Journal of Organometallic Chemistry, 87 (1975) 317—321

TRANSITION METAL COMPLEXES OF DITHIO LIGANDS

I. REACTIONS OF THE CYANODITHIOFORMATE ION WITH CYCLOPENTADIENYLMETAL CARBONYL HALIDES

LARRY J. EPLEY and LARRY W. HOUK*

Department of Chemistry, Memphis State University, Memphis, Tennessee 38152 (U.S.A.)

(Received October 7th, 1974)

Summary

The cyclopentadienylmetal carbonyl halides $C_5H_5Mo(CO)_3Cl$, $C_5H_5W(CO)_3Cl$, $C_5H_5CoCOI_2$ and $C_5H_5CoCOC_3F_7I$ react with the cyanodithioformate ion $^-S_2C_2N$ to yield the following derivatives: $C_5H_5Mo(CO)_2(S_2C_2N)$, $C_5H_5W(CO)_2(S_2C_2N)$, $C_5H_5CoI(S_2C_2N)$, $C_5H_5Co(S_2C_2N)$ [SC(S)CN] and $C_5H_5CoC_3F_7(S_2C_2N)$. When acting as a bidentate the cyanodithioformate ligand is superior to other univalent dithio chelating agents as based upon its ability to remove charge from the metal.

Introduction

Whereas numerous accounts of the interaction of monoanionic dithio ligands (^-S_2R, where typically R = PF_2 [1-3], $P(OC_2H_5)_2$ [4, 5], $C=C(CN)_2$ [6], COC_2H_5 [5, 7, 8] and $CN(C_2H_5)_2$ [8-11]) with transition metal compounds are found in the literature, the cyanodithioformate ion ($^-S_2C_2N$) has been confined to three areas, (1) study of its organic chemistry [12-15] (2) the preparation of simple salts of main group metals [13, 16] and (3) its use as an intermediate in the synthesis of the well studied *cis*-1,2-dicyanoethylene-1,2-dithiolate dianion [11, 17-19].

This initial investigation is concerned with reactions of the cyanodithioformate ion (CNDF) with selected cyclopentadienylmetal carbonyl halides, the structures of resulting complexes, and the comparative bonding ability of CNDF with that of other dithio chelating agents.

Experimental

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and M-H-W Laboratory, Garden City, Michigan. Infrared spectra were recorded in methylene chloride solutions and potassium bromide pellets on a Model 621 Perkin—Elmer spectrometer. Proton NMR spectra were taken in chloroform-*d* on Varian Associates Model T-60 and HA-100 instruments with tetramethylsilane as an internal standard. Melting points were taken in open capillaries and are uncorrected. Mass spectra were recorded on a Varian Associates Model CH-7 spectrometer using a direct inlet probe heated from 100-150°. Chemicals were obtained from the following sources: $Mo(CO)_6$ and $W(CO)_6$ (Pressure Chemical Co.), $C_5H_5Co(CO)_2$ (Alpha Ventron), and C_3F_7I (Columbia Chemical Co.). Florisil (60-100 mesh) used for column chromatography was obtained from Fisher Scientific Co. The starting materials $C_5H_5Mo(CO)_3Cl$ [20], $C_5H_5W(CO)_3Cl$ [20], $C_5H_5CoCOI_2$ [21], $C_5H_5CoCOC_3F_7I$ [22], $NaS_2C_2N \cdot 3DMF$ [16] (DMF = *N,N*-dimethylformamide), and $(C_2H_5)_4NS_2C_2N$ [13] were prepared from literature methods.

$C_5H_5Mo(CO)_2(S_2C_2N)$

$C_5H_5Mo(CO)_3Cl$ 0.71g (2.53 mmol) and $NaS_2C_2N \cdot 3DMF$ 0.87g (2.53 mmol) were stirred at ambient temperature in acetone for 72 h. After evaporation (25°, 40 mm) the residue was extracted with chloroform (5 ml) and placed on a Florisil column. Evaporation of the 50/50 benzene/CH_2Cl_2 eluant followed by two recrystallizations from CH_2Cl_2/heptane yielded violet crystals.

