Journal of Organometallic Chemistry, 465 (1994) 187–191

JOM 23895

Syntheses and electrochemical behaviour of novel dithiolatoniobium-(IV) and -(V) complexes with two η^5-cyclopentadienyl rings

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(Received March 30, 1993)

Abstract

Novel niobium(IV) complexes with two cyclopentadienyl rings and dmit, dmio or dddt were synthesized, and their voltammometric behaviour was investigated in acetonitrile and dichloromethane. These complexes in acetonitrile solution exhibited a reversible one-electron oxidation and a reversible one-electron reduction step, corresponding to niobium(V) and niobium(III) respectively, without any complicating side- or subsequent reactions. Among the three niobium(IV) complexes, the reduction potential of the complex with dddt was notably less negative than those of the complexes with dmit or dmio. This fact allows the preparation of the charge-transfer complexes with TCNQ. The niobium(V) dmit and dmio complexes with two cyclopentadienyl rings were also isolated as iodide salts by the oxidation of the corresponding niobium(IV) complex. These Nb^V complexes gave two one-electron reduction steps whose potentials were identical to those of Nb^{IV} and Nb^{III} for niobium(IV) dmit and dmio complexes.

Key words: Niobium; Thiolate; Electrochemistry; Cyclopentadienyl

1. Introduction

Recently the conductivity behaviour of organometallic compounds with 1,2-dithiolato-ligands has attracted interest [1]. Dmit (1,3-dithiol-2-thione-4,5-dithiolate), dmio (1,3-dithiol-2-one-4,5-dithiolate) and dddt (5,6-dihydro-1,4-dithiin-2,3-dithiolate) are 1,2-dithiolates, the most attractive for conducting organometallic compounds [2]. For example, Langmuir–Blodgett films of $[Au(dmit)_2]$ moiety exhibit remarkable conductivities at room temperature [3]. By appropriate selection of the central metal and the counter cation, dmit complexes which exhibit room-temperature conductivities and metallic behaviour have been prepared [4].

The conductivity behaviour of symmetrical and square-planar bis(dmit) and bis(dddt) complexes $[M(dmit)_2]$, (M = Ni, Pd, Pt, *etc.*) has been of interest to many investigators, but mixed-ligand dmit complexes have been studied in only a few cases [5–8]. There are only two reports of the synthesis of an organometallic compound with a cyclopentadienyl ring and dmit, $[Ti(cp)_2(dmit)]$ [7] and $[Co(cp)(dmit)]$ [8,9], which have synthetic potential for novel organosulfur compounds. The electrochemical behaviour of $[Co(cp)(dmit)]$ has been studied only by Shimizu *et al.* [9,10].

The present paper is an extension of the previous papers on some dithiocarbamates, $[Nb(cp)_2(S_2CNR_2)]PF_6$ (R = Me or Et; $R_2 = (CH_2)_4$) [11] and dithiophosphates $[Nb(cp)_2(S_2P(OR)_2)]PF_6$ (R = Me, Et, or Pr^i) [12]. We have also succeeded in isolating some complexes with both a NbS_2 three-membered ring and a dithiophosphate, $[Nb(cp)_2S_2(SP)S(OR)_2]$ (R = Me, Et, or Pr^i) [12] and have reported the electrochemical behaviour of the niobium dithiolato complexes $[Nb(cp)_2(S_2C_2R_2)]$ and $Nb(cp)_2(S_2C_2R_2)]PF_6$ (R = Me or Ph) [13].

The purposes of this study are to (1) to prepare several new Nb^{IV} and Nb^V dithiolato-complexes (Fig.

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SSDI 0022-328X(93)23895-5

1) which will be precursors for conducting organometallic complexes with organosulfur electron donors and (2) to elucidate their electrochemical behaviour and synthetic potential.

