Journal of Organometallic Chemistry, 260 (1984) 81–89
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF CARBONYL COMPLEXES (NN)M(CO)$_4$ (M = Mo, W; NN = 2,2′-BIPYRIDINE, 1,10-PHENANTHROLINE; 2,9-DIMETHYL-1,10-PHENANTHROLINE) WITH MERCURY HALIDES AND PSEUDOHALIDES

M.P. PARDO and M. CANO

Facultad de Ciencias Químicas, Departamento de Química Inorgánica, Universidad Complutense, Madrid - 3 (Spain)

(Received August 3rd, 1983)

Summary

The reactions of the mercury compounds HgX_2 with X = Cl, Br, CN, or SCN, with complexes (NN)M(CO)$_4$ (NN = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp); M = Mo, W) give complexes of the types: (dmp)(CO)$_3$M · nHgX$_2$ (M = Mo, X = Cl, $n = 1$; M = W, X = Cl, $n = 1.5$, X = Br, $n = 2$); (NN)(CO)$_3$MHg(SCN)$_2$ (NN = bipy, phen, dmp; M = Mo, W) and [(phen)(CO)$_3$Mo]$_2$Hg(CN)$_2$ depending on the mercuric derivative and NN-donor ligand employed.

The infrared and electronic absorption and conductance data show all the products to be tricarbonyl species. The reactions involve partial CO displacement without elimination of the NN-donor ligand.

Introduction

The reaction between complexes of transition basic metals and mercury halides as Lewis acids is one of the methods described in the literature for the preparation of compounds with metal–mercury bonds. Thus reactions of the (NN)M(CO)$_4$ complexes (M = Mo, W; NN = bipy, phen) with $HgCl_2$ and $HgBr_2$ have given compounds of the type (NN)(CO)$_3$MHgX$_2$ via an oxidative elimination reaction [1]. The resolution of the crystal structure of some of these derivatives has demonstrated the presence of M–Hg bonds [2]. Only in the case of the reaction of the complexes of the type (NN)W(CO)$_4$ were adducts of formula (NN)(CO)$_4$W · 2HgX$_2$ isolated; these give the tricarbonyl species mentioned above by CO elimination.

Kinetic studies [3–5] have shown that in all cases the reactions of the (NN)M(CO)$_4$ complexes proceed via intermediate adducts. The weakening of the M–CO bond in these adducts, produced by the electronic donation of the metal to the mercury, favours the CO elimination and so the formation of tricarbonyl species. Since a

0022-328X/84/$03.00

strong interaction between the metal basic complex and the mercury halide seems to result in the final formation of tricarbonyl species with metal–metal bonds we considered it of interest to use strong donor ligands which increase the basicity of the metal complex $(NN)M(CO)_4$, in order to throw light on the behaviour of mercury derivatives having a more electrofile character.

This paper describes the reactions of complexes of the type $(dmp)M(CO)_4$ (dmp = 2,9-dimethyl-1,10-phenanthroline; M = Mo, W) with mercury halides and the analogous reactions of $Hg(CN)_2$ and $Hg(SCN)_2$ with the $(NN)M(CO)_4$ complexes (M = Mo, W; NN = bipy, phen, dmp).

Results and discussion

A. Reactions of (dmp)M(CO)$_4$ (M = Mo, W) with HgX$_2$ (X = Cl, Br)

Tetracarbonyl complexes of the type $(dmp)M(CO)_4$ (M = Mo, W) react with $HgCl_2$ and $HgBr_2$ at room temperature under N_2; the colour of the solution changes and evolution of CO is observed.

The reaction of $(dmp)Mo(CO)_4$ with $HgBr_2$ gave a solid which decomposed with deposition of metallic mercury. In the other cases new compounds of the type $[(dmp)(CO)_3M \cdot nHgX_2]$ were isolated. The reaction can be represented as shown in eq. 1.

$$(dmp)M(CO)_4 + HgX_2 \rightarrow (dmp)(CO)_3M(HgX)(X) + CO \tag{1}$$

The representation is analogous to that proposed for the reactions involving bipy and phen as NN donor ligand.

