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NUCLEOPHILIC SUBSTITUTION BY ARENETHIOLATES AT THE CARBENE CARBON OF PENTACARBONYL(METHOXYMETHYLCARBENE)-METAL(0) COMPLEXES (METAL = Cr, Mo, or W)

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Summary

The phenylthiocarbene complexes, $[(CO)_5MC(CH_3)(SPh)]$ (M = Cr, Mo, or W) have been prepared in good yield by the reaction of $[(CO)_5MC(CH_3)(OCH_3)]$ (M = Cr, Mo, or W) with NaSPh in benzene/methanol in the presence of HCl. A series of *para*-substituted phenylthiocarbene complexes of tungsten, $[(CO)_5WC(CH_3)(SC_6H_4Y)]$, (Y = *p*-Br, *p*-F, *p*-H, *p*-CH_3, *p*-OCH_3 or *p*-OH) have also been prepared by the reaction of the appropriate arenethiolate ion with $[(CO)_5WC(CH_3)(OCH_3)]$. Poor nucleophiles such as *p*-nitrobenzenethiolate and pentafluorobenzenethiolate did not react with $[(CO)_5WC(CH_3)(OCH_3)]$ to form the corresponding phenylthiocarbene complex. A mechanism accounting for the formation of these phenylthiocarbene complexes is proposed. The complexes have been characterized by their infrared, electronic, mass, ^1H NMR, and ^{13}C NMR spectra. These spectroscopic data have been used to establish the structure of these complexes in solution and indicate that the phenyl ring bonded to sulfur is probably not coplanar with the "carbene" plane.

Introduction

Since the report of the first well defined complex of a transition metal containing a coordinated organic carbene moiety [1], numerous other "carbene" complexes of transition metals have been reported. For recent reviews see ref.2. A solvolysis reaction (eqn.1) of $[(CO)_5CrC(CH_3)(OCH_3)]$ in benzenethiol has recently been reported by Fischer and his co-workers [3] and the crystal and

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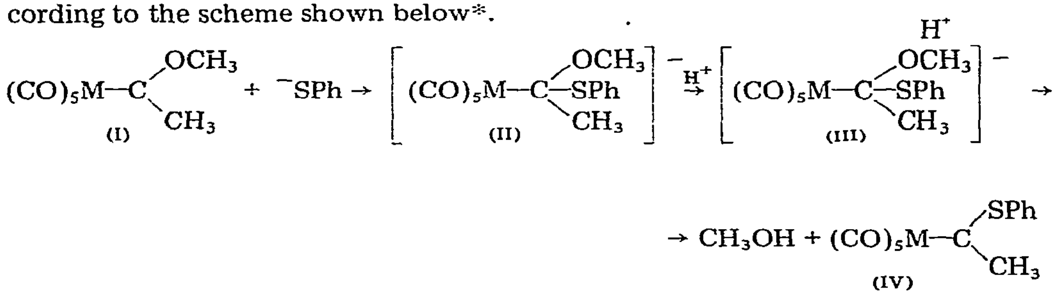
molecular structure of the solvolysis product has subsequently been determined [4]. During the course of investigating the coordinating properties of benzenethiol and its derivatives [5], we have investigated the reaction between $[(CO)_5MC(CH_3)(OCH_3)]$ (M = Cr, Mo or W) and sodium benzenethiolate in benzene/methanol and have found that reaction (2) proceeds smoothly at room temperature and provides a facile synthetic route to phenylthiocarbene complexes of Group VIb metals.

$$[(CO)_5CrC(CH_3)(OCH_3)] + HSPh \rightarrow [(CO)_5CrC(CH_3)(SPh)] + CH_3OH \qquad (1)$$

$$\underset{(I)}{[(CO)_5MC(CH_3)(OCH_3)]} + NaSPh + HCl \rightarrow \underset{(IV)}{[(CO)_5MC(CH_3)(SPh)]} + CH_3OH + NaCl \qquad (2)$$

Results and Discussion

The appropriate methoxycarbene complex, (I), and sodium benzenethiolate are allowed to react in benzene/methanol and then methanolic HCl is added to form the product, (IV). After removal of the precipitated NaCl, the phenylthiocarbene complex may be eluted from a "florisil" column with hexane and recrystallized from hexane/ether at —78°. If the methoxycarbene complex, (I), is first allowed to react with HCl, followed by the addition of benzenethiolate ion, the phenylthiocarbene complex, (IV), is not formed. These observations suggest that there is an inital nucleophilic attack by the benzenethiolate ion at the carbene carbon of (I) to form the anionic intermediate, (II), which is subsequently protonated by the acid at the methoxy oxygen atom, (III), followed by elimination of methanol to form the phenylthiocarbene complex, (IV), according to the scheme shown below[*].



