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1,4-DICYANOBUTENE-BRIDGED BINUCLEAR RHODIUM(I) COMPLEXES AND THEIR CATALYTIC ACTIVITIES

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Summary

Reactions of $Rh(ClO_4)(CO)(PPh_3)_2$ with dicyano olefins, *cis*-$NCCH=CHCH_2CH_2CN$ (*c*-DC1B), *trans*-$NCCH=CHCH_2CH_2CN$ (*t*-DC1B), *trans*-$NCCH_2CH=CHCH_2CN$ (*t*-DC2B), and $NCCH_2CH_2CH_2CH_2CN$ (DCB) produce the binuclear dicationic rhodium(I) complexes, $[(CO)(PPh_3)_2RhNC\text{–}A\text{–}CNRh(PPh_3)_2(CO)](ClO_4)_2$ (NC–A–CN = *c*-DC1B (**1**), *t*-DC1B (**2**), *t*-DC2B (**3**), DCB (**4**)). Complexes **1** and **2** are catalytically active for the hydrogenation of *c*-DC1B and *t*-DC1B, respectively, to give DCB, while complex **3** catalyzes the isomerization of *t*-DC2B to give *c*-DC1B and *t*-DC1B, and the hydrogenation of *t*-DC2B to DCB at 100 °C.

Introduction

Monocyano olefins (L) react with $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh [1], Ir [2]) to give $[ML(CO)(PPh_3)_2]ClO_4$ (L is coordinated through the nitrogen atom of the cyano group) which are catalytically active for the hydrogenation, isomerization and oligomerization of L. Here, we report on the synthesis of new dicationic binuclear rhodium(I) complexes of dicyano olefins (NC–A–CN) and their catalytic activities for the hydrogenation and isomerization of NC–A–CN.

Results and discussion

Coordination of cyano olefins to rhodium

Reaction of $Rh(ClO_4)(CO)(PPh_3)_2$ with 1,4-dicyanobutene and 1,4-dicyanobutane produce the new rhodium(I) complexes according to eq. 1 (see Experimental for details). Attempts to prepare the monomeric complexes of NC–A–CN, $[Rh(NC\text{–}A\text{–}CN)(CO)(PPh_3)_2]ClO_4$, by using an excess of NC–A–CN (NC–A–CN/Rh = 10), have been unsuccessful and give only the binuclear complexes, **1**–**4**. Iridium analogues, $[(CO)(PPh_3)_2IrNC\text{-}A\text{-}CNIr(PPh_3)_2(CO)](ClO_4)_2$

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and their hydrido complexes, $[(CO)(PPh_3)_2(H)_2IrNC\text{-}A\text{-}CNIr(H)_2(PPh_3)_2(CO)](ClO_4)_2$ have also been prepared [3]. A report on a dicationic binuclear complex with a bridging dicyano compound which coordinates through the nitrogen atoms, $[(dppm)_2(CO)MnNCCH_2CH_2CNMn(CO)(dppm)_2](ClO_4)_2$ (dppm = bis(diphenylphosphino)methane) has been previously published [4]. Complexes **1–4** have been characterized by elemental analyses, conductance measurements (see Experimental), and spectroscopic data. They are diamagnetic; soluble in polar solvents such as chloroform and dichloromethane, insoluble in non-polar solvents such as benzene and hexane; stable in the solid state and in solution under nitrogen at room temperature.

$$2Rh(ClO_4)(CO)(PPh_3)_2 + NC\text{–}A\text{–}CN \rightarrow$$

$$\underset{\textbf{(1–4)}}{[(CO)(PPh_3)_2RhNC\text{–}A\text{–}CNRh(PPh_3)_2(CO)]}(ClO_4)_2 \qquad (1)$$

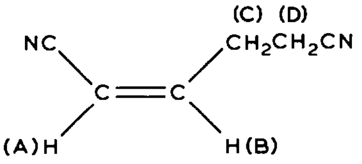
NC–A–CN: (1) *cis*-$NCCH{=}CHCH_2CH_2CN$ (*c*-DC1B),
(2) *trans*-$NCCH{=}CHCH_2CH_2CN$ (*t*-DC1B),
(3) *trans*-$NCCH_2CH{=}CHCH_2CN$ (*t*-DC2B),
(4) $NCCH_2CH_2CH_2CH_2CN$ (DCB).

