Electrochemical reductive carbon-to-carbon coupling of σ-ethynyl complexes of transition metals

L. I. Denisovich, T. V. Filatova, M. G. Peterleitner, N. A. Ustynyuk, V. N. Vinogradova, and L. I. Leont'eva*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The electrochemical properties of σ-ethynyl complexes of chromium subgroup metals were studied by cyclic voltammetry and preparative-scale electrolysis. The redox cycle of $C_5H_5(CO)_3CrC{\equiv}CPh$ was shown to give the bis-carbyne complex $(\eta^5\text{-}C_5H_5)(CO)_2Cr{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}Cr(CO)_2(\eta^5\text{-}C_5H_5)$ formed *via* the reductive $C_\beta{-}C_\beta$ coupling of ethynyl moieties. The influence of the nature of the metal atom and the ligand environment on the course of this reaction was considered.

Key words: chromium, molybdenum, and tungsten σ-ethynyl complexes; reductive coupling, cyclic voltammetry, preparative-scale electrolysis, bis-carbyne complexes.

Currently, the ligand—ligand type dimerization processes induced by electron transfer are a general method for the synthesis of different classes of binuclear organometallic compounds.[1—3] The oxidatively induced dimerization of transition metal σ-1-alkynyl derivatives $[M]{-}C{\equiv}CR$ occurs as the $C_\beta{-}C_\beta$ coupling of intermediate 17-e $\{[M]{-}C{\equiv}CR\}^{\cdot+}$ radical cations to give binuclear bis-vinylidene $\{[M]{=}C{=}C(R){-}C(R){=}C{=}[M]\}^{2+}$ complexes ($[M] = Fe(dppe)(\eta^5\text{-}C_5H_5)$, R = Me;[4] $[M] = Fe(dppe)(\eta^5\text{-}C_5Me_5)$, R = H;[5] $[M] = Mo(dppe)(\eta^7\text{-}C_7H_7)$, R = Bu^n, Ph [6]). In the case of R = H, these compounds can undergo deprotonation to form corresponding binuclear μ-η^1,η^1-butadiynediyl $[M]{-}C{\equiv}C{-}C{\equiv}C[M]$ compounds ($[M] = Fe(dppe)(\eta^5\text{-}C_5Me_5)$).[4] At the same time, the dimerization processes of σ-ethynyl complexes induced by their reduction have not been studied previously. To search for new approaches to the synthesis of bis-vinylidene ($[M]{=}C{=}C(R){-}C(R){=}C{=}[M]$) and bis-carbyne ($[M]{\equiv}C{-}C(R){=}C(R){-}C{\equiv}[M]$) complexes, in this work the reduction of σ-phenylethynyl compounds $(\eta^5\text{-}C_5R_5)(CO)_3MC{\equiv}CPh$ (**1—3**: R = H, **1**: M = Cr, **2**: M = Mo, **3**: M = W; **4—6**: R = Me, **4**: M = Cr, **5**: M = Mo, **6**: M = W), *trans*-$(\eta^5\text{-}C_9H_7)(CO)_2(PPh_3)MoC{\equiv}CPh$ (**7**), *trans*-$(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)WC{\equiv}CPh$ (**8**) and $(\eta^5\text{-}C_9H_7)(CO)_3WC{\equiv}CPh$ (**9**) was studied by cyclic voltammetry (CV) and preparative-scale electrolysis. The prerequisite to performing this work was the synthesis of the bis-carbyne complex $(\eta^5\text{-}C_5H_5)(CO)_2Cr{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}Cr(CO)_2(\eta^5\text{-}C_5H_5)$ (**10**) by the reduction of complex **1** with a K/Na alloy.[7] The oxidation of compounds **1—9** was also studied by CV. The data obtained are listed in Table 1.