The chromium complex rapidly decomposes in the solid state and in solution when exposed to light. The molybdenum derivative behaves in a similar fashion although decomposition appears to occur at a somewhat slower rate, whereas the tungsten derivative is quite stable as a solid and in solution.

Reaction (2) was also carried out with $[(CO)_5WC(CH_3)(OCH_3)]$ and a number of *para*-substituted benzenethiolates in order to examine the effect of sub-

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[*] After completion of our study, a report describing the isolation and characterization of the diphenylcarbene complex, $[(CO)_5WC(Ph)_2]$, came to our attention [6]. This particular complex was prepared via a similar synthetic route reported here for the phenylthiocarbene complexes, i.e., reaction of $[(CO)_5WC(Ph)(OCH_3)]$ with LiPh followed by the addition of HCl.

stituents in a series of phenylthiocarbene complexes of the type, $[(CO)_5MC(CH_3)(SC_6H_4Y)]$ where Y is *p*-Br, *p*-F, *p*-H, *p*-CH_3, *p*-OCH_3, or *p*-OH. Weak nucleophiles such as *p*-$O_2NC_6H_4S^-$ and $F_5C_6S^-$ did not react with $[(CO)_5WC(CH_3)(OCH_3)]$ via reaction (2) to form the corresponding phenylthiocarbene complex, (IV). The presence of acid resulted in the decomposition of $[(CO)_5WC(CH_3)(OCH_3)]$.

Infrared spectral data obtained in hexane are given in Table 1. The data for $[(CO)_5CrC(CH_3)(SPh)]$ are in good agreement with those reported by Fischer et al. [3] and are consistent with C_{4v} local symmetry for the $(CO)_5M$ group. Examination of the data in Table 1 indicates that $\nu(CO)(A_1\ (2))$ *trans* to the thiocarbene moiety is insensitive to the nature of the *para*-substituent, Y. This observation differs from that reported for the complexes, $[(CO)_5CrC(Ar)(OCH_3)]$ [7], $[(CO)_5CrC(Ar)(NH_2)]$ [8], and $[(CO)_5CrC(CH_3)(NHAr)]$ [9], where Ar = a substituted phenyl ring. In these latter complexes, the electronic effect of the substituent(s) associated with the Ar group manifests itself in the stretching frequency (or force constant) for the CO ligand *trans* to the "carbene" ligand.

The thiocarbene complexes of Cr, Mo, and W reported here exhibit a characteristic charge transfer band (metal-to-"carbene") in the visible region between ≈ 445—470 nm of their electronic spectra. These data are given in Table 2 and representative spectra are shown in Fig. 1. It may be noted that the position of the charge transfer band in the tungsten complexes at ≈445 nm is insensitive to the nature of the *para*-substituent, Y. Also, the asymmetry of this band on its long wavelength side suggests that it is overlapping another intense band at ≈ 480 nm.

The parent ion for each complex was observed in their respective mass spectra but the complexes fragment differently in the mass spectrometer as indicated below where L = $C(CH_3)SPh$ or $C(CH_3)SC_6H_4Y$.

$$(CO)_5CrL^+ \rightarrow (CO)_4CrL^+ \xrightarrow{-2\,CO} (CO)_2CrL^+ \rightarrow (CO)CrL^+ \rightarrow CrL^+ \qquad (3)$$

$$(CO)_5MoL \rightarrow (CO)_4MoL^+ \rightarrow (CO)_3MoL^+ \rightarrow (CO)_2MoL^+ \rightarrow (CO)MoL^+ \rightarrow MoL^+ \qquad (4)$$

$$(CO)_5WL^+ \xrightarrow{-2\,CO} (CO)_3WL^+ \rightarrow (CO)_2WL^+ \rightarrow (CO)WL^+ \rightarrow WL^+ \qquad (5)$$

Only the molybdenum complex loses CO in a stepwise fashion.