2. Experimental details

2.1. Measurements

Cyclic and hydrodynamic voltammetry were performed with an EG&G RARC 175 universal programmer in combination with a SOTELEM Potentiostat/Galvanostat, P/T stat Z1. Their voltammograms were recorded with SEFRAM model TGM, 164 recorder. Electrochemical measurements were conducted in both 0.1 mol dm^{-3} tetraethylammonium hexafluorophosphate (TEAH)-acetonitrile and tetrabutylammonium hexafluorophosphate (TBAH)-dichloromethane solutions at ambient temperature (20°C) under a pure argon. A platinum disk electrode ($\phi = 2$ mm) from Tacussel EDI 101T was used as the working electrode for both cyclic and hydrodynamic voltammetry. The counter electrode was a Pt coil. The reference electrode was a silver–silver ion electrode, Ag/Ag$^+$ (0.1 mol dm^{-3} AgClO$_4$ in acetonitrile). All the potentials cited here are referred to this electrode. The reversible half-wave potential of the ferricinium-ferrocene couple in acetonitrile solution and in dichloromethane solutions were 0.025 V and 0.160 V respectively against this reference electrode.

X-band ESR spectra were recorded on a Bruker ESP300 spectrometer, in dichloromethane, and IR spectra were measured on a Bruker IFS45 WHR FTIR spectrophotometer as KBr pellets. Mass spectra were recorded with a Kratos Profile HV-400 spectrophotometer. The conductivity of the solutions was measured using a Tacussel CD 7D.

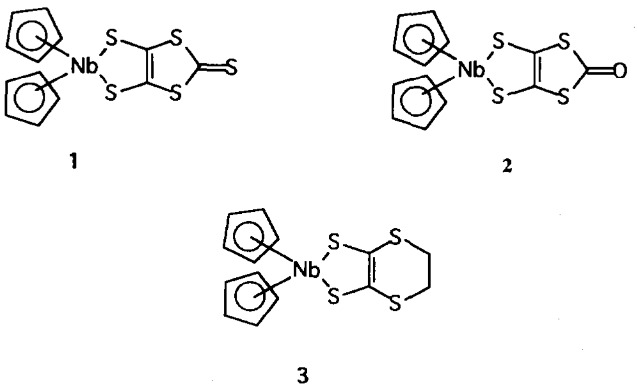

Fig. 1. Niobium(IV) dithiolato complexes prepared in this study.

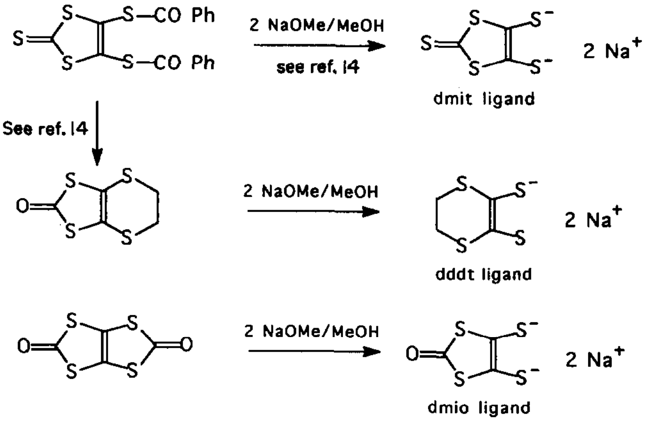

Fig. 2. Synthetic schemes for Na$_2$dmit, Na$_2$dmio and Na$_2$dddt.

2.2. Materials

The solvents and reagents were dried prior to use when necessary. All operations of the preparation procedure of niobium complexes were performed under an argon using Schlenk techniques. The starting material, [Nb(cp)$_2$Cl$_2$], was prepared according to the literature [15] and identified by IR spectrophotometry. The sulfur donors were prepared using the Varma's method [14]. The sodium salts were isolated as solids before use (Fig. 2).

