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Preliminary communication

SYNTHESES AND CHARACTERISATION OF SOME TRIPHENYLCYANOBORATE COMPLEXES OF RHODIUM(III), RUTHENIUM(II) AND PALLADIUM(II)

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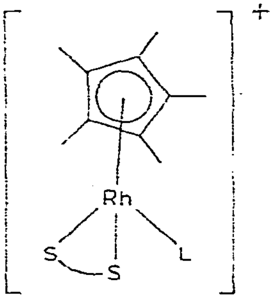
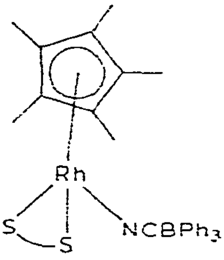
Summary

The triphenylcyanoborate (N-bonded) complexes $\{\eta^5\text{-}(C_5Me_5)Rh(S{-}S)NCBPh_3\}$ ($S{-}S^- = {}^-S_2PMe_2$, ${}^-S_2PPh_2$, ${}^-S_2CNMe_2$), $\{\eta^6\text{-}(C_6H_6)Ru(S_2PPh_2)NCBPh_3\}$ and $[Pd(S_2CNEt_2)(PMe_2Ph)(NCBPh_3)]$ have been synthesised and characterised by both spectroscopic and X-ray structural methods.

Recently the syntheses of $[\eta^5\text{-}(C_5Me_5)Rh(S{-}S)_2]$ (I) and $[\eta^5\text{-}(C_5Me_5)RhCl(S{-}S)]$ (II) ($S{-}S^- = {}^-S_2CNMe_2$, ${}^-S_2PR_2$ [R = Me, Ph]) by treatment of $[\eta^5\text{-}(C_5Me_5)RhCl_2]_2$ with Na(S—S) in 1/4 and 1/2 molar ratios, respectively were reported [1]. Treatment of II with methanol followed by addition of $NaBPh_4$ gives the solvated cations $\{\eta^5\text{-}(C_5Me_5)Rh(S{-}S)(MeOH)\}BPh_4$ which are very useful precursors for generating a range of cations $[\eta^5\text{-}(C_5Me_5)Rh(S{-}S)L]BPh_4$ (III: L = PPh_3, $PMePh_2$, $AsPh_3$, C_5H_5N, CO, etc.) However, attempts to synthesise $[\eta^5\text{-}(C_5Me_5)Rh(S{-}S)\{C_2(CN)_4\}]BPh_4$ by treatment of II with excess tetracyanoethylene in methanol, followed by addition of $NaBPh_4$ to the result-



(III)



(IV)

ing orange-yellow solutions gave non-conducting yellow solids (IV: S—S$^-$ = (a) $^-S_2PMe_2$; (b) $^-S_2PPh_2$; (c) $^-S_2CNMe_2$). The analytical data (C, H, N) of IV are, however, consistent with the formulation [η^5-(C_5Me_5)Rh(S—S)$NCBPh_3$], e.g. found for IVc: C, 60.7; H, 5.7; N, 4.6. Calcd.: C, 61.3; H, 5.7; N, 4.5%

Additional evidence for the formulation of IV as zwitterionic complexes containing the triphenylcyanoborate anion is based on spectroscopic data. For example, the infrared spectra of all these compounds contain a C—N stretching frequency band at ca. 2180 cm^{-1}, indicative of nitrile rather than isonitrile coordination of the $^-NCBPh_3$ group [2], and all show bands characteristic of bidentate coordination of the dithioacid ligands. The mass spectrum of IVc has a peak at *m/e* 626 corresponding to $\{\eta^5\text{-}(C_5Me_5)Rh(S_2CNMe_2)NCBPh_3\}^+$ together with a fragmentation pattern consistent with this formulation. Furthermore, the ^{1}H NMR spectrum of IVc in $CDCl_3$ at 303 K has the expected three signals at δ 1.79 (C_5Me_5), 3.17 ($^-S_2CNMe_2$) and 7.21 ppm ($^-NCBPh_3$) of relative intensity 5/2/5.