Pertinent ^1H NMR data are given in Table 3. In addition to resonances due to the SC_6H_4Y group, the spectra are characterized by a singlet at $\delta \approx 3.0$ ppm

TABLE 1

INFRARED SPECTRAL DATA IN n-HEXANE

Complex	$\nu(CO)$ (cm^{-1})		
	$A_1(1)$	E	$A_1(2)$
$[(CO)_5CrC(CH_3)(SPh)]$	2061s	1961vs	1961vs
$[(CO)_5MoC(CH_3)(SPh)]$	2067s	1990s	1964vs
$[(CO)_5WC(CH_3)(SC_6H_4Br)]$	2068s	1958vs	1958vs
$[(CO)_5WC(CH_3)(SC_6H_4F)]$	2068s	1958vs	1958vs
$[(CO)_5WC(CH_3)(SC_6H_5)]$	2068s	1956vs	1956vs
$[(CO)_5WC(CH_3)(SC_6H_4CH_3)]$	2067s	1958vs	1958vs
$[(CO)_5WC(CH_3)(SC_6H_4OCH_3)]$	2067s	1958vs	1958vs
$[(CO)_5WC(CH_3)(SC_6H_4OH)]$	2068s	1959vs	1959vs

TABLE 2

ELECTRONIC SPECTRAL DATA

Complex	λ_{max} (nm)	ϵ_{max} ($M^{-1} \cdot cm^{-1}$)
$[(CO)_5CrC(CH_3)(SPh)]$	463	1.4×10^4
	242	14.8×10^4
	222	16.5×10^4
$[(CO)_5MoC(CH_3)(SPh)]$	455	1.5×10^4
	342	3.2×10^3
	247	14.3×10^4
	224	14.6×10^4
$[(CO)_5WC(CH_3)(SC_6H_4Br)]$	445	2.9×10^4
	$(476)^a$	(1.9×10^4)
	356	6.7×10^3
	240	1.1×10^5
	234	1.1×10^5
$[(CO)_5WC(CH_3)(SC_6H_4F)]$	443	2.17×10^4
	$(477)^a$	(1.4×10^4)
	357	5×10^3
	241	7.3×10^4
	224	8.0×10^4
$[(CO)_5WC(CH_3)(SC_6H_5)]$	445	1.7×10^4
	$(477)^a$	$(1,1 \times 10^4)$
	358	4.1×10^3
	240	6.2×10^4
	223	6.8×10^4
$[(CO)_5WC(CH_3)(SC_6H_4CH_3)]$	444	3.8×10^4
	$(475)^a$	(3.0×10^4)
	358	8.7×10^3
	241	1.0×10^5
	227	1.3×10^5
$[(CO)_5WC(CH_3)(SC_6H_4OCH_3)]$	447	4.2×10^4
	$(482)^a$	(2.7×10^4)
	357	1.0×10^4
	239	2.9×10^5
$[(CO)_5WC(CH_3)(SC_6H_4OH)]$	445	6.4×10^4
	$(469)^a$	(4.3×10^4)
	356	1.5×10^4
	238	1.1×10^5
	231	1.2×10^5

[a] Not well resolved.

due to the methyl protons of the "carbene" ligand. The ^1H NMR spectra in chloroform-*d* and acetone-d_6 for the complexes, $[(CO)_5MC(CH_3)(SPh)]$ (M = Cr, Mo, or W) are unchanged when the temperature is lowered to −60° indicating that there is no *cis—trans* isomerization occurring in solution with respect to a rotation about the C(carbene)—S bond for all three complexes. Isomerization of this type has been observed for $[(CO)_5CrC(CH_3)(OCH_3)]$ [10]. A change in the nature of the *para*-substituent, Y, in the tungsten complexes does not alter this behaviour in $CDCl_3$. The data in Table 3 show that the chemical shift for the methyl protons of the "carbene" ligand in the $[(CO)_5WC(CH_3)(SC_6H_4Y)]$ complexes is also somewhat insensitive to the nature of the *para*-substituent, Y.