The compounds obtained can be formulated as $(dmp)(CO)_3Mo \cdot HgCl_2$, $(dmp)(CO)_3W \cdot 1.5HgCl_2$ and $(dmp)(CO)_3W \cdot 2HgBr_2$ on the basis of their analytical data (Table 1). They are yellow-orange microcrystalline solids, insoluble in non-polar solvents and sligthly soluble in polar solvents. They are unstable to air on prolonged exposure, and undergo photochemical reactions in light. Their suspensions in acetone produce a deposit of metallic mercury. Table 1 lists some properties of the products isolated.

The reaction times are much longer for the tungsten complexes than for the molybdenum complexes.

The conductance measurements in DMF solution (Table 1) confirm the neutral character of the complexes. There is no increase in the conductance upon addition of an excess of HgX_2 to the solution.

IR spectra. The infrared spectra were recorded in the 4000–200 cm^{-1} region in KBr disks and in Nujol mulls. Since the complexes have low solubilities their solution IR spectra were not recorded. Table 2 gives the values of the most characteristic infrared frequencies with their assignments.

The derivatives obtained show three $\nu(CO)$ bands in the 1990–1860 cm^{-1} region, in contrast with the four bands typical of the tetracarbonyl species. These bands are modificated with respect to the parent compounds. This can be attributed to an increment in the formal oxidation state of the metal atom as well as to a change in the stereochemistry and to effects of the substituents. However, the frequencies of the 3 bands is typical of the heptacoordinate tricarbonyl complexes [6].

The stretching and bending frequencies of the M–CO bonds, which appear in the 600–400 cm^{-1} region, were assigned by comparison with data for the

TABLE 1

ANALYTICAL AND OTHER DATA FOR THE NEW COMPOUNDS

Compound [a]	Colour	Yield (%)	Elemental analysis (Found (calcd.)(%)) C	H	N	M.p. [b] (°C)	Conductivity [c] Ω_M (ohm^{-1} cm^2 mol^{-1})
$dmp(CO)_3Mo \cdot HgCl_2$	yellow-orange	47	30.89 (30.92)	1.45 (1.81)	4.15 (4.24)	163–165	13.33
$dmp(CO)_3W \cdot 1.5HgCl_2$	orange	57	22.58 (23.11)	1.27 (1.35)	3.01 (3.17)	167–170	12.28
$dmp(CO)_3W \cdot 2HgBr_2$	orange	40	17.57 (17.05)	1.00 (1.00)	2.31 (2.34)	149–153	25.26
$bipy(CO)_3Mo \cdot Hg(SCN)_2$	orange	73	27.65 (27.75)	1.34 (1.22)	8.87 (8.57)	134	39.55
$bipy(CO)_3W \cdot Hg(SCN)_2$	orange	93	24.20 (24.31)	1.08 (1.08)	7.43 (7.55)	105–109	11.8
$phen(CO)_3Mo \cdot Hg(SCN)_2$	orange	79	30.04 (30.15)	1.40 (1.18)	8.16 (8.27)	139	20.48
$phen(CO)_3W \cdot Hg(SCN)_2$	orange	87	26.88 (26.68)	1.19 (1.04)	7.68 (7.32)	129	8.23
$dmp(CO)_3Mo \cdot Hg(SCN)_2$	yellow-orange	69	32.08 (32.34)	1.68 (1.70)	7.91 (7.94)	137–138	14.93
$dmp(CO)_3W \cdot Hg(SCN)_2$	orange	89	28.98 (28.78)	1.51 (1.50)	7.06 (6.86)	115	11.16
$[phen(CO)_3Mo]_2 \cdot Hg(CN)_2$	yellow	71	38.91 (39.53)	1.70 (1.64)	8.30 (8.64)	172–180	7.64

[a] Each compound is diamagnetic. [b] Decomposition temperature. [c] In DMF at 22°C for concentrations ca. 10^{-3}–10^{-4} *M*.

$[(C_5H_5)(CO)_3Mo]_2Hg$ species [7], but the assignment is slightly complicated by the presence in that region of some of the bands of the dmp ligand.

It is noteworthy that the bands attributed to the ν(M–CO) vibrations, which appear in the 360–380 cm^{-1} region, disappear in the products obtained from HgX_2. Only in the case of complexes with $HgCl_2$, are strong bands observed in the 300–265 cm^{-1} region, and these are attributed to the stretching vibrations of the Hg–Cl bond. These bands are strongly shifted with respect to those of the free $HgCl_2$ [8]. The value of the ν(HgCl) frequency of ca. 280 cm^{-1} is not very different from that in the HgX_3^- anion [9]. This suggests that the Hg–Cl bonds are weaker than in $HgCl_2$, because of the bonding of the Hg atom to the transition metal. However, the assignments in this zone are complicated by the possible appearance of bands of the NN donor ligand activated by coordination.