However, unequivocal proof of the solid state structure of IV comes from a preliminary X-ray structural analysis of IVa. Crystals of the complex from methanol are monoclinic, space group $P2_1/n$ with cell parameters a = 24.013 ± 0.006 Å, b = 9.368 ± 0.002 Å, c = 14.643 ± 0.001 Å, β = 106.70 ± 0.01°, Z = 4 and ρ = 1.329 kg m^{-3}. Data were collected to θ = 40° on a Nonius CAD4 diffractometer using filtered Cu-K_α radiation. A Patterson map allowed ready location of the Rh atom, which yielded phases with which a Fourier map was calculated. As the Rh atom appeared on the glide plane at y = ¼, superimposed mirror images of the structure resulted. Further inspection of the Patterson map allowed the Rh atom to be placed just off the plane and, together with the sulphur atoms, a map phased on these three revealed much of the centre of the molecule. A difference Fourier synthesis based on this extra information allowed the complete structure to be determined. Refinement of the structure with data to θ = 30° (838 reflections) gives a conventional R-factor of 0.07. Further refinement with all measured data is in progress. The structure of the central region of the molecule is shown in Fig. 1 whilst Table 1 lists the bond lengths and angles. No density other than diffraction ripple round the Rh atom has been detected on difference Fourier maps. Refinement of the two enantiomorphic

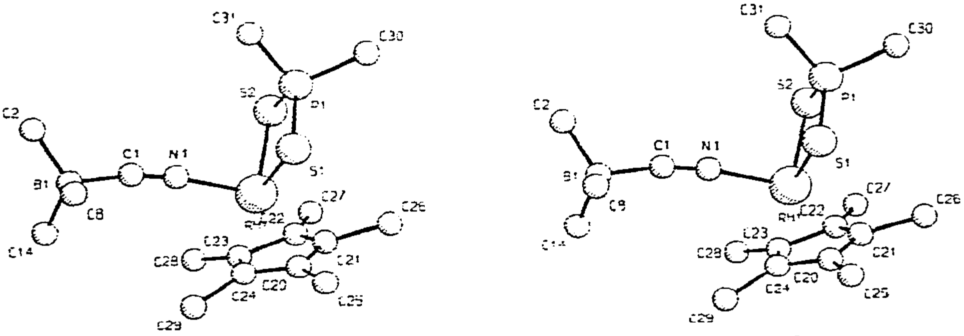


Fig. 1. View of the molecular geometry of $\{\eta^5\text{-}(C_5Me_5)Rh(S_2PMe_2)NCBPh_3\}$ (IVa). For clarity only the central part of the molecule is shown.

TABLE 1

Bond length (Å)		Bond angle (°)	
Rh—S(1)	2.41(1)	Rh—N—C	168.9(2.8)
Rh—S(2)	2.43(1)	N—C—B	167.6(2.6)
Rh—N	2.00(4)	Rh—S(1)—P	87.0(5)
Rh—C_5Me_5[a]	1.81	Rh—S(2)—P	86.5(4)
N—C	1.16(5)	N—Rh—S(1)	91.7(1.0)
C—B	1.58(5)	S(1)—Rh—S(2)	82.0(3)
S(1)—P	2.01(1)	N—Rh—C_5Me_5[a]	123.0
S(2)—P	2.01(1)	S(1)—Rh—C_5Me_5[a]	125.7
	Torsion angle about C—N: −30.0°		

[a] Distance to the centre of gravity of the pentamethylcyclopentadienyl ring.

(Rh—S_2) moieties gave *R*-factors of 0.39 and 0.50, the latter one being disregarded as incorrect.

Only two papers describing transition metal complexes of triphenylcyanoborate have been found in the literature (viz. $\{\eta^5\text{-}(C_5H_5)M(PPh_3)_2NCBPh_3\}$ (M = Fe, Ru) [3], $\{\eta^5\text{-}(C_5H_5)Ru(PPh_3)_2CNBPh_3\}$ [3] and $\{(PPh_3)CuNCBPh_3\}_n\text{-}CHCl_3$ [2] and all these compounds have been prepared by means of direct reaction with $NaBPh_3CN$.

In this work, the BPh_3CN^- anion is generated in situ, possibly by reaction of hydrogen cyanide with BPh_4^-. Earlier studies on $C_2(CN)_4$ have shown that hydrogen cyanide is readily released on reaction with alkoxide ions in the presence of certain catalysts [4].

Finally, it should be noted that this rather unusual reaction is not confined to rhodium. Thus, reaction of $\{\eta^6\text{-}(C_6H_6)Ru(S_2PPh_2)Cl\}$ with a methanolic solution of $C_2(CN)_4$ and $NaBPh_4$ gives $\{\eta^6\text{-}(C_6H_6)Ru(S_2PPh_2)NCBPh_3\}$ and $\{Pd(S_2CNEt_2)(PMe_2Ph)Cl\}$ on treatment with $AgBF_4$/THF, (which gives $\{Pd(S_2CNEt_2)(PMe_2Ph)(THF)\}^+$ [5]), followed by $C_2(CN)_4$ and $NaBPh_4$ in methanol gives $\{Pd(S_2CNEt_2)(PMe_2Ph)NCBPh_3\}$.

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