^1H NMR data clearly suggest a $[Rh(PPh_3)_2]_2$ (NC–A–CN) moiety for each of **1–4** (see the ratios of the protons of PPh_3 to those of NC–A–CN in Table 1). The absence of the spin coupling between ^{103}Rh and the olefinic protons in **1–3** suggests that the coordination of NC–A–CN does not occur through the olefinic π-system of NC–A–CN. Upfield shifts have been observed for the protons of saturated and unsaturated nitriles upon coordination through the nitrogen atom to $Ru(NH_3)_5^{2+}$ [5], $Rh(CO)(PPh_3)_2^+$ [6] and $Ir(H)_2(CO)(PPh_3)_2^+$ [7]. There are several factors that may affect the shielding of protons, as previously discussed [5]. Further investigation is necessary to explain the significant upfield shifts of the protons of NC–A–CN upon coordination to $Rh(CO)(PPh_3)_2^+$ (see Table 1). Infrared spectral data (Table 2) unambiguously indicate that each NC–A–CN in **1–4** is coordinated to rhodium through both of the nitrogen atoms of the two cyano groups, rather than through the π-system of the olefinic group. It is well-known that $\nu(C{\equiv}N)$ of a cyano compound increases upon coordination through the nitrogen atom [8,9], and decreases upon coordination through the π-system of the cyano group [9,10]. The two $\nu(C{\equiv}N)$ observed for each of **1** and **2** are considerably higher than those of free *c*-DC1B and *t*-DC1B, respectively, which suggests that *c*-DC1B and *t*-DC1B are coordinated through both of the nitrogen atoms of the two cyano groups. Both **3** and **4** show only one $\nu(C{\equiv}N)$ which is significantly higher than that of free *t*-DC2B and DCB, indicating that *t*-DC2B and DCB in **3** and **4** are also coordinated through both nitrogen atoms of the two cyano groups. A slight change in $\nu(C{=}C)$ of NC–A–CN upon coordination (Table 2) also supports the nitrogen-bonded NC–A–CN in **1–4**. A strong and broad absorption at ca. 1100 cm^{-1}, observed for all complexes, is attributed to the tetrahedral (Td) anion ClO_4^- [11], this supports the fact that **1–4** are 1 : 1 electrolytes as confirmed by the conductance measurements (see Experimental).

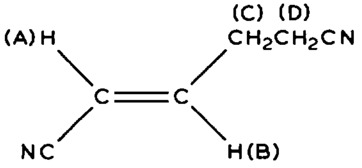
UV-VIS spectral data for **1–4** (Table 2) also support the fact that **1–4** are four-coordinated rhodium(I) complexes and that NC–A–CN in **1–4** is coordinated through the nitrogen atoms. It is well-known that the related rhodium(I) complexes,

TABLE 1

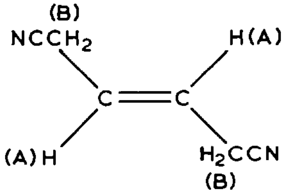
^1H NMR SPECTRAL DATA FOR $[(CO)(PPh_3)_2RhNC\text{-}A\text{-}CNRh(PPh_3)_2(CO)](ClO_4)_2$ (**1**: NC–A–CN = *cis*-$NCCH{=}CHCH_2CH_2CN$ (*c*-DC1B); **2**: NC–A–CN = *trans*-$NCCH{=}CHCH_2CH_2CN$ (*t*-DC1B); **3**: NC–A–CN = *trans*-$NCCH_2CH{=}CHCH_2CN$ (*t*-DC2B); **4**: NC–A–CN = $NCCH_2CH_2CH_2CH_2CN$ (DCB)) IN $CDCl_3$ AT 25 °C AT 60 MHz.