$C_5H_5W(CO)_2(S_2C_2N)$

$C_5H_5W(CO)_3Cl$ 0.50g (1.35 mmol) and $NaS_2C_2N \cdot 3DMF$ 1.0g (2.90 mmol) were stirred at 56° in acetone for 72 h. After solvent evaporation the residue was extracted with 6 X 20 ml portions of hexane. Crystals were obtained by slow evaporation of the hexane under a stream of dry nitrogen.

$C_5H_5CoC_3F_7(S_2C_2N)$

$C_5H_5CoCOC_3F_7I$ 0.30g (0.67 mmol) and $NaS_2C_2N \cdot 3DMF$ 0.23g (0.67 mmol) were stirred at 56° in acetone for 18 h. Solvent evaporation followed by two recrystallizations from CH_2Cl_2/heptane yielded the product.

$C_5H_5CoI(S_2C_2N)$

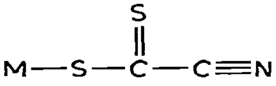
$C_5H_5CoCOI_2$ 0.50g (1.23 mmol) and $[(C_2H_5)_4N](S_2C_2N)$ 0.29g (1.25 mmol) were stirred at 25° in acetone for 2 h. After evaporation of the solvent the residue was extracted into CH_2Cl_2, washed with water, and dried by filtering through anhydrous Na_2SO_4. The pure product was obtained by two recrystallizations from CH_2Cl_2/heptane.

$C_5H_5Co(S_2C_2N)_2$

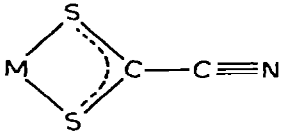
$C_5H_5CoCOI_2$ 0.50g (1.23 mmol) and $NaS_2C_2N \cdot 3DMF$ 1.10g (3.22 mmol) were heated at 56° in acetone for 12 h. The solvent from the filtered solution was evaporated and the residue was dissolved in CH_2Cl_2 and placed on a Florisil column. Elution with 50/50 CH_2Cl_2/acetone followed by recrystallization from CH_2Cl_2/heptane yielded the product.

Results and discussion

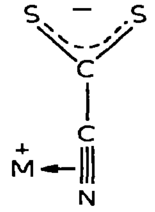
Discounting bridged dimeric or polymeric species (Table 1), three modes of bonding appear plausible between the ligand and metal in the $C_5H_5M(CO)_x$-$(CNDF)_y$ (M = Mo, W, Co) derivatives prepared in this study.



(I)



(II)



(III)

Since III should cause a drastic reduction in ν(CN) which was not observed, structures I and II appear to be the most likely candidates for these cyclopentadienylmetal derivatives of the CNDF ion.

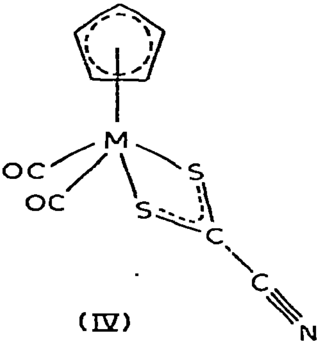
When $C_5H_5M(CO)_3Cl$ (M = Mo, W) were allowed to react with CNDF in acetone solution, two new ν(CO) bands appeared concurrently with a red to violet color change. Although transient $C_5H_5M(CO)_3(CNDF)$ species are probably generated, their presence was never revealed by frequent monitoring of the ν(CO) region. However, minute quantities of these fugitive tricarbonyls were quite possibly present with their ν(CO) bands hidden beneath those of $C_5H_5M(CO)_3Cl$ or emerging $C_5H_5M(CO)_2(CNDF)$. Subsequent purification yielded violet crystals of $C_5H_5M(CO)_2(CNDF)$ adopting the half-sandwich structure IV.

