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REACTION OF SOME TERTIARY PHOSPHINES AND PHOSPHITES WITH $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)]$

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Summary

Reaction of the 16 electron monomer $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)]$ with various tertiary phosphines and phosphites (L) gives readily the 18 electron monomers $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)L]$ which for L = $P(OR)_3$ have $J(\underline{P}C_5\underline{H}_5)$ ca. 6 Hz but $J(\underline{P}C_5\underline{H}_5) = 0$ for L = PR_3.

Although a large number of η^5-cyclopentadienyl metal complexes containing 1,2-dithiolene ligands have been synthesised and characterised in the last fifteen years [1], relatively little work has been published on the reactions of these complexes with Lewis bases. In this short paper, we now wish to report the reactions of $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)]$ with various tertiary phosphines and phosphites (L) which produce readily the air stable, crystalline compounds $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)L]$.

Results and discussion

The compound $[Co(C_5H_5)(S_2C_2\{CN\}_2)]$ first synthesised by Locke and McCleverty in 1966 by reaction of $[Co(C_5H_5)(CO)_2I]$ with $Na_2[S_2C_2(CN)_2]$ [2] was shown by X-ray analysis [3] in 1968 to be a genuine monomer in the solid state of structure I. Furthermore, osmometric molecular weight measurements in acetone and mass spectroscopic studies at 70 eV confirm that this monomeric structure is retained in both solution and gas phase (see Experimental section).

As expected for this 16 electron monomer, reaction readily occurs with various tertiary phosphines and phosphites (L) to give the stable 18 electron monomers $[Co(C_5H_5)(S_2C_2\{CN\}_2)L]$ (II). These adducts have been fully characterised by elemental analyses, osmometric molecular weight measurements in acetone and IR spectroscopic studies which show the two ν(CN) stretching vibrations expected for the dithiolate ligand in such compounds (Table 1).

TABLE 1

Complex	Colour	M.p. (°C)	Yield [a]	
			g	%
$Co(C_5H_5)(S_2C_2\{CN\}_2)(P\text{-}n\text{-}Pr_3)$	Brown plates	154—155	0.13	81
$Co(C_5H_5)(S_2C_2\{CN\}_2)(P\text{-}n\text{-}Bu_3)$	Dark yellow-brown plates	152—153	0.13	72
$Co(C_5H_5)(S_2C_2\{CN\}_2)(PPh_2Cl)$	Brown prisms	190—192 (dec.)	0.11	61
$Co(C_5H_5)(S_2C_2\{CN\}_2)(PEt_2Ph)$	Dark brown prisms	174—175	0.15	89
$Co(C_5H_5)(S_2C_2\{CN\}_2)(PEtPh_2)$	Dark brown prisms	185—186	0.16	85
$Co(C_5H_5)(S_2C_2\{CN\}_2)(PPh_3)$	Dark brown prisms	200—201	0.16	80
$Co(C_5H_5)(S_2C_2\{CN\}_2)(P(OMe)_3)$	Brown-green needles	182—183	0.09	57
$Co(C_5H_5)(S_2C_2\{CN\}_2)(P(OEt)_3)$	Brown-green needles	161—162	0.13	78
$Co(C_5H_5)(S_2C_2\{CN\}_2)(P(OPh)_3)$	Brown prisms	93—94	0.18	84

[a] Yield based on 0.10 g of $[Co(C_5H_5)(S_2C_2\{CN\}_2)]$. [b] Calculated figures in parentheses. [c] Measured osmometrically in acetone at 37°C. [d] ±0.01; J(PH) (Hz) in parentheses. [e] Measured in acetone solution. [f] Measured in Nujol mulls.