Since ^{13}C NMR spectroscopy has recently proven to be a sensitive probe to study the properties of transition metal "carbene" complexes [11—13], it was decided to record the ^{13}C NMR spectra of the tungsten derivatives, $[(CO)_5WC(CH_3)(SC_6H_4Y)]$ in order to further investigate the apparent lack of any substantial substituent effect noted above in this series of complexes. Pertinent ^{13}C

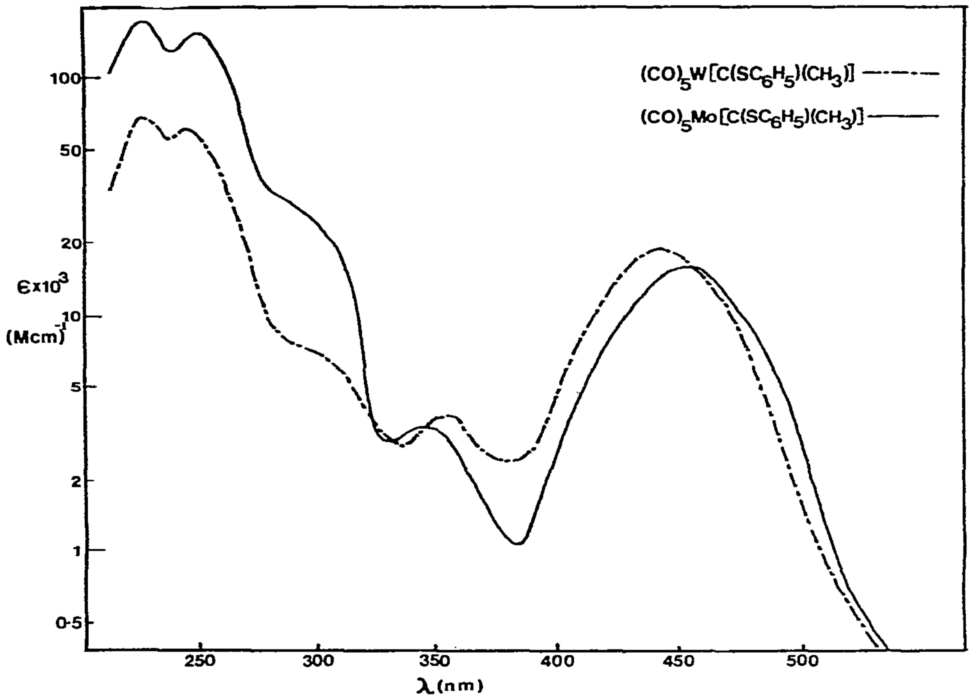

Fig. 1. Electronic spectra of W and Mo complexes.

NMR data ($CDCl_3$ solution) are given in Table 4. It may be noted that the shieldings of the two types of carbonyl carbon atoms (*cis* and *trans* to the "carbene" ligand) are essentially invariant to the nature of the *para*-substituent, Y. The shieldings of the "carbene" carbons which vary from ca. 331 to 333 ppm, are also relatively insensitive to the nature of Y. This behaviour contrasts with that reported for $[(CO)_5WC(C_6H_4Y)(OCH_3)]$ and $[(CO)_5CrC(C_6H_4Y)(OCH_3)]$ [12] (Y = an electron-withdrawing or an electron-releasing substituent). The shielding of the "carbene" carbon in these particular complexes was noted to be *significantly* dependent on the nature of Y.

TABLE 3

^1H NMR DATA

Complex	$\delta(CH_3)^a$ (ppm)		
$[(CO)_5CrC(CH_3)(SPh)]$	3.29	$(3.40)^b$	
$[(CO)_5MoC(CH_3)(SPh)]$	3.21	$(3.35)^b$	
$[(CO)_5WC(CH_3)(SC_6H_4Br)]$	3.02		
$[(CO)_5WC(CH_3)(SC_6H_4F)]$	3.03		
$[(CO)_5WC(CH_3)(SC_6H_5)]$	3.04	$(3.22)^b$	
$[(CO)_5WC(CH_3)(SC_6H_4CH_3)]$	3.04		$\delta(CH_3)$, 2.38
$[(CO)_5WC(CH_3)(SC_6H_4OCH_3)]$	3.05		$\delta(OCH_3)$, 3.83
$[(CO)_5WC(CH_3)(SC_6H_4OH)]$	3.05		$\delta(OH)$, 5.21

^{a}Value in $CDCl_3$ unless otherwise indicated. ^{b}Value obtained in acetone-d_6.

TABLE 4

^{13}C SHIELDINGS^{a} FOR THE COMPLEXES, [$(CO)_5WC(CH_3)(SC_6H_4Y)$]

Para-substituent, Y	δ(CH_3)	δ(carbene)	δ(CO) (*trans*)	δ(CO) (*cis*)
Br	49.5	331.1	207.4	196.8
F	49.1	332.4	207.7	197.1
H	49.3	332.0	207.5	197.1
CH_3^{b}	49.1	332.8	207.8	197.4
CH_3O^{c}	49.0	333.3	207.5	197.1
OH	49.0	333.3	207.7	197.1

[a] In ppm (± 0.1)(downfield positive) from TMS. [b] δ(*p*-CH_3) 21.4 ppm. [c] δ(*p*-OCH_3) 55.3 ppm.