Experimental

All the operations except for TLC were carried out under an Ar atmosphere. Chromatography was performed using silica gel (Aldrich, 70—230 mesh, 60 Å). ^1H and ^{13}C NMR spectra were recorded on Bruker WP-200 and Varian VXR 400 spectrometers. Cyclic voltammograms were recorded using a PI-50-1

Table 1. Potentials of oxidation (E^{ox}/V) and reduction (E^{red}/V) peaks of the complexes

Compound	E^{ox}	$-E^{red}$	$-E_a{}^a$	G^b
$C_5H_5(CO)_3Cr{-}C{\equiv}C{-}Ph$	1.13	1.84	0.52	2.97
$C_5H_5(CO)_3Mo\text{-}C{\equiv}C{-}Ph$	1.23	1.72	0.37	2.95
$C_5H_5(CO)_3W{-}C{\equiv}C{-}Ph$	1.18	1.80	0.44	2.98
$C_5Me_5(CO)_3Cr{-}C{\equiv}C{-}Ph$	0.93	1.87		2.80
$C_5Me_5(CO)_3Mo{-}C{\equiv}C{-}Ph$	1.06	1.88		2.94
$C_5Me_5(CO)_3W{-}C{\equiv}C{-}Ph$	1.04	1.93		2.97
$C_9H_7(CO)_2(PPh_3)Mo{-}C{\equiv}C{-}Ph$	0.94	1.98	0.37	2.92
$C_5H_5(CO)_2(PPh_3)W{-}C{\equiv}C{-}Ph$	0.67^c	2.32	0.44	2.99
$C_9H_7(CO)_3W{-}C{\equiv}C{-}Ph$	0.98	1.54		2.52
$[Cr]{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}[Cr]^d$	0.95	0.97^c 1.11^c		
$[Mn]{=}C{=}C(Ph){-}C(Ph){=}C{=}[Mn]^e$	0.56^c 0.70^c	1.91 2.66		

Note. The reaction conditions were THF, 0.1 *M* Bu_4NBF_4, as supporting electrolyte, $C = 2 \cdot 10^{-3}$ mol L^{-1}, $V = 200$ mV s^{-1}, glassy-carbon electrode, *vs.* SCE.

[a] E_a are the potentials of anodic peaks observed after cathodic potential scan.

[b] $G = (E^{ox} - E^{red})$.

[c] Reversible process; $E_a = (E_{p.a.} + E_{p.c.})/2$.

[d] $[Cr] = C_5H_5(CO)_2Cr$.

[e] $[Mn] = C_5H_5(CO)_2Mn$.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1955—1958, October, 1998.

1066-5285/98/4710-1901 $20.00

potentiostat and potential-controlled electrolysis was conducted using a P-5827M potentiostat. IR spectra were recorded on an UR-20 instrument.

Complexes **1**—**6** and **9** were synthesized by refluxing corresponding potassium carbonylmetallates $(\eta^5\text{-}C_5R_5)(CO)_3M^-K^+$ (M = Cr, Mo, W; R = H, Me) and $(\eta^5\text{-}C_9H_7)(CO)_3W^-K^+$ with PhC≡CCl in THF for 4—6 h. The procedure for performing the reactions and isolating the complexes was analogous to that we described previously.[8] The syntheses of compounds **7**, **8** also have been described previously.[9]

Redox cycles of complexes 1, 5, and 6. The reduction of compound **1** (0.12 g), or compound **5** (0.11 g), or compound **6** (0.10 g) was carried out at a Hg cathode at a potential of −1.9 V (compound **1**) or −2.3 V (compounds **5**, **6**) until complete disappearance of the initial compounds. The quantity of electricity consumed corresponded to 2 F mol^{-1} (**1**), 1.6 F mol^{-1} (**5**), and 1.7 F mol^{-1} (**6**). The oxidation of the solutions obtained was performed at a potential of 0.2 V. The formation of compound **10** as a result of the redox cycle of compound **1** was confirmed by comparing the CV and TLC data with those of the specimen of compound **10** obtained according to the known procedure.[7]

After performing the redox cycles of compounds **5** and **6**, the solutions were evaporated; the products were extracted with benzene (30—40 mL), filtered from the supporting electrolyte, concentrated to 5 mL, and chromatographed on plates with SiO_2 (with a benzene—ether mixture (1 : 1 as eluent). The biscarbyne complexes **11** and **12** were precipitated from hexane.