TABLE 1

PHYSICAL PROPERTIES AND ANALYSES OF CYCLOPENDADIENYLMETAL CARBONYL COMPLEXES OF THE CYANODITHIOFORMATE LIGAND

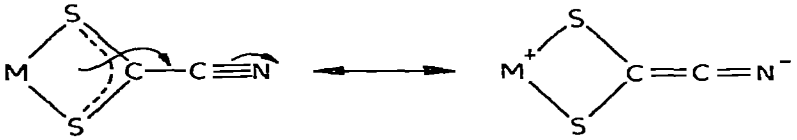
Compound	Color	Yield (%)	M p (°C)[a]	Analyses[b] found (calcd.) (%)			
				C	H	N	S
$C_5H_5Mo(CO)_2(CNDF)$[c]	violet	65	75-77	34.11 (33 86)	1.55 (1.58)	4.41 (4.39)	19.88 (20.09)
$C_5H_5W(CO)_2(CNDF)$[c]	violet	60	98-100	26.72 (26.25)	1.23 (1.24)	3.54 (3.44)	15.75 (15.75)
$C_5H_5CoI(CNDF)$	purple-black	87	134-135	24.03 (23.81)	1.41 (1.43)	3.94 (3.97)	18.15 (18.16)
$C_5H_5Co(CNDF)_2$	purple-black	60	110-115	32.50 (32.91)	1.73 (1.53)	8.63 (8.56)	39.10 (39.05)
$C_5H_5CoC_3F_7(CNDF)$	purple-black	33	94-95	30.36 (30.39)	1.18 (1.28)	3.42 (3.54)	16.32 (16.22)

[a] Melt with decomposition. [b] Parent ions were observed in the mass spectra run at 50° and 150° between 10-70eV (no higher mol. wt. ions observed). [c] Mol. wt. by v.p.o., for $C_5H_5Mo(CO)_2(CNDF)$, found. 310. calcd: 319.2, for $C_5H_5W(CO)_2(CNDF)$, found· 400, calcd: 407.1.



(IV)

Even though the $\tau(C_5H_5)$ values for specific metal systems appear to be rather insensitive to ligand effects, the ν(CO) frequencies (Table 2) reveal an effective bonding order CNDF > S_2PF_2 > $S_2CN(C_2H_5)_2$ for bidentate sulfur chelating agents. Based upon this inference from ν(CO) values, CNDF is superior to all dithio ligands previously reported. The following resonance pair apparently contributes to this removal of charge from the metal and the resulting lower ν(CN) value for CNDF as a bidentate ligand. Consistent with all the prior data the ν(CO) frequencies are lower for tungsten than for the molybdenum derivative.



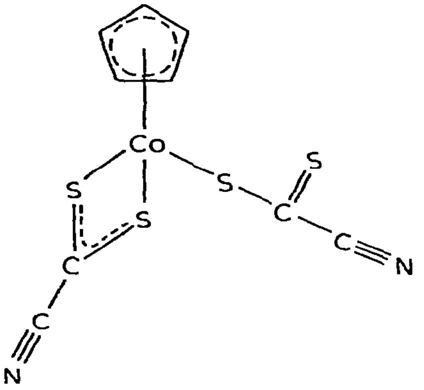
Both $C_5H_5CoCOI_2$ and $C_5H_5CoCOIC_3F_7$ reacted with one mole of CNDF displacing an iodide ion and the carbon monoxide to produce $C_5H_5CoI(CNDF)$ and $C_5H_5CoC_3F_7(CNDF)$, respectively. When $C_5H_5CoCOI_2$ and the ligand were allowed to interact in a 1/2 molar ratio, a molecule containing one bidentate and one monodentate CNDF ligand resulted. The $C_5H_5Co(CNDF)_2$ formulation is supported by the two ν(CN) stretching bands observed (monodentate, 2232 cm^{-1}; bidentate, 2220 cm^{-1}).

TABLE 2

INFRARED AND NMR SPECTRA OF CNDF COMPOUNDS

Compound	ν(CO),[a] cm^{-1}		ν(CN),[a] cm^{-1}	$\tau(C_5H_5)$[b]
$C_5H_5Mo(CO)_2(CNDF)$	1997 vs	1940 s	2185 w	4 55
$C_5H_5W(CO)_2(CNDF)$	1989 vs	1926 s	2181 w	4 32
$C_5H_5CoI(CNDF)$			2221 w	4.45
$C_5H_5Co(CNDF)_2$			2232 w, 2220 m	4 32
$C_5H_5CoC_3F_7(CNDF)$			2200 w	4.55
$C_5H_5Mo(CO)_2(S_2PF_2)$[c]	1980 vs	1889 s		4.50
$C_5H_5Mo(CO)_2[S_2CN(C_2H_5)_2]$[c]	1931 vs	1839 s		4 52

[a] Run in methylene chloride. [b] Run in chloroform-*d*. [c] Ref. 1.



Acknowledgement

We wish to express our appreciation to the Memphis State University Research Foundation for partial support of this work.

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