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π-CYCLOPENTADIENYLS OF NICKEL(II)

VII. CARBON DISULFIDE INSERTION REACTIONS WITH THIOLATONICKEL COMPOUNDS

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SUMMARY

Mononuclear thiolatonickel compounds (I) and dinuclear thiolatonickel compounds (II) readily undergo carbon disulfide insertion, producing the stable (alkyl trithiocarbonato)nickel compounds (III) and (IV), respectively.

INTRODUCTION

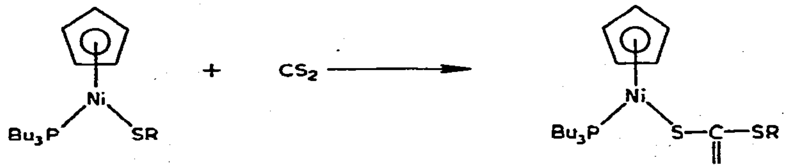
A few cases of carbon disulfide insertion reactions with thiolato-transition metal compounds have been reported. Though stable alkyl(aryl) trithiocarbonato compounds of molybdenum and tungsten have been obtained from the reactions of $[\pi\text{-}C_5H_5M(CO)_2SR]_2$ and $\pi\text{-}C_5H_5M(CO)_3SR$ (M = Mo, W) with carbon disulfide[1], only the unstable (alkyl trithiocarbonato)nickel compound seemed to be formed in the reaction between carbon disulfide and certain μ-(alkylthiolato)nickel compounds[2].

In this paper the preparation and properties of stable (alkyl trithiocarbonato)-nickel compounds are reported. They were formed from the reactions of carbon disulfide with mononuclear and dinuclear thiolatonickel compounds previously prepared by us[3,4].

RESULTS AND DISCUSSION

The reaction of CS_2 with the mononuclear thiolatonickel compound (I)

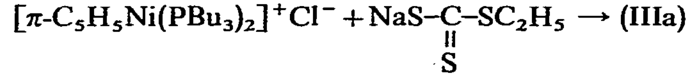
The mononuclear thiolatonickel compound (I)[3] undergoes CS_2 insertion readily at room temperature, producing the stable (alkyl trithiocarbonato)nickel compound (III).



(I)
(Ia, R = C_2H_5 ; Ib, R = $CH_2C_6H_5$)

(III)
(IIIa, R = C_2H_5 ; IIIb, R = $CH_2C_6H_5$)

The compound (IIIa) can also be obtained directly from the reaction of sodium ethyl trithiocarbonate[5] with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ [6] in aqueous solution:



$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + NaS\text{-}\underset{\underset{S}{\|}}{C}\text{-}SC_2H_5 \longrightarrow \text{(IIIa)}$$

The IR and NMR data for (III) are given in Table 1. The IR spectrum of (IIIa) shows the characteristic out of plane deformation band of π-cyclopentadienyl at about 800 cm^{-1}, and the strong C=S stretching frequency[7] at about 1000 cm^{-1}. The proton NMR spectrum of the protons of the ethyl trithiocarbonate in (IIIa) shows a triplet at τ 8.82 due to the methyl protons, though it is overlapped by the peaks of the protons of PBu_3, and a quartet at τ 7.00 due to the methylene protons, and that of the benzyl trithiocarbonate in (IIIb) shows a peak at τ 2.87 due to the aromatic protons and a singlet at τ 5.72 due to the methylene protons.

TABLE 1

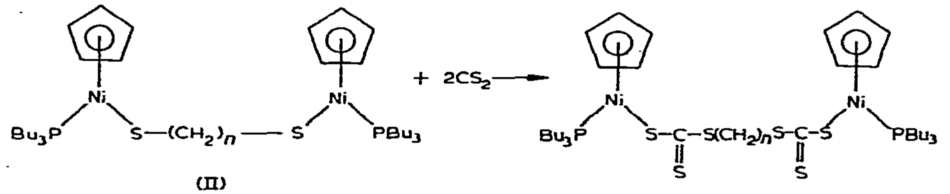
PMR AND IR DATA FOR COMPOUNDS (III) AND (IV)

Compound	*PMR data*[a] *(ppm)*				*IR data (cm^{-1})*	
	τ(π-C_5H_5),	*τ(PBu_3)*	*τ(S–CH_2)*	*τ(Other)*	*γ(π-C_5H_5)*	*ν(C=S)*
(IIIa)	4.86 (s)[b]	8.3–9.3[c]	7.00 (q)	8.82[c] (S–C–CH_3)	795	1003
(IIIb)	4.85 (s)	8.2–9.2	5.72 (s)	2.87 (C_6H_5)	797	1015
(IVa)	4.84 (s)	8.3–9.2	6.82 (s)		787	1015
(IVb)	4.87 (s)	8.2–9.2[d]	6.99 (t)	[d]	795	1010
(IVc)	4.87 (s)	8.3–9.2[e]	7.10 (t)	[e]	785	995

[a] In CS_2 solution, TMS internal standard. [b] s: singlet; t: triplet; q: quartet. [c] τ(PBu_3)+τ(C–C–CH_3]. [d] τ(PBu_3)+τ[S–C$(CH_2)_2$C–S]. [e] τ(PBu_3)+τ[S–C$(CH_2)_4$C–S].