The yield of compound **11** was 7% (0.014 g). ν_{CO} $(CH_2Cl_2)/cm^{-1}$: 1935, 1995. ^1H NMR $(C_6D_6, \delta$, a mixture of *cis*- and *trans*-isomers): 1.42, 1.66 (C_5Me_5); 6.7—7.3 (C_6H_5). ^{13}C NMR $(C_6D_6, \delta$, a mixture of *cis*- and *trans*-isomers): 358.76, 341.2 (Mo≡C—); 234.9, 229.7 (CO); 157.3, 141.1 (—C(Ph)=); 124—126, 119.7, 121.0 $(C_6H_5$, *ipso*-, *ortho*-, *meta*-, *para*-); 104.0, 102.0 $(C—CH_3)$; 9.4, 9.3 (CH_3).

The yield of compound **12** was 9% (0.018 g); ν_{CO} $(CH_2Cl_2)/cm^{-1}$: 1930, 1995. ^1H NMR $(C_6D_6, \delta$, a mixture of *cis*- and *trans*-isomers): 1.6, 1.84 (C_5Me_5); 6.85—7.75 (C_6H_5). ^{13}C NMR $(C_6D_6, \delta$, a mixture of *cis*- and *trans*-isomers): 349.4, 337.2 (W≡C—); 232.7, 227.9 (CO); 155.6, 139.0 (—C(Ph)=); 123—125, 120, 119 $(C_6H_5$, *ipso*-, *ortho*-, *meta*-, *para*-); 102.9, 99.1 $(C—CH_3)$; 9.1, 9.0 (CH_3).

Redox cycle of complex 10. The reduction of compound **10** (0.09 g) was carried out in THF solution (0.2 *M* Bu_4NBF_4) at a Hg cathode at a potential of −1.6 V. The starting current (30 mA) was linearly reduced to 2 mA over the electrolysis period (40 min), which corresponded to complete disappearance of the initial compound (CV monitoring). The quantity of electricity consumed (Q_{exp} = 30 K) corresponded to addition of two electrons (Q_{theor} = 31.6 K; n = 2). After electrolysis, the IR spectrum of the solution contained the absorption bands at 1780, 1860, 1905, 1945, and 1970 cm^{-1}. The oxidation of the solution obtained was carried at a potential of 0.1 V. The starting current (25 mA) was linearly reduced to 4 mA (Q_{exp} = 29 K) over the electrolysis period. After the electrolysis, the peaks of the initial complex **10** were observed on the CV of the solution; the heights of the peaks corresponded to 30% of the initial compound **10** recovered after performing the redox cycle. The presence of compound **10** in the solution was also confirmed by TLC (silica gel, with benzene as eluent).

Results and Discussion

The σ-ethynyl complexes **1**—**9** studied can undergo electrochemical oxidation and reduction at a glassy-carbon electrode in THF solution. The potentials of the peaks observed on CVs are listed in Table 1. The diffusion-controlled oxidation and reduction peaks correspond to the transfer of an electron and to electrochemically irreversible processes, except for those of complex **8** whose oxidation occurs reversibly.

The observed changes in the oxidation and reduction potentials of complexes **1**—**9** are due to the influence of the nature of the metal and the ligand environment. Replacement of CO by the more electron-donor PPh_3 ligand makes the oxidation easier and hampers the reduction of the complexes (*cf.* **3** and **8**). Replacement of the C_5H_5 ligand (complexes **1**—**3**) by the pentamethylcyclopentadienyl (complexes **4**—**6**) has an analogous effect, whereas replacement of the C_5H_5 ligand (complex **3**) by the $\eta^5—C_9H_7$ (indenyl) ligand (complex **9**) leads to an appreciable decrease in both the oxidation and the reduction potentials. Changes in the oxidation and reduction potentials depending on the nature of the metal atom are not associated with the metal position in the Group VIB. The oxidation of the molybdenum complex (**2**) is more difficult while its reduction occurs more readily as compared to those of analogous chromium and tungsten complexes (**1** and **3**).