2.2.1. [Nb^{IV}(cp)$_2$(dmit)] (1)

Treatment of [Nb(cp)$_2$Cl$_2$] (0.294 g, 1 mmol) with Na$_2$dmit (0.242 g, 1 mmol) in stirred CH$_2$Cl$_2$ (80 cm^3) at 20°C resulted in a color change from red to green. After 15 h, the resulting solution was filtered and the filtrate was evaporated to dryness. The solid was washed with 10 cm^3 of cold CH$_2$Cl$_2$ and then dried under reduced pressure to afford dark greenish brown crystals in 65% yield. Anal. Found: C, 37.13; H, 2.50; S, 38.22%. C$_{13}$H$_{10}$NbS$_5$: Calc. C, 37.22; H, 2.40; S, 35.96%. The complex was soluble in dichloromethane, acetone and acetonitrile. An ion peak (M$^+$) of 418 was observed in the mass spectrum. Two peaks for ν(C=S) were observed at 1055 and 1030 cm^{-1} in IR (KBr) spectra. Compound **1** is a non-conductor.

2.2.2. [Nb^V(cp)$_2$(dmit)]I (1a)

The chemical oxidation of [Nb^{IV}(cp)$_2$(dmit)] (0.419 g, 1 mmol) by iodine (0.127 g, 0.5 mmol) was performed at room temperature using dichloromethane as solvent (50 cm^3). A violet precipitate was immediately obtained. This was filtered off and washed with dichloromethane and then dried under reduced pressure. Yield 80%. Anal. Found: C, 28.00; H, 1.83; S, 29.40; I, 25.2%. C$_{13}$H$_{10}$INbS$_5$: Calc. C, 28.58; H, 1.83; S, 29.83; I, 23.26%.

Molar conductivity (Λ) for 1 mol dm^{-3} in nitromethane was 81 S cm^2 mol^{-1}, corresponding to a 1:1 electrolyte [16]. The two peaks observed at 1085 and 1010 cm^{-1} for ν(C=S) were shifted to a higher wave number compared with those of the corresponding niobium complex.

2.2.3. [Nb^{IV}(cp)$_2$(dmio)] (2)

[Nb(cp)$_2$Cl$_2$] (0.294 g, 1 mmol) was treated with Na$_2$dmio (0.242 g, 1 mmol) in stirred CH_2Cl_2 at 20°C for 15 h. Otherwise the procedure was similar to that for **1**. Yield, 67%. Anal. Found: C, 38.48; H, 2.58; S, 30.63%. $C_{13}H_{10}NbOS_4$: Calc. C, 38.71; H, 2.50; S, 31.81%. The complex is soluble in dichoromethane, acetone and acetonitrile. An ion peak (M$^+$) of 403 was observed in mass spectrum. Two peaks for ν(C=O) were observed at 1650 and 1600 cm^{-1} in the IR spectrum.

2.2.4. [Nb^V(cp)$_2$(dmio)]I (2a)

[Nb^V(cp)$_2$(dmio)] (0.402 g, 1 mmol) was treated with I_2 (0.127 g, 0.5 mmol) in stirred CH_2Cl_2 at 20°C for 15 h. The procedure was otherwise similar to that for **1a**. Yield 80%. Anal. Found: C, 28.5; H, 1.86; S, 22.5. $C_{13}H_{10}OINbS_4$: Calc. C, 29.45; H, 1.9; S, 24.19. Molar conductivity in nitromethane ($c = 1$ mmol dm^{-3}, $\Lambda =$ 98 S/cm^2 mol^{-1}) corresponds to a 1:1 electrolyte [16]. Two peaks assignable to ν(C=O) were observed in the IR spectrum at 1680 and 1620 cm^{-1}.

2.2.5. [Nb^{IV}(cp)$_2$(dddt)] (3)

[Nb(cp)$_2$Cl$_2$] (0.294 g, 1 mmol) was treated with Na$_2$dddt (0.226 g, 1 mmol) in stirred CH_2Cl_2 (50 cm^3) at 35°C. After 48 h, the resulting solution was filtered and the filtrate was evaporated to dryness. The solid was washed with 10 cm^3 of cold CH_2Cl_2, dried under reduced pressure and recrystallized from dichloromethane–pentane at -50°C. Yield 60%. Anal. Found: C, 39.7; H, 3.3; S, 32.5. $C_{14}H_{14}NbS_4$: Calc. C, 41.69; H, 3.47; S, 31.76. Two peaks assigned to ν(CH) in IR spectrum were observed at 2923 and 2854 cm^{-1}. Complex **3** was not an electrolyte in solution.