The presence of a band at 376 cm^{-1} in the tungsten tricarbonyl complexes $(dmp)(CO)_3W \cdot n HgX_2$ is attributed to the presence of additional lattice HgX_2 molecules. No such effect is observed for the bipy and phen derivatives.

Electronic spectra. The electronic spectra of the $(dmp)(CO)_3M \cdot n HgX_2$ complexes were recorded in the 650–250 cm^{-1} region. Table 3 summarizes the absorption maxima (with assignments) and intensities (log ϵ) for these compounds and for the starting complexes.

In all the complexes four bands are observed in the 400–272 nm region. The absortion maximum at lower wavelength is assigned to the L–L transition according to the data given in the literature for other phen complexes [10]. The bands of strong

TABLE 2

INFRARED SPECTRAL DATA

Compound	ν(CO)	ν(CN)	δ(MCO)+ ν(MCO)	ν(HgX)
bipyMo(CO)$_4$	2000 vs, 1912 s, 1865 s, 1810 s			
bipyW(CO)$_4$	1998 vs, 1897 s, 1855 s, 1800 s			
phenMo(CO)$_4$	2000 vs, 1908 vs, 1860 vs, 1817 vs			
phenW(CO)$_4$	1995 vs, 1897 vs, 1863 vs, 1840 vs			
dmpMo(CO)$_4$	2006 vs, 1903 vs, 1860 vs, 1810 vs			
dmpW(CO)$_4$	2000 vs, 1900 vs, 1852 vs, 1804 vs			
dmp(CO)$_3$Mo·HgCl$_2$	1982 vs, 1903 v, 1873 vs		597 m 580 s 495 vs 472 s 450 m	300 m, 278 s
dmp(CO)$_3$W·1.5HgCl$_2$	1980 vs, 1910 sh, 1895 vs, 1860 vs		598 m 573 s 555 s 484 s 455 m	376 s, 285 s, 265 s
dmp(CO)$_3$W·2HgBr$_2$	1980 vs, 1920 sh, 1895 vs, 1860 vs		597 m 575 s 555 s 502 s 480 s	
bipy(CO)$_3$Mo·Hg(SCN)$_2$	1942 vs, 1860 vs, 1835 vs	2114 s, 2098 s	597 s 508 s 475 m 448 m	
bipy(CO)$_3$W·Hg(SCN)$_2$	1978 vs, 1902 sh, 1883 vs, 1850 vs	2105 s, 2082 s	580 s 508 s 473 m 457 vs	237 vs
phen(CO)$_3$Mg·Hg(SCN)$_2$	1960vs, 1867 vs	2112 s, 2095 s	588vs 513 vs 485 m 455 s	235 s
phen(CO)$_3$W·Hg(SCN)$_2$	1960 vs, 1905 s, 1875 sh, 1860 vs	2120 s, 2095 s	598 m 587 m 523 m 482 m 458 m	
dmp(CO)$_3$Mo·Hg(SCN)$_2$	1975 vs, 1900 vs, 1860 vs	2100 s, 2080 sh	587 s 575 m 465 m 455 m	235 m
dmp(CO)$_3$W·Hg(SCN)$_2$	1963 vs, 1885 vs, 1850 vs	2100 sh, 2080 s	593 m 575 vs 469 s 455 m	240 vs
[phen(CO)$_3$Mo]$_2$·Hg(CN)$_2$	1975 sh, 1945 vs, 1910 sh, 1862 vs, 1820 vs	2100 sh, 2090 m	592 s 523 s 485 m 457 m	325 m