In this case the value of the intrinsic electrochemical gap[10] (defined as the difference between E^{ox} and E^{red}) remains virtually constant for the studied series of related complexes **1**—**9**. This indicates that the structural factors affect slightly the energies of the redox orbitals of the complexes studied. The irreversible character of the observed peaks indicates the high reactivity of the radical ions formed as a result of one-electron oxidation and reduction of neutral initial complexes. However, our attempts to characterize the transformation products of the radical cations (RC) formed in the oxidation of the complexes failed. No pronounced peaks that could be identified and assigned to the reduction of the obtained products were observed on the cathodic parts of CVs of the studied complexes after anodic polarization. This result indicates that the RC formed in the oxidation of the complexes are unstable and differ from the RC of previously studied σ-ethynyl [M]—C≡C—R complexes whose electrochemical and chemical oxidation occur with the formation of stable RC.[4—6] It is likely that the radical cation of complex **5** is more stable than the RC generated from complexes **1**—**4** because in this case the observed oxidation peak is reversible.

As has already been noted, the electrochemical reduction of complexes **1**—**9** occurs irreversibly. However, the peaks in the interval from −0.4 to −0.5 V (Fig. 1, *a*, Table 1) appeared on the anodic parts of CVs in all cases after cathodic potential scan. These peaks can be assigned to the oxidation of transformation products of radical anions (RA) formed in the reduction of initial σ-ethynyl complexes. To elucidate the nature of such products, the potential-controlled preparative-scale electrolysis (PCE) of chromium complex **1** was conducted at the potential corresponding to the reduction peak of

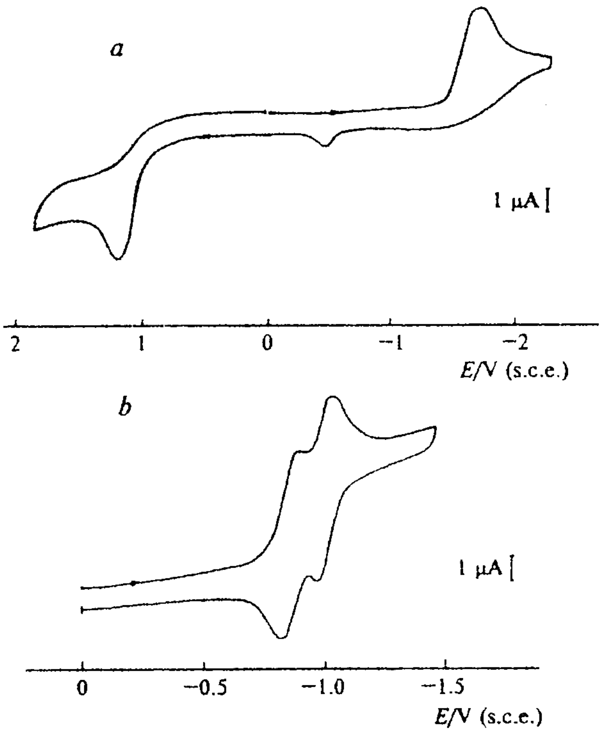
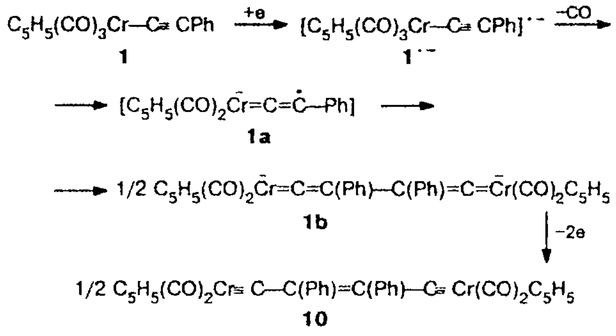


Fig. 1. Cyclic voltammograms (THF, 0.1 *M* Bu_4NBF_4, $C = 2 \cdot 10^{-3}$ mol L^{-1}, $v = 200$ mV s^{-1}, glassy-carbon electrode, *vs.* SCE): *a*, $C_5H_5(CO)_3Cr{-}C{\equiv}C{-}Ph$; *b*, $C_5H_5(CO)_2Cr{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}Cr(CO)_2C_5H_5$.