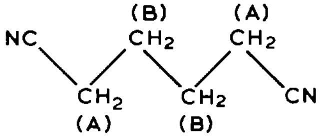
(*c*-DCIB)



(*t*-DCIB)



(*t*-DC2B)



(DCB)

Compound	Chemical shift, ppm ^{a}				
	H(A)	H(B)	H(C)	H(D)	$P(C_6H_5)_2$
c-DC1B	5.70(d) ^{b}	6.41(m) ^{b}	2.49(m)		
1	4.80(d,1H) ^{c}	5.31(m,1H) ^{c}	1.09(m,2H)	1.80(m,2H)	7.50(m,60H)
t-DC1B	5.39(d) ^{d}	6.60(m) ^{d}	2.41(m)		
2	4.89(d,1H) ^{e}	5.71(m,1H) ^{e}	1.50(m,2H)	1.89(m,2H)	7.50(m,60H)
t-DC2B	5.80(m)	3.21(m)			
3	4.21(t,2H)	2.49(d,4H)			7.50(m,60H)
DCB	2.80(m)	2.41(m)			
4	1.59(m,4H)	0.31(m,4H)			7.50(m,60H)

^{a} Relative to Me_4Si. ^{b} $J(H(A)\text{-}H(B))$ 12.0 Hz. ^{c} $J(H(A)\text{-}H(B))$ 20.0 Hz. ^{d} $J(H(A)\text{-}H(B))$ 11.1 Hz. ^{e} $J(H(A)\text{-}H(B))$ 17.4 Hz.

$RhA(CO)(PPh_3)_2$ (A = monodentate ligand) show an absorption band in the region of 350–400 nm which shifts with respect to the type of ligating atom A [12]. $RhA(CO)(PPh_3)_2$ shows an absorption band at 365–381 nm when A is the ligand that coordinating through the nitrogen atom in groups such as N_3, NCO, NO_2, NCS [12] and monocyano olefins [1].

Catalytic activities

We have previously found that $[Rh(CH_2{=}CHCN)(CO)(PPh_3)_2]ClO_4$ (**5**) and $[Rh(CH_3CH{=}CHCN)(CO)(PPh_3)_2]ClO_4$ (**6**) are catalytically active for the hydrogenation and oligomerization of $CH_2{=}CHCN$ and $CH_3CH{=}CHCN$, respectively, at room temperature while $[Rh(CH_2{=}C(CH_3)CN)(CO)(PPh_3)_2]ClO_4$ (**7**) and $[Rh(CH_2{=}CHCH_2CN)(CO)(PPh_3)_2]ClO_4$ (**8**) do not show these features at room temperature [1,13]. At elevated temperature, however, complexes **7** and **8** catalyze the hydrogenation, isomerization (of $CH_2{=}CHCH_2CN$ to $CH_3CH{=}CHCN$) and

TABLE 2

SELECTED IR AND UV-VIS ABSORPTION DATA FOR $[(CO)(PPh_3)_2RhNC\text{-}A\text{-}CNRh(PPh_3)_2(CO)](ClO_4)_2$ (**1**: NC–A–CN = *cis*-$NCCH{=}CHCH_2CH_2CN$ (*c*-DC1B); **2**: NC–A–CN = *trans*-$NCCH{=}CHCH_2CH_2CN$ (*t*-DC1B); **3**: NC–A–CN = *trans*-$NCCH_2CH{=}CHCH_2CN$ (*t*-DC2B); **4**: NC–A–CN = $NCCH_2CH_2CH_2CH_2CN$ (DCB)).

Compound	Infrared absorption (cm^{-1}) [a]			UV-VIS absorption (nm) [b]
	$\nu(C{\equiv}N)$	$\nu(C{=}C)$	$\nu(C{\equiv}O)$	
c-DC1B	2245, 2220	1626		
1	2289, 2260	1628	2003	380(6880)
t-DC1B	2247, 2222	1637		
2	2292, 2268	1625	2018	381(6660)
t-DC2B	2250			
3	2293		2026	375(6870)
DCB	2244			
4	2288		2001	376(6220)

[a] In Nujol. [b] In CH_2Cl_2 at 25 °C under nitrogen. Extinction coefficients are given in parentheses.

