

### Preliminary communication

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## REACTIONS OF $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ WITH $\text{XCN}$ ( $\text{X} = \text{Br}, \text{I}$ )

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### Summary

Oxidative additions of  $\text{XCN}$  ( $\text{X} = \text{Br}, \text{I}$ ) to  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  give  $(\eta\text{-C}_5\text{H}_5)_2\text{TiX}(\text{CN})$ , ( $\text{X} = \text{Br}, \text{I}$ ). The compounds were characterized by elementary analyses and IR and  $^1\text{H}$  NMR spectra.

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The carbonyl ligands of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  are known to be readily eliminated in reactions with alkyl or aryl disulfides or acetylenes [1-3]. We have now found that addition of  $\text{XCN}$  ( $\text{X} = \text{Br}, \text{I}$ ) to the ethereal solutions of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  immediately causes evolution of carbon monoxide and quantitative formation of the yellow solid  $(\eta\text{-C}_5\text{H}_5)_2\text{TiX}(\text{CN})$  ( $\text{X} = \text{Br}, \text{I}$ ) previously unknown.

Table 1 lists IR spectral data for the two new compounds; the bands from the  $\text{C}_5\text{H}_5$  rings appear at 3000, 1400, 1100 and 800  $\text{cm}^{-1}$ , some being doublets because of the asymmetry of these molecules. The presence of these bands indicate that no  $\sigma\text{-}\pi$  rearrangement takes place [5]. The band at 1100  $\text{cm}^{-1}$  indicates that there is no substitution on the  $\text{C}_5\text{H}_5$  ring. The bands corresponding to  $\nu(\text{C}\equiv\text{N})$  appear at 2120  $\text{cm}^{-1}$ , and there are no bands in the  $\nu(\text{CO})$  region. The bands corresponding to  $\nu_{\text{as}}(\text{Ti-R})$ , ( $\text{R} = \eta\text{-C}_5\text{H}_5$ ), appear around 400  $\text{cm}^{-1}$ , higher than in  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  [4], probably due to the increase in the oxidation level of Ti; we assign the band at 300  $\text{cm}^{-1}$  to the symmetric vibration mode of the Ti-R bond; the band from  $\nu(\text{Ti-Br})$  appears at 240  $\text{cm}^{-1}$ , and that from  $\nu(\text{Ti-I})$  at 140  $\text{cm}^{-1}$ .

In the  $^1\text{H}$  NMR spectra of both compounds, two signals appear at about  $\tau$  3-3.5 ppm, corresponding to the protons of the cyclopentadienyl rings. The presence of these two signals indicates the absence of free rotation in the  $\text{C}_5\text{H}_5$  rings (probably due to steric hindrance by the relatively large ligands I, Br and CN) which makes the protons nonequivalent.

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TABLE 1

IR SPECTRA OF  $R_2TiX(CN)^a$ 

X = I	X = Br	Assignment <sup>b</sup> (Cs)
3090 w	3090 w	$\nu(CH) A'$
2127 m	2130 w	$\nu(C=N) A'$
1442 m	1440 m	$\omega(CC) A' + A''$
1435 m	1435 m	
1255 w	1253 w	$\delta(CH) A''$
1120 w	1120 w	$\gamma(CH) A'$
1018 m	1020 m	$\delta(CH) A' + A''$
1005 m	1008 m	
	850 (sh)	
815 s	810 s	$\gamma(CH) A' + A''$
720 s	730 s	
585 w	589 w	$\delta(R) A'$
420 w	418 (sh)	$\pi_{as}(R) A' + A''$
405 m	407 m	$\nu_{as}(TiR) A''$
353 w	360 w	$\nu(TiC) A'$
335 w	340 w	$\delta(TiCN) A'$
295 w	295 w	$\nu_s(TiR) A'$
	240 m	$\nu(TiBr) A'$
220 w	220 w	$\delta_{as}(RMR) A'$
140 s		$\nu(TiI) A'$

<sup>a</sup>R =  $\eta-C_5H_5$ ; s = strong; vs = very strong; w = weak; vw = very weak; m = medium; (sh) = shoulder.

<sup>b</sup> $\delta$  = deformation in the plane,  $\gamma$  = deformation out of the plane,  $\pi$  = tilting.

## Experimental

All the reactions were carried out under  $N_2$ . Analyses for C, H and N were carried out in the Centro Nacional de Química Orgánica (Madrid-Spain).

The  $Ti^{4+}$  was determined as  $TiO_2$ , and the halogens as silver halides by Volhard's method.

The  $(\eta-C_5H_5)_2Ti(CO)_2$  and the cyanogen halides were synthesised and purified by literature methods [6-7].

**Preparation of  $(\eta-C_5H_5)_2TiI(CN)$ .** In a 100 ml two-neck flask fitted with a  $N_2$  inlet, a magnetic stirrer and a pressure-equalized dropping funnel, 2.34 g (10 mmol) of  $(\eta-C_5H_5)_2Ti(CO)_2$  were dissolved in 50 ml of anhydrous ether. A solution of 1.60 g (10.6 mmol) of ICN in 20 ml of anhydrous ether was added dropwise. A yellow solid immediately appeared, and evolution of CO is observed. The solid was filtered off, washed with ether, and dried in vacuum. Anal.: Found: C, 38.72; H, 2.97; N, 3.98; I, 37.90; Ti, 13.67.  $C_{11}H_{10}NiTi$  calcd.: C, 39.8; H, 3.02; N, 4.22; I, 38.36; Ti, 14.5%.  $^1H$  NMR (acetone- $d_6$ ),  $\tau$  (CH) 3.22 and 3.29 ppm.

**Preparation of  $(\eta-C_5H_5)_2TiBr(CN)$ .** When 2.34 g (10 mmol) of  $(\eta-C_5H_5)_2Ti(CO)_2$  in ether were added to 1.12 g (10.6 mmol) of BrCN in 20 ml of ether a yellow solid precipitated. This was filtered off, washed with ether, and dried in high vacuum. Anal.: Found: C, 45.54; H, 3.85; N, 4.87; Br, 27.87; Ti, 16.32.  $C_{11}H_{10}NBrTi$  calcd.: C, 46.70; H, 3.52; N, 4.92; Br, 28.16; Ti, 16.90%.  $^1H$  NMR (acetone- $d_6$ ):  $\tau$  (CH) 3.22 and 3.29 ppm.

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