this compound. The presence of the anodic peak on the CV of the solution after performing electrolysis at the same potential (−0.5 V) as that of the anodic response peak of complex **1** observed on the CV (see Fig. 1, *a*) may indicate the identity of the products formed as a result of the reduction process on the time scale of CV and PCE. It was established that the oxidation potential of the product obtained (the anodic peak at −0.5 V) is independent of the material the electrode is made of (mercury electrode or glassy-carbon electrode). Such a result rules out the reductive cleavage of the σ-Cr—C bond with the formation of $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]^-$, as was observed for $(\eta^5\text{-}C_5H_5)(CO)_3M{-}R$ (M = Mo, W; R = Alk, Ar[11]), since it is known[12] that the oxidation potential of $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]^-$ depends on the material the electrode is made of. The difference between the IR spectra of the solution recorded after performing the electrolysis (the ν(CO) bands are at 1780 and 1880 cm^{-1}) and those of $(\eta^5\text{-}C_5H_5)(CO)_3Cr)^-$ (the ν(CO) bands are at 1743, 1793, and 1897 cm^{-1}) makes it possible to suggest that anionic products other than $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]^-$ can be formed under PCE conditions. It was found that the preparative oxidation of the electrolysis products results in the red solution from which the substance identical to the bis-carbyne chromium complex (compound **10**) obtained previously was isolated by extraction and chromatography on SiO_2 in 30% yield.[7] Thus, the redox cycle resulted in the $C_\beta{-}C_\beta$ coupling product of the ethynyl moieties; based on the generalization of the results, its formation can be illustrated by the following scheme:

Scheme 1



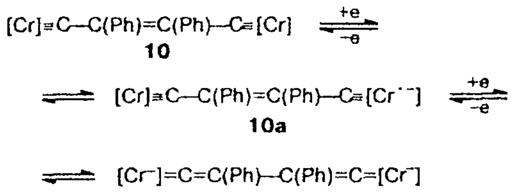
According to Scheme 1, the 19-e radical anion $1^{\cdot -}$ formed after addition of an electron undergoes decarbonylation, resulting in the 18-e radical anion **1a**. The $C_\beta{-}C_\beta$ dimerization of **1a** gives the binuclear dianionic bis-vinylidene complex **1b** that is oxidized to give the bis-carbyne complex **10**.

Then, the preparative electrochemical reduction of pentamethylcyclopentadienyl complexes **4—6** was carried out. The $(\eta^5\text{-}C_5Me_5)(CO)_2M{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}M(CO)_2(\eta^5\text{-}C_5Me_5)$ bis-carbyne complexes (**11**: M = Mo, **12**: M = W) were obtained in low yields (3—5%) after performing the redox cycles of molybdenum and tungsten complexes. We failed to isolate the analogous chromium compound (M = Cr) because of its instability. We believe that the redox cycles of complexes **4—6** occur *via* the same stages as the redox cycle of complex **1** shown in Scheme 1, *viz.*, the electron addition, the CO elimination, the radical anion dimerization, and the final oxidation. The structures of **11** and **12** were confirmed by ^1H and ^{13}C NMR spectroscopy data that virtually coincide with the spectral data obtained for the chromium bis-carbyne complex **10** whose structure was established by X-ray analysis.[7] The low yields of bis-carbyne complexes **10—12** suggest the existence of alternative channels for transforming the intermediates formed in the reduction of compounds **1—6**. One of such channels can be the further reduction of radical anions of the type **1a** to unstable dianions. This assumption is in agreement with the observed increase in the quantity of electricity consumed in the reduction of complexes **1—6** to 1.6—1.8 F mol^{-1}. It cannot be ruled out that the key stage of the carbon—carbon bond formation in the coupling of the two radical anions (see Scheme 1) is electrostatically hampered, which also would lead to decreasing the yield of the dimeric product.

It was found that the C(4)-bis-carbyne complex **10** can undergo electrochemical oxidation and reduction.