The ^1H NMR spectra of these compounds are of interest in that whereas the tertiary phosphine complexes show a single η^5-C_5H_5 resonance at ambient temperature, the tertiary phosphite complexes exhibit a sharp 1 : 1 doublet of separation ca. 6 Hz. Heteronuclear spin decoupling experiments show that this phenomenon is due to long range ^{31}P—^1H spin—spin coupling interactions rather than the presence of two conformational isomers. In agreement with this, the ^{13}C-$\{^1H\}$ NMR spectrum of $[Co(C_5H_5)(S_2C_2\{CN\}_2)(P\{OMe\}_3)]$ shows a η^5-C_5H_5 doublet ($J(PC_5H_5)$ 5.4 Hz) whereas no splitting was observed in the ^{13}C NMR spectra of any of the tertiary phosphine complexes.

Long range coupling between the protons of a π-bonded carbocyclic ring and phosphorus containing ligands directly attached to a transition metal ion is a well established phenomenon although it is rather surprising that the effect here is so large when $L = P(OR)_3$ but not detectable when $L = PR_3$ *. Thus, for example, in $[Mo(\eta^7\text{-}C_7H_7)(CO)LI]$ complexes, $J(\underline{P}C_7\underline{H}_7)$ for $L = P(OMe)_3$ is 3.0 Hz whereas for $L = PPh_3$, $J(\underline{P}C_7\underline{H}_7)$ is 2.1 Hz [4].

A possible explanation may be due to a difference in the Co—P bond lengths in these tertiary phosphine and phosphite complexes, e.g., for $[Mo(\eta^5\text{-}C_5H_5)(CO)_2IL]$ it has been shown by X-ray analyses that the Mo—P bond length is considerably shorter when $L = P(OMe)_3$ compared to $L = PPh_3$ [5]. Reduction in the Co—P bond length here would presumably increase the degree of transmission of the nuclear spin—spin coupling effect in the tertiary

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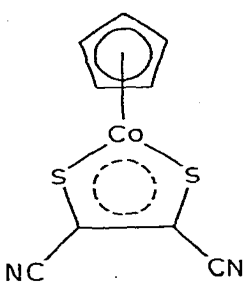
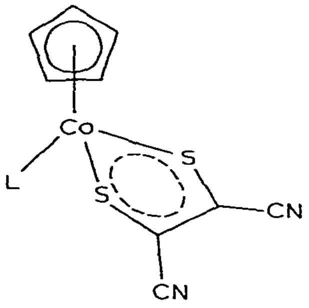
* No splitting is observed in the ^1H NMR spectrum of the tertiary phosphine complexes even at —90°C in CD_2Cl_2, indicating that it is unlikely that fast intermolecular exchange of free and bound PR_3 groups is responsible for the failure to observe a finite J value.

Analyses [b]				M [c]	^{1}H NMR (C_5H_5 resonance) (δ value) [d]	Infrared	
C	H	Co	N			ν(CN) [e] (cm^{-1})	ν(C=C) [f] (cm^{-1})
50.7(50.9) 53.9(54.1)	6.1(6.1) 6.9(6.9)	— 12.8(12.7)	6.5(6.6) 6.0(6.0)	— 439(466)	5.11 (s) 5.16 (s)	2207, 2200 2208, 2199	1429 1426
51.9(52.0)	3.1(3.1)	—	5.6(5.8)	—	5.14 (s)	2210, 2195	1417
50.0(50.3)	4.5(4.5)	13.9(13.7)	5.4(5.6)	401(430)	4.96 (s)	2210, 2195	1414
56.6(57.2)	4.2(4.2)		5.5(5.8)	—	4.99 (s)	2210, 2198	1410
61.7(61.6)	3.8(3.8)	11.4(11.2)	5.4(5.3)	—	5.02 (s)	2212, 2198	1410
36.8(37.1)	3.6(3.6)	15.2(15.2)	7.2(7.2)	362(388)	5.49 (d) (6.0)	2218, 2205	1411
42.0(41.9)	4.9(4.7)	13.7(13.7)	6.4(6.5)	400(430)	5.37 (d) (5.8)	2216, 2200	1417
55.1(55.1)	3.4(3.5)	10.2(10.3)	4.8(4.9)	—	5.20 (d) (5.8)	2210, 2195	1410

phosphite complexes. However, X-ray analyses are now necessary to establish this postulated difference in bond length in these tertiary phosphine and tertiary phosphite complexes.