Since there is little observable effect due to the substituent, Y, in the infrared, electronic, ^{1}H NMR, and ^{13}C NMR spectra of [$(CO)_5WC(CH_3)(SC_6H_4Y)$], it seems likely that the phenyl ring bonded to sulfur in these complexes is essentially perpendicular to the carbene plane. However, it must be pointed out that free rotation about the S—C_6H_4Y bond or the fact that a sulfur atom intervenes between the "carbene" carbon and the substituted phenyl ring may be responsible for the absence of any substantial substituent effect in the spectra of these complexes. However, these two effects would appear to be less likely in view of the fact that the sulfur atom in a series of substituted thioanisoles, $CH_3SC_6H_4Y$, is capable of transmitting the electronic effect of Y to the CH_3 group [14]. The phenyl ring in [$(CO)_5CrC(CH_3)(SPh)$] has been shown to be perpendicular to the "carbene" plane in the solid state [14]. In this particular complex the phenylthio and methyl groups are *cis* to one another relative to the C("carbene")—S bond. Consequently, it is reasonable to speculate that the phenyl ring in the [$(CO)_5WC(CH_3)(SC_6H_4Y)$] complexes as well as [$(CO)_5MoC(CH_3)(SPh)$] will also be perpendicular to the "carbene" plane. Also, because of the similarity in the chemical shifts of the methyl protons for the phenylthiocarbene complexes described here, the *cis* arrangement of the SC_6H_4Y and CH_3 groups would appear to be the preferred isomer of these complexes.

Experimental

(1). Materials

Samples of molybdenum and tungsten hexacarbonyls were kindly donated by Climax Molybdenum, Inc., Ann Arbor, Michigan. Chromium hexacarbonyl was purchased from Strem Chemicals, Inc., Danvers, Massachusetts. Sodium benzenethiolate was prepared by stirring equimolar amounts of sodium metal and thiophenol in dry ether at room temperature for 72 h. The salt was filtered off, washed with dry ether and used immediately. The salts, *p*-$CH_3C_6H_4SNa$ and *p*-$CH_3OC_6H_4SNa$, were prepared in a similar manner. A sample of *p*-hydroxybenzenethiol was a gift from Crown Zellerbach, Inc., Camas, Washington. Trimethoxyonium fluoroborate [15] and the pentacarbonylmetal methylmethoxycarbene complexes, [$(CO)_5MC(CH_3)(OCH_3)$] (M = Cr, Mo, or W) [16] were prepared according to methods outlined in the literature. Other chemicals used were reagent grade or better. Reactions were performed under an atmosphere of nitrogen but work-ups were carried out in the open. Microanalyses were carried out by Chemalytics, Inc., Tempe, Arizona. Melting points were determined on a Fisher—Johns melting point apparatus and are uncorrected.

(2). Preparation of the complexes, $[(CO)_5MC(CH_3)(SPh)]$ (M = Cr, Mo, or W)

The following general procedure was used to prepare these complexes. A sample (0.8 g) of the appropriate $[(CO)_5MC(CH_3)(OCH_3)]$ complex (M = Cr, Mo, or W) was dissolved in 80 ml of oxygen-free benzene. To this solution was then added 0.8 g of sodium benzenethiolate dissolved in 15—20 ml of methanol and the resulting solution was stirred at room temperature for about 5 min whereupon 15 ml of methanolic HCl (6% v/v) was added dropwise to the stirred solution over a period of about 20 min. Upon addition of the HCl solution, the reaction solution became deep red in colour and NaCl precipitated. The resulting mixture was then stirred at room temperature for 1 h. In the case of the molybdenum complex, the time of stirring was confined to a period of less than ½ h in order to avoid decomposition. After completion of the reaction, the volume of the reaction mixture was reduced to about one third of its original volume. At this point, 80 ml of water and 100 ml of n-hexane were added to it in succession. The aqueous layer was discarded and the organic layer was dried over anhydrous Na_2SO_4. The Na_2SO_4 was then filtered and the solution evaporated to dryness leaving a dark red oily residue. A "florisil" column (50 × 3 cm) was charged with this residue and eluted with n-hexane. The deep red effluent was collected and its volume reduced. This concentrated solution was then cooled to —78° and the desired product precipitated from solution. This was air-dried and recrystallized from hexane/ether (1/1) as deep red needle-like crystals which were finally dried in air at room temperature. Analytical data are given in Table 5.