TABLE 3

ELECTRONIC SPECTRAL DATA

Compound	Concentration (mol l^{-1})	λ (nm)	log ϵ	Assignment
$dmpMo(CO)_4$	5.69×10^{-5}	430	3.69	CT M → L_{NN}
		390sh	3.75	$d \to d$
		290	4.49	CT M → π^*(CO)
		273	4.78	$\pi L_{NN} \to \pi^* L_{NN}$
$dmpW(CO)_4$	5.66×10^{-5}	435	3.56	CT M → L_{NN}
		390sh	3.58	$d \to d$
		290	4.38	CT M → π^*(CO)
		273	4.48	$\pi L_{NN} \to \pi^* L_{NN}$
$dmp(CO)_3Mo \cdot HgCl_2$	5.69×10^{-5}	430	3.69	CT M → L_{NN}
		390	3.75	$d \to d$ + CT M → π^*(CO)
		292	4.49	CT M → π^*(CO)
		272	4.78	$\pi L_{NN} \to \pi^* L_{NN}$
$dmp(CO)_3W \cdot 1.5HgCl_2$	1.96×10^{-4}	452	3.33	CT M → L_{NN}
		360	3.34	$d \to d$ + CT M → π^*(CO)
		300	4.19	CT M → π^*(CO)
		285	4.23	$\pi L_{NN} \to \pi^* L_{NN}$
$dmp(CO)_3W \cdot 2HgBr_2$	6.66×10^{-4}	442	3.31	CT M → L_{NN}
		328	3.82	$d \to d$ + CT M → π^*(CO)
		285	4.54	CT M → π^*(CO)
		272	4.58	$\pi L_{NN} \to \pi^* L_{NN}$
$bipy(CO)_3Mo \cdot Hg(SCN)_2$	1.01×10^{-4}	400	3.40	CT M → L_{NN}
		320	3.92	$d \to d$ + CT M → π^*(CO)
		285	4.26	CTM → π^*(CO)
$bipy(CO)_3W \cdot Hg(SCN)_2$	5.32×10^{-5}	435	3.43	CT M → L_{NN}
		345	3.62	$d \to d$ + CT M → π^*(CO)
		295	4.26	CT M → π^*(CO)
		287	4.28	CT M → π^*(CO)
$phen(CO)_3Mo \cdot Hg(SCN)_2$	8.80×10^{-5}	410	3.50	CT M → L_{NN}
		325	3.56	$d \to d$ + CT M → π^*(CO)
		295	4.07	CT M → π^*(CO)
		272	4.38	$\pi L_{NN} \to \pi^* L_{NN}$
$phen(CO)_3W \cdot Hg(SCN)_2$	7.51×10^{-5}	450	3.45	CT M → L_{NN}
		350	3.59	$d \to d$ + CT M → π^*(CO)
		292	4.28	CT M → π^*(CO)
		273	4.52	$\pi L_{NN} \to \pi^* L_{NN}$
$dmp(CO)_3Mo \cdot Hg(SCN)_2$	5.07×10^{-5}	370	3.75	$d \to d$ + CT M → π^*(CO)
		298	4.28	CT M → π^*(CO)
		275	4.50	$\pi L_{NN} \to \pi^* L_{NN}$
$dmp(CO)_3W \cdot Hg(SCN)_2$	4.85×10^{-5}	445	3.50	CT M → L_{NN}
		365	3.86	$d \to d$ + CT M → π^*(CO)
		300	4.34	CT M → π^*(CO)
		277	4.56	$\pi L_{NN} \to \pi^* L_{NN}$
$[phen(CO)_3Mo]_2 \cdot Hg(CN)_2$	3.05×10^{-5}	445	3.80	CT M → L_{NN}
		390sh	3.76	$d \to d$ + CT M → π^*(CO)
		293sh	4.40	CT M → π^*(CO)
		272	4.79	$\pi L_{NN} \to \pi^* L_{NN}$

intensity which appear as shoulders can be attributed to M → CO charge transfer transitions [11]. The maxima about 400 nm with log ϵ ca. 3–4, are probably due to CT M → L transitions accompanied by *d–d* transitions. In $(NN)M(CO)_4$ and (π-arene)$M(CO)_3$ complexes, bands with such log ϵ values have been assigned to *d–d* transitions. The values of these coefficients may be due to the low symmetry of the complexes [10–12].

According to this assignment there is a substantial shift of the bands attributed to *d–d* transitions compared with those of the starting complexes. This can be attributed to the change in the environment of the transition metal atom upon the formation of additional M–Hg bonds and the CO elimination.