(I)



(II)

Experimental

Microanalyses (C,H,N) were obtained with a Perkin—Elmer 240 elemental autoanalyser and cobalt analyses on a Varian Techtron A5 atomic absorption spectrometer. Molecular weights were determined in acetone on a Hitachi model 115 osmometer calibrated with benzil. Infrared spectra were recorded in the region 4000—250 cm^{-1} on a Perkin—Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were obtained in potassium bromide cells. ^{1}H NMR spectra were obtained on a Varian Associates HA-100 spectrometer in $CDCl_3$ at 298 K and ^{13}C NMR spectra on a Varian Associates XL-100 spectrometer operating in the pulse and Fourier-transform mode at 25.2 MHz. Heteronuclear decoupling experiments were carried out on the HA-100 spectrometer using a second radio frequency field provided by the Schlumberger FS30 frequency synthesiser. Mass spectra were recorded on an A.E.I. MS902 spectrometer and melting points were determined with a Köfler hot-stage microscope and are uncorrected.

All solvents were dried and degassed before use and all reactions were carried out under an atmosphere of nitrogen.

Cyclopentadienyl(maleonitriledithiolato)cobalt

This complex was prepared by the published method [2] in 60% yield and by the following method in 70% yield. The compounds $[Co(\eta^5\text{-}C_5H_5)COI_2]$ (5.00 g) and $Na_2[S_2C_2(CN)_2]$ (4.56 g) (1/2 molar ratio) were dry mixed and then added to 100 cm^3 of methanol and acetone (1/1, v/v) at 233 K. The purple solution was allowed to warm to room temperature and then most of the solvent removed under vacuum. The precipitated crystals were filtered off and more product was obtained by concentrating further and then adding 50 cm^3 of n-hexane. After washing with diethyl ether, the complex was recrystallised from acetone/water [yield 2.26 g (70%), m.p. 282—283°C; mol. wt. (acetone) 252; calculated 264], mass spectrum (principal peaks): *m/e* 264, $[Co(C_5H_5)(S_2C_2\{CN\}_2)]^+$; 188, $[Co(C_5H_5)S_2]^+$; 124, $[Co(C_5H_5)]^+$; 65, $C_5H_5^+$; 59, Co^+.

General method of preparation of the tertiary phosphine complexes

The compound $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)]$ (0.10 g) was dissolved in 25 cm^3 of acetone and ethanol (1/1, v/v) and treated with the appropriate tertiary phosphine (in 1/1 molar ratio) dissolved in 25 cm^3 of the same solvent mixture. The solution was then refluxed for 30 min to give a yellowish-brown solution which was filtered hot. The volume was reduced by overnight evaporation and the resulting solid filtered off. Addition of n-hexane yielded more product. The complexes were purified by recrystallisation from acetone/n-hexane or, in the cases of PPh_2Cl and PPh_3, by dry column chromatography [6].

General method of preparation of the tertiary phosphite complexes

The compound $[Co(\eta^5\text{-}C_5H_5)(S_2C_2\{CN\}_2)]$ (0.10 g) in 25 cm^3 of acetone was added to the appropriate tertiary phosphite (1/1 molar ratio) dissolved in 25 cm^3 of acetone. All solutions turned a yellowish-green on shaking and on standing overnight precipitated product. Further product was obtained on addition of 50 cm^3 of n-hexane to the solution and the complexes were purified by recrystallisation from acetone/n-hexane.

An attempt to prepare the $P(OMe)_3$ complex in a 1/1 (v/v) mixture of acetone and ethanol resulted in the formation of the $P(OEt)_3$ complex due to transesterification of the tertiary phosphite groups.

Elemental analyses, molecular weights, yields, colours, position of the C_5H_5 resonance in the ^{1}H NMR spectrum and ν(CN), ν(C=C) stretching vibration positions in the IR spectrum of all these complexes are given in Table 1.

Acknowledgement

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References

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