The reaction of CS_2 with the dinuclear thiolatonickel compound (II)

The dithiol dianion bridged nickel compounds (II)[4] similarly undergo CS_2 insertion readily at room temperature, producing the stable compounds (IV).



(II)
(IIa, n=2 ; IIb, n=4 ; IIc, n=6)

(IV)
(IVa, n=2 ; IVb, n=4 ; IVc, n=6)

When the compound (II) is dissolved in CS_2, it gives a red solution though the solid (IIa) is reddish brown, while (IIb) and (IIc) are green. After the CS_2 solution had been set aside for about an hour at room temperature, we obtained the reddish brown compounds (IV).

The IR and NMR data for (IV) are given in Table 1. The IR spectra of (IVa), (IVb) and (IVc) resemble that of (IIIa). The proton NMR spectrum of (IVa) in CS_2 solution shows bands at τ 8.3–9.2 (intensity 54) due to the protons of PBu_3, a sharp singlet at τ 4.84 (intensity 10) due to the π-C_5H_5 protons and a singlet at τ 6.82 (intensity 4) due to the S_2CS–$(CH_2)_2$–SCS_2 protons; these results indicate that two molecules of CS_2 insert symmetrically into (IIa).

The proton NMR spectra of (IVb) and (IVc) similarly support the proposed structure, though some of the methylene protons of the respective alkyl trithiocarbonate are overlapped by the peaks of the PBu_3 protons.

EXPERIMENTAL

The complexes (I) and (II) were prepared as previously described[3,4]. Benzene and n-hexane were purified in the usual way. IR spectra were recorded on a Jasco IR-G spectrometer. Proton NMR spectra were recorded on a Jeol-JNM-4H-100 NMR spectrometer with TMS as internal standard. All experiments were conducted under dry nitrogen.

The reaction of (Ia) with CS_2

The carbon disulfide solution of (Ia) was set aside for about 12 h at room temperature, then the solution was evaporated *in vacuo*. The resulting residue was recrystallized from n-hexane to give reddish brown crystals, m.p. 85.5–86.5°, in 80% yield. (Found: C, 51.92; H, 8.37. $C_{20}H_{37}NiPS_3$ calcd.: C, 51.87; H, 8.00%.)

The reaction of (Ib) with CS_2

A similar procedure with (Ib) and CS_2 gave (IIIb) as reddish brown crystals, m.p. 76.5–77.5°, in 78% yield. (Found: C, 57.47; H, 7.42; S, 17.49. $C_{25}H_{39}NiPS_3$ calcd.: C, 57.17; H, 7.43; S, 18.29%.)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $NaSCS_2C_2H_5$

Addition of $NaSCS_2C_2H_5$[5] (2 mmoles) in 20 ml of THF to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ [6] in 50 ml of water at room temperature gave compound (IIa) in 90% yield.

The reaction of (IIa) with CS_2

The carbon disulfide solution of (IIa) was set aside for 1 h at room temperature, then evaporated *in vacuo*. The residue was recrystallized from benzene–n-hexane to give (IVa) as reddish brown crystals, m.p. 88.8–89.0°, in 88% yield. (Found: C, 51.55; H, 7.84. $C_{38}H_{68}Ni_2P_2S_6$ calcd.: C, 50.93; H, 7.59%.)

The reaction of (IIb) with CS_2

A similar procedure with (IIb) and CS_2 gave (IVb) as reddish brown crystals, m.p. 82.0–83.0°, in 62% yield. (Found: C, 52.54; H, 8.35; S, 19.82. $C_{40}H_{72}Ni_2P_2S_6$ calcd.: C, 51.98; H, 7.79; S, 20.79%.)

The reaction of (IIc) with CS_2

From the reaction with (IIc), (IVc) was similarly obtained as reddish brown crystals, m.p. 80.5–81.0°, in 68% yield. (Found: C, 53.39; H, 8.35. $C_{42}H_{76}Ni_2P_2S_6$ calcd.: C, 52.97; H, 7.98%.)

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