(3). Preparation of $[(CO)_5WC(CH_3)(SC_6H_4Y)]$ ($Y = p\text{-}CH_3$, $p\text{-}OCH_3$)

These complexes were prepared following the procedure described above for $[(CO_5WC(CH_3)(SPh)]$

TABLE 5

ANALYTICAL DATA

Complex	Found (calcd) (%)		M.p. (°C)	Yield (%)	Mol. wt.[a], found (calcd.)
	C	H			
$[(CO)_5CrC(CH_3)(SPh)]$	47.29 (47.55)	2.43 (2.44)	67	75	328 (328)
$[(CO)_5MoC(CH_3)(SPh)]$	41.70 (41.93)	2.38 (2.15)	70	60	372 (372)
$[(CO)_5WC(CH_3)(SC_6H_4Br)]$	29.01 (28.95)	1.26 (1.30)	93-94	90	539 (539)
$[(CO)_5WC(CH_3)(SC_6H_4F)]$	32.51 (32.64)	1.36 (1.46)	88	80	478 (478)
$[(CO)_5WC(CH_3)(SC_6H_5)]$	33.91 (33.88)	1.74 (1.55)	76	75	460 (460)
$[(CO)_5WC(CH_3)(SC_6H_4CH_3)]$	35.38 (35.44)	1.94 (2.11)	75	86	474 (474)
$[(CO)_5WC(CH_3)(SC_6H_4OCH_3)]$	34.26 (34.29)	1.78 (2.04)	72	70	490 (490)
$[(CO)_5WC(CH_3)(SC_6H_4OH)]$	32.60 (32.77)	1.46 (1.68)	124	72	476 (476)

[a] Parent ion in the mass spectrometer.

(4). *Preparation of* $[(CO)_5WC(CH_3)(SC_6H_4)](Y = p\text{-}Br, p\text{-}F)$

A solution of p-$BrC_6H_4S^-$ or p-$FC_6H_4S^-$ was prepared by adding 0.5 g of NaOH to 1.5 ml of the appropriate thiol dissolved in 30 ml of methanol. This mixture was stirred until the neutralization was completed whereupon 30 ml of benzene were added. To this solution were then added 1.2 g of $[(CO)_5WC(CH_3)$-(OCH_3) and the resulting solution stirred for about 10 min at room temperature. Methanolic HCl (15 ml, 6% v/v) was added to complete the reaction sequence. The reaction mixture was then worked-up as before. The crude products were recrystallized from n-hexane and air dried. Analytical data are given in Table 5.

(5). *Preparation of* $[(CO)_5WC(CH_3)(SC_6H_4OH)]$

A solution of p-$^-OC_6H_4S^-$ was prepared by adding 1.0 g of NaOH to 1.5 g of p-hydroxythiophenol dissolved in 30 ml of methanol. To this solution was added 40 ml of benzene with stirring followed by the addition of 40 ml of methanolic HCl (6% v/v). The reaction mixture was worked-up as before but the complex was extracted using a $CHCl_3/H_2O$ mixture rather than a n-hexane/H_2O mixture. The complex was eluted from "florisil" using $CHCl_3$. The complex was precipitated from solution by cooling to −40° and recrystallized from $CHCl_3$. Analytical data are given in Table 5.

(6). *Physical measurements*

Infrared spectra were recorded on a Beckman IR-12 double beam recording spectrophotometer using NaCl liquid cells (0.1 mm). The instrument was calibrated with CO in the ν(CO) region and the reported frequencies are believed to be reliable within $\pm$ 2 cm^{-1}. Proton NMR spectra were recorded on a Varian HA-100 spectrometer. Electronic spectral data were recorded with the aid of a Beckman Acta C III double beam recording spectrophotometer. A Varian CH7 mass spectrometer was used to obtain the mass spectra at an ionizing potential of 70eV and an ionizing current of 100 mA. ^{13}C NMR spectra were measured on a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.2 MHz. All spectra were determined with noise-modulated proton decoupling. The spectra were recorded in chloroform-*d* solutions in 5 mm sample tubes and were calibrated using the solvent resonances as secondary calibrations [17]. A time delay of 3 sec was used between pulses.

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