oligomerization of $CH_2{=}CHCH_2CN$ and $CH_3CH{=}CHCN$ [14]. In this study, it has been found that complexes **1**–**3** are catalytically active for the hydrogenation and isomerization of NC–A–CN at elevated temperature (Figs. 1 and 2). These complexes do not show catalytic activity at room temperature. The rate of hydrogenation of *t*-DC1B is practically the same as that of *c*-DC1B, (see Fig. 1). The isomerization of *c*-DC1B (or *t*-DC1B) to $NCCH_2CH{=}CHCH_2CN$ with **1** (or **2**) has not been observed under the experimental conditions for the catalytic hydrogenation shown in Fig. 1, while the isomerization of *t*-DC2B to *c*-DC1B and *t*-DC1B occurs in the presence of **3** (see Fig. 2). It is apparent from Fig. 2 that DCB is produced by the hydrogenation of *c*-DC1B and *t*-DC1B which are the isomerization products of *t*-DC2B. It is, however, uncertain whether DCB is also formed by the direct hydrogenation of *t*-DC2B (without going through the isomerization step), or

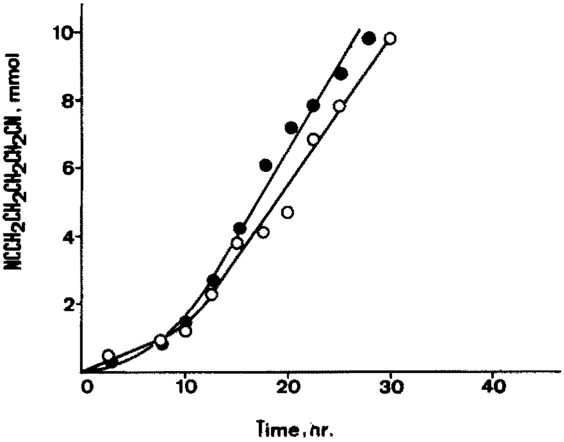


Fig. 1. Hydrogenation of *cis*-$NCCH{=}CHCH_2CH_2CN$ (10 mmol) with $[(CO)(PPh_3)_2Rh\text{-}cis\text{-}NCCH{=}CHCH_2CH_2CN\text{-}Rh(PPh_3)_2(CO)](ClO_4)_2$ (0.05 mmol) (○——○) and *trans*-$NCCH{=}CHCH_2CH_2CN$ (10 mmol) with $[(CO)(PPh_3)_2Rh\text{-}trans\text{-}NCCH{=}CHCH_2CH_2CN\text{-}Rh(PPh_3)_2(CO)](ClO_4)_2$ (0.05 mmol) (●——●) in chlorobenzene (5 ml) at 100 °C under hydrogen ($p(H_2) = 1$ atm).

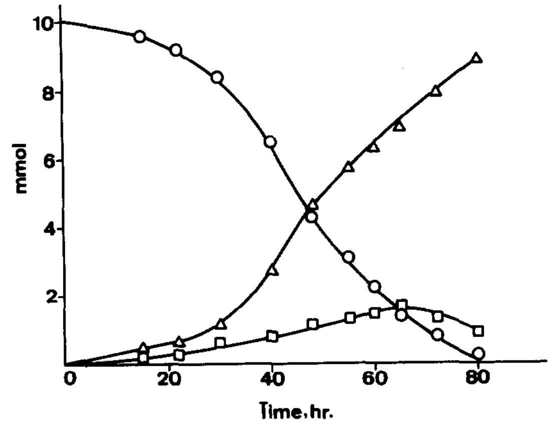


Fig. 2. Hydrogenation and isomerization of *trans*-$NCCH_2CH{=}CHCH_2CN$ (10 mmol) with $[(CO)(PPh_3)_2Rh$-*trans*-$NCCH_2CH{=}CHCH_2CNRh(PPh_3)_2(CO)](ClO_4)_2$ (0.05 mmol) in chlorobenzene (5 ml) at 100 °C under hydrogen ($p(H_2)$ 1 atm). ○——○, *trans*-$NCCH_2CH{=}CHCH_2CN$; □——□, mixture (1:1) of *cis*- and *trans*-$NCCH{=}CHCH_2CH_2CN$; △——△, $NCCH_2CH_2CH_2CH_2CN$.

whether it is formed at all. It should be mentioned that the isomerization of *t*-DC2B to DC1B also occurs in the absence of H_2. The rate, however, is considerably slower than that under H_2: less than 0.5 mmol (5%) of *t*-DC2B were isomerized after 65 h under N_2 while 1.7 mmol (17%) of DC1B were observed after 65 h under H_2, under the same experimental conditions (given in Fig. 2).