B. Reactions of the (NN)M(CO)$_4$ complexes with Hg(SCN)$_2$

The reactions of the (NN)M(CO)$_4$ complexes (M = Mo, W; NN = bipy, phen, dmp) with Hg(SCN)$_2$ at room temperature with short reaction time give new products in all cases. All the reactions were carried out in acetone, under N$_2$ at 1/1 and 1/2 molar ratios. Addition of Hg(SCN)$_2$ to the suspension of the starting carbonyls causes dissolution of the complexes accompanied by CO evolution and the formation of an orange precipitate. The compounds formed can be formulated as the tricarbonyl species (NN)(CO)$_3$MHg(SCN)$_2$. Their analytical data and some properties are listed in Table 1.

The new products are unstable in the air and decompose in polar solvents with deposition of metallic mercury. On exposure to light they undergo a photochemical reaction with a gradual change in colour. They are insoluble in most solvents except DMF and DMSO. The solutions in the latter solvents change in colour with time. The conductances in DMF solutions correspond to non-ionic species.

IR spectra. The IR spectra in the 4000–200 cm^{-1} region show bands characteristic of the presence of the CO and NN ligand, and also bands like those of the substrate Hg(SCN)$_2$. The spectra show three bands attributed to the ν(CO) vibrations in the 1940–1835 cm^{-1} region. The pattern of bands for these products is very different to those for the parent tetracarbonyl complexes, which show a four-band spectrum. The tricarbonyl derivatives obtained in this paper can be formulated as seven-coordinated complexes with a coordination geometry analogous to that of (bipy)(CO)$_3$Mo(HgCl)(Cl) [2].

The bands appearing between 2080 and 2100 cm^{-1} are assigned to ν(CN) vibrations of the SCN groups. The splitting observed can be attributed either to the presence of different coordination modes of the SCN group to the metals and/or to solid state effects. In complexes with MoHgSCN bonds [13] the ν(CN) stretching vibration appears at ca. 2100 cm^{-1} and the MoNCS band appears between 2123 and 2048 cm^{-1} [9].

The presence of the characteristic vibrations of the NN ligand complicated the assignment of the ν(CS), but a band which appears in the 790–805 cm^{-1} region can be tentatively assigned to this frequency.

The ν(HgSCN) vibration is assigned to a band which appears at ca. 240 cm^{-1}. This value is similar to that found in complexes with M–HgSCN bonds [14].

In the light of all the data, the new Hg(SCN)$_2$ derivatives may be regarded as seven-coordinate complexes formed via an "oxidative elimination" reaction of the type:

$$\text{(NN)M(CO)}_4 + \text{Hg(SCN)}_2 \rightarrow \text{(NN)(CO)}_3\text{M(HgSCN)(SCN)} + \text{CO} \qquad (2)$$

C. Reactions of the (NN)M(CO)$_4$ (M = Mo, W) with Hg(CN)$_2$

The reactions of compounds of the type (NN)M(CO)$_4$ (M = Mo, W; NN = bipy, phen, dmp) with $Hg(CN)_2$ give new derivatives only in the case of the phen-Mo complex. The product isolated can be formulated on the basis of its analytical data as $[(phen)(CO)_3Mo]_2 \cdot Hg(CN)_2$. It contains two $(phen)(CO)_3M$ units for each $Hg(CN)_2$ group. Analogous compositions have been found in the salts of heavy metal atoms of the type $[(C_5H_5)(CO)_3Mo]_2Hg$ obtained by reaction of $[(C_5H_5)(CO)_3M]^-$ complexes with $Hg(CN)_2$.

The product is unstable in air and light, insoluble in most solvents, and behave as a non-electrolyte in DMF. Its solutions in DMF and DMSO decompose with time.

The IR spectrum shows bands at ca. 2090–2100 cm^{-1} (Table 2) which are assigned to the $\nu(CN)$ vibration. These frequencies are substantially shifted with respect to those of free $Hg(CN)_2$. The low value suggests an increase in the ionic nature of the interaction of a CN group and in the negative charge on the nitrogen atom [14].

The $\nu(HgCN)$ vibration is tentatively assigned to a band at 325 cm^{-1}. The shifting of this frequency with respect to its value in the free $Hg(CN)_2$ is similar to that found in the complexes of $Hg(CN)_2$ with traditional bases [15–17].

As in the cases mentioned above the $[(phen)(CO)_3Mo]_2Hg(CN)_2$ complex exhibit $\nu(CO)$ bands in the 2000–1800 cm^{-1} region, i.e. at frequencies very different from those of starting carbonyl complex.