3. Results and discussion

The ESR spectra of **1**, **2** and **3** in dichloromethane at room temperature showed hyperfine splitting, with ten peaks corresponding to a nuclear spin 9/2. The values of A and g for **1**, **2** and **3** were listed in Table 1. The values for **1** and **2** were comparable with those of other Nb^{IV} complexes already reported [11,12]. The values obtained for complex **3** show that the delocalization of the unpaired electron onto the dddt is greater than that for dmit and dmio.

TABLE 1. A and g values in ESR spectra of **1**, **2** and **3** in dichloromethane at room temperature

Compound	A (mT)	g
1	8.35	1.988
2	8.32	1.988
3	7.95	1.999

The solubility of the compounds **1a** and **2a** is very low in the usual solvents. The ^{1}H NMR spectra in CD_3COCD_3 did not allow us to infer a precise configuration.

Cyclic voltammograms (CV) of [Nb(cp)$_2$Cl$_2$] in dichloromethane show a reversible one-electron coupled peak in the anodic process, corresponding to Nb^{IV} → Nb^V, and a large irreversible peak in the cathodic process because the solvent is catalytically reduced by the anion [NbCp$_2$Cl$_2$]$^-$. Similar behaviour has been observed in the case of the electrochemical reduction of [Nb(Me$_3$SiC$_5$H$_4$)$_2$Cl$_2$] in dichloromethane [17]. However, in acetonitrile solutions, the CV of the cathodic branch changed to a Nernstian one-electron process corresponding to Nb^{IV} → Nb^{III}, coupled with a fast subsequent homogeneous chemical reaction (Fig. 3). The product generated by the following chemical reaction gave an oxidation peak at -1.03 V, attributable to the oxidation of [Nb^{III}(cp)$_2$Cl(CH$_3$CN)] produced by a ligand replacement reaction from [Nb^{III}(cp)$_2$Cl$_2$]$^-$. A similar mechanism has been observed with other nucleophiles [18].

As shown in Fig. 4, the CV of **1** gave a single coupled cathodic peak and a single coupled anodic peak. The cathodic and anodic peak currents (i_{pc} and i_{pa}) in both oxidation and reduction processes were equal in magnitude and independent of scan rate (v). The i_{pc}/i_{pa} ratio was unity, independent of scan rate, and both the peak currents were proportional to $v^{1/2}$. The separation of the peak potentials was 60 mV in both oxidation and reduction processes, independent of scan rate between 0.02 and 0.2 V s^{-1}. The CV for **2** and **3** showed the similar results. In addition, the cyclic voltammometric behaviour of **1**, **2** and **3** in dichloromethane was basically the same as in acetonitrile for the half-wave potentials of the oxidation and reduction.

Cyclic voltammetric studies on **1**, **2** and **3** in acetonitrile and dichloromethane solutions confirmed that they undergo a reversible oxidation and a reversible reduction process without any complicating side- or subsequent chemical reactions.

The hydrodynamic voltammogram using a rotating disk electrode for these complexes showed an anodic and a cathodic step with limiting currents corresponding to the peaks in CV. The conventional log plot analysis of these steps in the hydrodynamic voltammograms in acetonitrile and dichlorometane solutions revealed that both oxidation and reduction processes are Nernstian one-electron processes. The limiting current was proportional to $w^{1/2}$, where w is rotating angular velocity (Fig. 5); therefore, the limiting currents were controlled by convective diffusion.

The Nb^{IV} complexes were unstable and gradually decomposed in air-free acetonitrile solutions. This instability may be due to replacement of the dithiolato moiety by solvent molecules. In air-free dichloromethane solutions, these complexes were stable.

