used. The crystal structure of **2** can also be solved in the space group *Pnam*. In this case, molecule **2** is located on a mirror plane *m* and contains the disordered CF_3 fragments and NO and CH_2 groups (R = 0.061, R_w = 0.082). The atomic coordinates in the structure of **2** and the complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database.

We thank S. E. Nefedov for performing X-ray diffraction study at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences), A. E. Gekhman for help in analyzing the reaction solutions by GLC-mass spectrometry, S. G. Sakharova for recording the ^1H NMR spectra, and N. A. Minaeva for measuring the IR spectra.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32519) and by the Russian Federation Government Program "Leading Scientific Schools" (Project No. 96-15-97577).

References

1. S. Cenini, M. Pizotti, and C. Crotti, *Metal Catalyzed Deoxygenation Reactions by Carbon Monoxide of Nitroso and Nitro Compounds*, in *Aspects of Homogeneous Catalysis*, Ed. R. Ugo and D. Reidel, Dordrecht (The Netherlands), 1988, **6**, 97.
2. Yu. B. Yan and B. K. Nefedov, in *Sintezy na osnove oksidov ugleroda* [*Syntheses Based on Carbon Oxides*], Khimiya, Moscow, 1987, 125 (in Russian).
3. A. L. Balch and D. Petridis, *Inorg. Chem.*, 1969, **8**, 2247.
4. T. A. Stromnova, S. T. Orlova, I. P. Stolyarov, S. B. Katser, and I. I. Moiseev, *Dokl. Akad. Nauk SSSR*, 1997, **352**, 68 [*Dokl. Chem.*, 1997, **352** (Engl. Transl.)].
5. R. G. Pritchard, G. S. Heaton, and I. M. El-Nahhal, *Acta Crystallogr. C* (*Cryst. Struct. Commun.*), 1989, **45**, 815.
6. P. L. Stanghellini and R. Rossetti, *Atti Accad. Sci. Torino*, 1970, **105**, 391.
7. J. A. Smieja and W. L. Gladfelter, *Inorg. Chem.*, 1986, **25**, 2667.
8. D. L. Ramage, G. L. Geoffroy, A. L. Rheingold, and B. S. Haggerty, *Organometallics*, 1992, **11**, 1242.
9. T. A. Stromnova, L. G. Kuz'mina, M. N. Vargaftik, G. Ya. Mazo, Yu. T. Struchkov, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 720 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27** (Engl. Transl.)].
10. T. A. Stromnova, M. N. Vargaftik, and I. I. Moiseev, *J. Organomet. Chem.*, 1983, **252**, 113.
11. T. A. Stromnova, N. Yu. Tikhonova, L. K. Shubochkin, and I. I. Moiseev, *Koord. Khim.*, 1993, **19**, 450 [*Russ. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
12. *Organic Syntheses, An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals*, Coll. Vol. 3, *A Revised Edition of Annual Vols. 20—29*, Ed. E. C. Horning, J. Wiley, New York, 1955.
13. *Organic Solvents*, Eds. A. Weissberger, E. Proskauer, J. Riddic, and E. Toops, Interscience Publishers, New York—London, 1955.

Received July 23, 1999