Preliminary communication

π-Cyclopentadienyls of nickel(II)
XI. The preparation of π-C₅H₅NiSC(S)R complexes

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SUMMARY

Treatment of the complexes π-C₅H₅NiPBu₃SC(S)R, obtained from the reaction between $[\pi$-C₅H₅Ni(PBu₃)₂]$^+$Cl$^-$ and the species SC(S)R$^-$, in aqueous solution, with HCl results in the complexes π-C₅H₅NiSC(S)R.

When an ether solution of π-C₅H₅NiPBu₃ SC(S)CH₂C₆H₅, obtained from the reaction between $[\pi$-C₅H₅Ni(PBu₃)₂]$^+$Cl$^-$ [1] and SC(S)CH₂C₆H₅, is treated with aqueous HCl, the solution changes from brown to purple. From this solution black crystals of molecular formula π-C₅H₅NiSC(S)CH₂C₆H₅ (I), m.p. 92–93° (Found: C, 53.65; H, 4.25. C₁₃H₁₂NiS₂ calcd.: C, 53.61; H, 4.12%) are obtained.

The proton NMR spectrum of (I) in CS₂ shows singlets at τ2.86 (phenyl protons), τ4.82 (π-cyclopentadienyl protons) and τ6.31 (methylene protons of the CH₂—C₆H₅ group) (Table 1).

An apparent molecular weight determination shows complex (I) to be monomeric (mol.wt. 268 by cryoscopy in benzene, calcd. 291). It is thus clear that SC(S)CH₂C₆H₅$^-$ acts as bidentate ligand in (I) as in complex Mn(CO)₄SC(S)C₆H₅ [2] and in general metal salts of dithioacids [3].

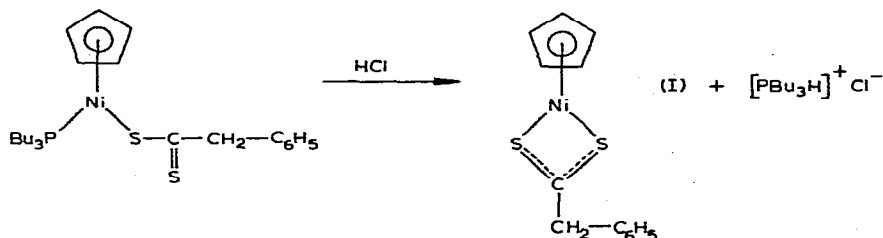(I) reacts with PBu₃ in hexane to give π-C₅H₅NiPBu₃SC(S)CH₂C₆H₅.

TABLE 1

THE PROTON NMR SPECTRUM DATA OF π-C$_5$H$_5$NiSC(S)R

R	Chemical shift (internal TMS)			
	$\tau(\pi$-C$_5$H$_5)$	$\tau(-C_6H_5)$	$\tau(CH_2)$	$\tau(CH_3)$
C$_6$H$_5$	4.69 s [a]	2.00~2.98		
CH$_2$C$_6$H$_5$	4.82 s	2.86 s	6.31 s	
C$_2$H$_5$	4.80 s		7.49 q	8.78 t

[a] s singlet; t triplet; q quartet.

The complexes π-C$_5$H$_5$NiSC(S)C$_6$H$_5$ and π-C$_5$H$_5$NiSC(S)C$_2$H$_5$ were obtained in a similar manner; proton NMR spectral data of all compounds are listed in Table 1.

REFERENCES

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