The corresponding peak potentials are given in Table 1. Oxidation occurs with irreversible transfer of two electrons, which indicates the instability of the oxidation products formed. The reduction of complex **10** occurs in two reversible one-electron stages (see Fig. 1, *b*); in addition to CV data, this is also confirmed by the result of the redox cycle of complex **10** we performed using PCE (the potentials of electrolysis were $E^{red} = -1.6$ V and $E^{ox} = 0.1$ V). The observed successive transfer of two electrons in the reduction of binuclear complex **10** studied implies an intermediate formation of a complex with metal atoms in different oxidation states (a mixed-valence complex) (Scheme 2).

Scheme 2



$$[Cr]{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}[Cr] \underset{-e}{\overset{+e}{\rightleftharpoons}}$$

10

$$\rightleftharpoons [Cr]{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}[Cr^{\cdot -}] \underset{-e}{\overset{+e}{\rightleftharpoons}}$$

10a

$$\rightleftharpoons [Cr^{-}]{=}C{=}C(Ph){-}C(Ph){=}C{=}[Cr^{-}]$$

$[Cr] = (\eta^5\text{-}C_5H_5)(CO_2)Cr$

As is known,[13] the potential difference between the two reduction stages may correlate with the degree of electron delocalization in the mixed-valence complex formed. According to the previously accepted classification,[13] on the basis of the observed potential difference between the first and the second reduction stages (0.14 V) the intermediate mixed-valence chromium complex **10a** can be placed in the class of compounds with a weak electron density delocalization due to conjugation in the bridging C(4) group connecting the chromium atoms. The mixed-valence manganese complex generated in the one-electron oxidation of compound **13** (see Table 1) can also be placed in the same class of compounds. It follows from the data in Table 1 that the difference in potentials between the two one-electron reversible oxidation stages of bis-vinylidene complex **13**, as well as that of bis-carbyne chromium complex **10**, is 0.14 V. The observed reduction peaks of the manganese complex are irreversible and have not been considered in detail in this work.

Thus, our results showed that in addition to the known oxidative C_β—C_β coupling of ethynyl fragments, the reductive C_β—C_β coupling can occur in the complexes studied in this work and containing carbonyl ligands rather than phosphine ligands. The structure of initial complexes suggests the formation of bis-carbyne compounds rather than bis-vinylidene compounds as in the case of oxidative coupling. The study of the reductive dimerization processes of σ-ethynyl complexes, in which the carbon—carbon bond formation stage will be determined by the coupling of two electroneutral radicals, is currently in progress. The results of these investigations will be published separately.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32773).

References

1. N. G. Connely, *Chem. Soc. Rev.*, 1989, **18**, 153.
2. A. D. Astruc, *Chem. Rev.*, 1989, **89**, 1189.
3. O. V. Gusev, M. A. Ievlev, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, P. V. Petrovskii, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1997, **534**, 57.
4. R. S. Iyer and J. P. Selegue, *J. Am. Chem. Soc.*, 1987, **109**, 910.
5. R. L. Beddoes, C. Bitcon, A. Ricalton, and M. W. Whiteley, *J. Organomet. Chem.*, 1989, **367**, C21.
6. N. LeNarvor, L. Toupet, and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129.
7. N. A. Ustynyuk, V. N. Vinogradova, V. G. Andrianov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1984, **268**, 73.
8. A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, V. N. Korneva, and N. A. Ustynyuk, *J. Organometal. Chem.*, 1979, **166**, 217.
9. N. A. Ustynyuk, V. N. Vinogradova, V. N. Korneva, D. N. Kravtsov, V. G. Andrianov, and Yu. T. Struchkov, *J. Organometal. Chem.*, 1984, **277**, 285.
10. K. P. Butin, V. V. Strelets, and O. A. Reutov, *Metalloorg. Khim.*, 1990, **3**, 814 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
11. L. I. Denisovich, S. P. Gubin, Yu. A. Chapovskii, and N. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 924 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968, **17** (Engl. Transl.)].
12. K. M. Kadish, D. A. Lacombe, and J. E. Anderson, *Inorg. Chem.*, 1986, **25**, 2246.
13. P. Zanello, S. Tamburini, P. A. Vigato, and G. A. Mazzocchin, *Coord. Chem. Rev.*, 1987, **77**, 165.

Received December 30, 1997