Electronic spectra. The electronic spectra of the $Hg(SCN)_2$ and $Hg(CN)_2$ derivatives were recorded in the 900–200 nm region. They are very similar to those obtained for the seven-coordinate species prepared by reaction of some tetracarbonyl complexes and HgX_2.

In all cases the spectra show four absortion maxima in the 450–270 nm region (Table 3). The assignment of these maxima was based on the criteria mentioned above. The similarities in the shape and positions of the bands suggests the existence of equivalent enviroments in the metal atom in the two types of complex.

Experimental

All reactions were carried out under oxygen-free dry nitrogen using standard Schlenk tube techniques and freshly distilled, dried, and degassed solvents.

Reagents

The $(NN)M(CO)_4$ complexes (M = Mo, W; NN = bipy, phen) were prepared as previously described [18–20].

(dmp)Mo(CO)$_4$. $Mo(CO)_6$ (1.3 g, 5 mmol) and 2,9-dimethyl-1,10-phenanthroline (1.09 g, 5 mmol) were heated in xylene under reflux until CO evolution was complete. The orange product which crystallised out on cooling was filtered off and washed with ethanol and light petroleum. The excess of molybdenum hexacarbonyl was removed in vacuum. The yield was almost quantitative.

(dmp)W(CO)$_4$. Tungsten hexacarbonyl (2.9 g; 5.6 mmol) and 2,9-dimethyl-1,10-phenanthroline (1.3 g; 5.6 mmol) in ethanol (40 ml) were heated at 110°C in an evacuated tube for 48 h. Then solution was cooled and the red solid formed was filtered off, washed with ethanol and dried under vacuum. The excess of tungsten hexacarbonyl was removed by sublimation. The yield was 1.92 g (68%).

Commercially available mercuric salts were used without purification.

Analyses

C, H, N analyses were carried out by the Elemental Micro-Analyses Ltd. Laboratories, Amberley, Beaworthy (Devon) England.

Physical measurements

Infrared spectra in the 4000–200 cm^{-1} region were recorded on a Perkin–Elmer 325 spectrophotometer as KBr discs or Nujol mulls.

Conductance measurements were performed with DMF solutions at room temperature with a Philips conductivity bridge, Model No CM 4144 and a cel PR9512/00.

Electronic spectra in the 900–267 nm region were scanned in DMF solution on a Kontron Uvikon 820 spectrophotometer.

Preparation of the complexes

$(dmp)(CO)_3Mo \cdot nHgX_2$ complexes ($M = Mo$, $X = Cl$, $n = 1$; $M = W$, $X = Cl$, $n = 1.5$; $X = Br$, $n = 2$). The compounds were obtained by addition of a solution of the corresponding mercury halide in acetone to a suspension of $(dmp)M(CO)_4$ (M = Mo, W) in the same solvent. The mixture was stirred until CO evolution was complete. The solid, which separated out was filtered off, washed with acetone and dried under vacuum.

$(NN)(CO)_3MHg(SCN)_2$ complexes ($M = Mo$, W; NN = bipy, phen, dmp). These compounds were prepared in acetone, in the dark under N_2. The reactions were carried out in 1/1 and 1/2 molar ratio, the same product being isolated in both cases.

As a typical example, 0.32 g (1 mmol) of $Hg(SCN)_2$ was added to a 15 ml suspension of 0.45 g (1 mmol) of $(bipy)W(CO)_4$ in dry acetone. The mixture was stirred, and when the gas evolution was complete the solid formed was filtered off, washed with acetone, and dried under vacuum.

$[(phen)(CO)_3Mo]_2Hg(CN)_2$. This complex was prepared in the dark under N_2 by stirring a suspension of of 0.39 g (1 mmol) of $(phen)Mo(CO)_4$ and 0.54 g (2 mmol) of $Hg(CN)_2$ in 30 ml dry acetone for 70 h. After a few minutes the reagents dissolved. The yellow precipitate formed was filtered off, washed with acetone, and dried under vacuum.

Acknowledgement

Financial support for this work from the Comision Asesora de Investigación, Científica y Técnica (CAIAYT) is gratefully acknowledged (Project No. 3727/79). The authors thank P. Tigeras for recording the IR spectra.

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