Consequently, the electrode reactions of **1**, **2** and **3** should correspond to the oxidation of Nb^{IV} to Nb^{V} and the reduction of Nb^{IV} to Nb^{III}. The electrode reaction of these complexes in acetonitrile and dichloromethane were basically the same except for the half-wave potentials for the oxidation and reduction. The reversible half-wave potentials ($E^{r}_{1/2}$) of Nb^{IV} dithiolato-complexes together with those of the Nb^{V} complexes are listed in Table 2.

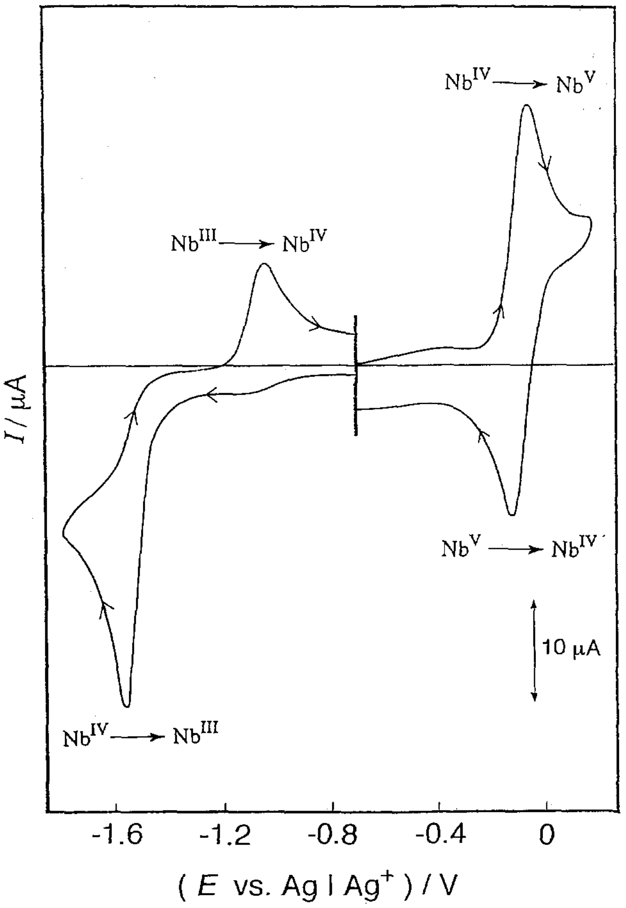

Fig. 3. Cyclic voltammogram of $[Nb(cp)_2Cl_2]$ in acetonitrile solution. Conc. = 1 mmol dm^{-3}, scan rate = 0.1 V s^{-1}, at 20°C.