Experimental

Methods

A standard vacuum line and Schlenk-type glassware were used in handling the metal complexes. ^1H NMR, IR and UV-VIS spectra were recorded with Varian 60 MHz (EM-360A), Shimadzu IR-440 and Shimadzu UV-240 spectrophotometers. Conductance measurements were carried out with a Wiss-Tech. Werkstätten Weinheim/Obb. conductometer in the presence of the corresponding dicyanides in chloroform at 25 °C. Elemental analyses were performed at Spang Microanalytical Laboratory, Eagle Harbor, MI.

Materials

$Rh(ClO_4)(CO)(PPh_3)_2$ was prepared by a standard method [8]. All solvents were dried and distilled before use. *cis*-1,4-Dicyano-1-butene (b.p. = 195 °C at 2 mmHg) and *trans*-1,4-dicyano-1-butene (b.p. = 175 °C at 2 mmHg) were separated from the mixture (*cis*/*trans* = ca. 1.0, Fluka) by fractional distillation at reduced pressure (2 mmHg). *trans*-1,4-Dicyano-2-butene (Fluka) and 1,4-dicyanobutane (Aldrich) were used as purchased.

Synthesis

$[(CO)(PPh_3)_2Rh$-cis-$NCCH{=}CHCH_2CH_2CN$-$Rh(PPh_3)_2(CO)](ClO_4)_2$ (1). *Cis*-$NCCH{=}CHCH_2CH_2CN$ (0.054 g, 0.5 mmol) was added to $Rh(ClO_4)(CO)(PPh_3)_2$

(0.75 g, 1.0 mmol) in benzene solution (70 ml) under nitrogen at 25 ° C, and immediately yellow microcrystals of **1** separated, these were collected by filtration, washed with benzene (50 ml), and dried in vacuum. The yield was 0.73 g (90%). Anal. Found: C, 60.02; H, 4.08; N, 1.69; Cl, 4.41; P. 7.56. $C_{80}H_{66}Cl_2N_2O_{10}P_4Rh_2$ calc: C, 59.39; H, 4.11; N, 1.73; Cl, 4.38; P. 7.66%. Molar conductance, 62 ohm^{-1} cm^2 mol^{-1} ([Rh] = 5.0 × 10^{-5} *M* in dichloromethane) *.

[(CO)(PPh$_3$)$_2$Rh-trans-NCCH=CHCH$_2$CH$_2$CN-Rh(PPh$_3$)$_2$(CO)](ClO$_4$)$_2$ (**2**), *[(CO)(PPh$_3$)$_2$Rh-trans-NCCH$_2$CH=CHCH$_2$CN-Rh(PPh$_3$)$_2$(CO)](ClO$_4$)$_2$* (**3**) and *[(CO)(PPh$_3$)$_2$Rh-NCCH$_2$CH$_2$CH$_2$CH$_2$CN-Rh(PPh$_3$)$_2$(CO)](ClO$_4$)$_2$* (**4**). These compounds which were prepared in the same manner as described for **1**, gave satisfactory elemental analyses and showed molar conductance values close to that of **1**.

Catalyses

In all experiments, the following procedure was used with 0.05 mmol (0.08 g) of **1** (or **2**–**4**) and 10 mmol (1.08 g) of the corresponding NC–A–CN in 5 ml of chlorobenzene. The rhodium complex and the corresponding NC–A–CN were mixed with chlorobenzene and placed in a bomb reactor (Parr 1341; volume 360 ml), which was then immediately flushed with hydrogen, and sealed. Hydrogen was introduced into the reactor until the pressure reached 1 atm at 25 ° C. The reactor was then placed in an oven maintained at 100 ° C. The hydrogen pressure in the reactor at 100 ° C was 1.25 atm. The reactor was cooled at intervals to 25 ° C, at which temperature no catalytic reactions could occur. The reactor was opened under nitrogen, and the solution was analyzed by ^{1}H NMR spectroscopy.

Acknowledgements

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* Molar conductance of a standard 1:1 electrolyte, $(n\text{-}Bu)_4NClO_4$ in dichloromethane at 25 ° C is 34 ohm^{-1} cm^2 mol^{-1}.