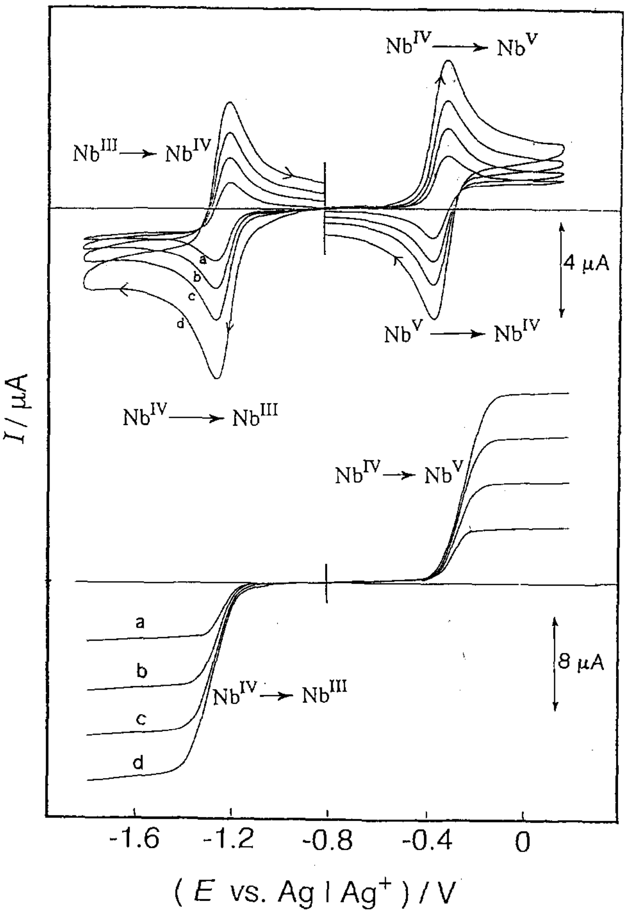

Fig. 4. Cyclic and hydrodynamic voltammograms of **1** in acetonitrile solutions: (a) conc. = 1 mmol dm^{-3}, scan rate = a, 0.02; b, 0.05; c, 0.1; d, 0.2 V s^{-1}, at 20°C. (b) conc. = 1 mmol dm^{-3}, rotation number = a, 100; b, 400; c, 900; d, 1600 rev min^{-1}, at 20°C.

Both reversible oxidation and reduction half-wave potentials of **3** in acetonitrile solutions are about 0.3 V more negative than those of **1** and **2**. This difference can be explained on the basis of the strong electron-donating effect of the terminal ring in dddt on the central metal. This large negative potential shift for **3** suggested that we prepare the charge-transfer complexes between **3** and TCNQ, which is an electron-acceptor. If such charge-transfer complexes could be obtained, they should have super electric conductivity.

The oxidation and reduction half-wave potentials of **1** were slightly more positive than that of **2**. This fact cannot be explained by differences in the electron affinity of terminal sulfur, and oxygen atoms because the Pauling electron affinity of oxygen is larger than that of sulfur.

The voltammetric behaviour of the complexes **1a** and **2a** was the same, except for the reduction half-wave potentials. Cyclic and hydrodynamic voltammograms of

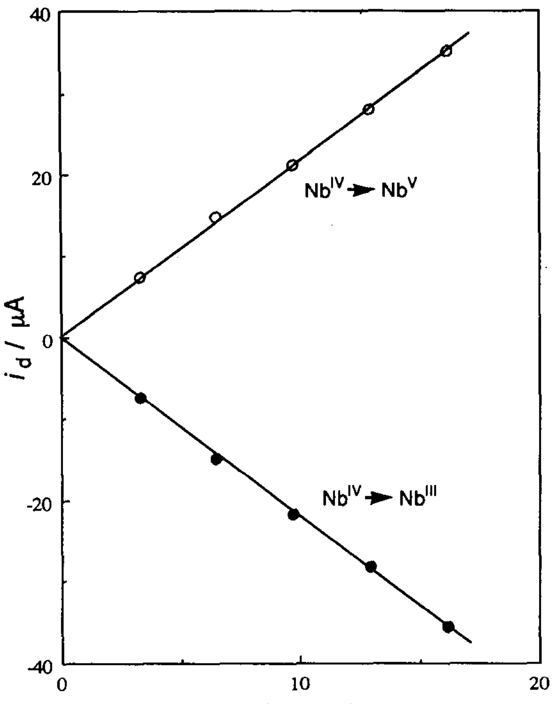

Fig. 5. Dependence of limiting current of hydrodynamic voltammetry on rotating angular velocity. Conditions are as in Figure 4(b). Rotation rate: 100, 400, 900, 1600, 2500 rev min^{-1}.

these complexes showed two one-electron reversible reduction processes, corresponding to Nb^{IV} and Nb^{III}. The reversible half-wave potentials obtained from hydrodynamic voltammograms for two steps reduction, $Nb^{V} \rightarrow Nb^{IV}$ and $Nb^{IV} \rightarrow Nb^{III}$, were in good agreement with that obtained from oxidation and reduction steps of the Nb^{IV} complexes, as shown in Table 2. The CVs of **1a** and **2a** also showed complicated peaks due to the oxidation of the iodide counter ion to iodine in the anodic branch. The mechanism of oxidation of iodide in aprotic medium has been described previously [19].

TABLE 2. Reversible half-wave potentials [a] of several Nb^{IV} and Nb^{V} dithiolato-complexes with two cyclopentadienyl rings in acetonitrile and dichloromethane

Complexes	$E^{r}_{1/2}$ (V)		Solvent
	Nb^{V}/Nb^{IV}	Nb^{IV}/Nb^{III}	
Nb^{IV} complexes			
$[Nb(cp)_2Cl_2]$	−0.08	−1.57 [b]	CH_3CN
	−0.01	−1.74 [c]	CH_2Cl_2
1	−0.33	−1.22	CH_3CN
2	−0.39	−1.27	CH_3CN
	−0.29	−1.24	CH_2Cl_2
3	−0.64	−1.53	CH_3CN
Nb^{V} complexes			
1a	−0.33	−1.22	CH_2Cl_2
2a	−0.39	−1.27	CH_3CN
	−0.38	−1.31	CH_2Cl_2

[a] *Vs.* Ag/0.1 mol dm^{-3} $AgClO_4$ in acetonitrile. [b] With fast subsequent chemical reaction. [c] Peak potential in CV.

4. Conclusion

Niobium(IV) complexes with dmit, dmio, or dddt exhibit reversible one-electron oxidation and reduction processes based on the central metal. The reversible half-wave potential of the niobium(IV)-dddt complex is much more negative than those of corresponding dmit and dmio complexes. This suggests that the dddt complex may be a good electron-donor for the preparation of charge-transfer complexes with electron acceptors such as TCNQ, and such charge-transfer complexes should have super electric conductivity. Niobium(V)-dmit and -dimo complexes were also prepared and isolated after chemical oxidation using iodine.

References

1 M.M. Ahmadd and A. Underhill, *J. Chem. Soc., Dalton Trans.*, (1982) 1065.
2 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishino, K. Kajita and Y. Sakaki, *Chem. Lett.*, (1987) 1819.
3 T. Nakamura, K. Kojima, M. Matsumoto, H. Tachibana, M. Tanaka, E. Manda and Y. Kawabata, *Chem. Lett.*, (1989) 367.
4 I. Hawkins and A.E. Underhill, *J. Chem. Soc., Chem. Commun.*, (1990) 1593.
5 R. Vicente, J. Ribas, X. Solans, M. Font-Altaba, A. Mari, P. de Loth and P. Cassoux, *Inorg. Chim. Acta, 132* (1987) 229.
6 G. Matsubayashi, M. Hirao and T. Tanaka, *Inorg. Chim. Acta, 1444* (1988) 217.
7 X. Yang, T.B. Rauchfuss and S.R. Wilkson, *J. Am. Chem. Soc., 111* (1989) 3465.
8 R.D. Bereman and H. Lu, *Inorg. Chim. Acta, 204* (1933) 53.
9 H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama and A. Sugimori, *Inorg. Chim. Acta, 175* (1990).
10 M. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama and A. Sugimori, *App. Organomet. Chem., 5* (1991) 221.
11 (a) J. Amaudrut, J.E. Guerchais and J. Sala-Pala, *J. Organomet. Chem., 157* (1976) C-10.
(b) B. Viard, *Thèse Besançon*, 1988, second part.
12 B. Viard, J. Sala-Pala, J. Amaudrut, J. Guerchais, C. Sanchez and J. Livage, *Inorg. Chem. Acta, 39* (1980) 99.
13 B. Viard, J. Amaudrut, J. Sala-Pala, A. Fakhr, Y. Mugnier and C. Moise, *J. Organomet. Chem., 292* (1985) 403.
14 K.S. Varma, A. Bury, N.J. Harris and A. Underhill, *Synthesis, 837* (1987).
15 C.R. Lucas, *Inorg. Synth., 16* (1976) 107.
16 W. Geary, *Coord. Chem. Rev., 9* (1967) 395.
17 A. Antinolo, M. Fajardo, A. Otero, Y. Mugnier, H. Nabaoui and H. Mourad, *J. Organomet. Chem., 414* (1991) 155.
18 A. Fakhr, Y. Mugnier, B. Gautheron and E. Laviron, *J. Organomet. Chem., 255* (1983) C 8.
19 E. Samuel, D. Guery and J. Vedel, *J. Organomet. Chem., 263* (1984) C 43.