was added MIC (2.2 mmol) and the reaction mixture was stirred at room temperature for the time given in Table I. The mixture was evaporated and ethyl ether (40 m*l*) was added to the residue. The supernatant was decanted from the black gum and the insoluble residue was washed three times with ethyl ether. The ether extracts were concentrated under reduced pressure and the crude product was purified by distillation.

General Procedure for Oxidative Cleavage of Oximes. To a solution of an oxime (2.0 mmol) in methylene chloride (5 m*l*) was added MIC (2.4 mmol). After being stirred at room temperature for the time given in Table II, the reaction mixture was evaporated and ethyl ether (40 m*l*) was added to the residue. The supernatant was decanted from black gum and the insoluble residue was washed three times with ethyl ether. The combined ether extracts were evaporated to dryness and the crude product was purified by distillation or by passing through a short column of silica gel.

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1,4-Dicyanobutene Bridged Binuclear Iridium (I, III) Complexes and Their Catalytic Activities
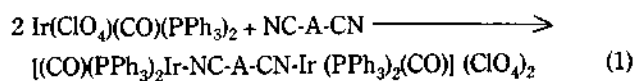
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Reactions of Ir(ClO$_4$)(CO)(PPh$_3$)$_2$ with dicyano olefins, *cis*-NCCH = CHCH$_2$CH$_2$CN (*c*DC1B), *trans*-NCCH = CHCH$_2$CH$_2$CN (*t*DC1B), *trans*-NCCH$_2$CH = CHCH$_2$CN (*t*DC2B), and NCCH$_2$CH$_2$CH$_2$CH$_2$CN (DCB) produce binuclear dicationic iridium (I) complexes, [(CO)(PPh$_3$)$_2$Ir-NC-A-CN-Ir(PPh$_3$)$_2$(CO)](ClO$_4$)$_2$ (NC-A-CN = *c*DC1B (**1a**), *t*DC1B (**1b**), *t*DC2B (**1c**), DCB (**1d**)). Complexes **1a-1d** react with hydrogen to give binuclear dicationic tetrahydrido iridium (III) complexes, [(CO)(PPh$_3$)$_2$(H)$_2$Ir-NC-A-CN-Ir(H)$_2$(PPh$_3$)$_2$ (CO)](ClO$_4$)$_2$ (NC-A-CN = *c*DC1B (**2a**), *t*DC1B (**2b**), *t*DC2B (**2c**), DCB (**2d**)). Complexes **2a** and **2b** catalyze the hydrogenation of *c*DC1B and *t*DC1B, respectively to give DCB, while the complex **2c** is catalytically active for the isomerization of *t*DC2B to give *c*DC1B and *t*DC1B and the hydrogenation of *t*DC2B to give DCB at 100°C.
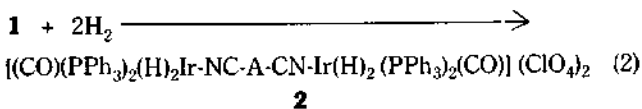
Introduction

We recently reported the synthesis and catalytic activities of monocyanoolefin complexes of rhodium(I)[1] and iridium(I, III),[2] [ML(CO)(PPh$_3$)$_2$] ClO$_4$ (M = Rh, Ir; L = monocyanoolefins coordinated through the nitrogen atom). It would be interesting to compare these monocyanoolefin complexes with the corresponding dicyanoolefin complexes. We now wish to report the synthesis of new cationic binuclear iridium(I) and tetrahydridodiiridium(III) complexes of bridging dicyanides, [(CO)(PPh$_3$)$_2$Ir-NC-A-CN-Ir(PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (**1**) and [(CO)(PPh$_3$)$_2$(H)$_2$Ir-NC-A-CN-Ir(H)$_2$(PPh$_3$)$_2$ (CO)] (ClO$_4$)$_2$ (**2**) (NC-A-CN = 1,4-dicyanobutene and 1,4-dicyanobutane), and their catalytic activities for the hydrogenation and isomerization of NC-A-CN. Attempts to prepare the mononuclear complexes,

$$2 \; Ir(ClO_4)(CO)(PPh_3)_2 + NC\text{-}A\text{-}CN \longrightarrow$$

$$[(CO)(PPh_3)_2Ir\text{-}NC\text{-}A\text{-}CN\text{-}Ir\,(PPh_3)_2(CO)]\,(ClO_4)_2 \qquad (1)$$

$$\mathbf{1}$$

$$\mathbf{1} + 2H_2 \longrightarrow$$

$$[(CO)(PPh_3)_2(H)_2Ir\text{-}NC\text{-}A\text{-}CN\text{-}Ir(H)_2\,(PPh_3)_2(CO)]\,(ClO_4)_2 \qquad (2)$$

$$\mathbf{2}$$

NC-A-CN = (a) *cis*-NCCH=CHCH$_2$CH$_2$CN (*c*DC1B), (b) *trans*-NCCH=CHCH$_2$CH$_2$CN (*t*DC1B), (c) *trans*-NCCH$_2$CH=CHCH$_2$CN (*t*DC2B), (d) NCCH$_2$CH$_2$CH$_2$CH$_2$CN (DCB)

[Ir(NC-A-CN)(CO)(PPh$_3$)$_2$] ClO$_4$ have been unsuccessful so far (see Experimental). There has been a report on a cationic binuclear Mn(I) complex of a bridging dicyano compound through the two nitrogen atoms, [(dppm)$_2$(CO)Mn-NCCH$_2$CH$_2$CN-Mn(CO)(dppm)$_2$] (ClO$_4$)$_2$ (dppm = bis(diphenylphosphino)methane).[3]

Experimental Section

Materials. Ir(ClO$_4$)(CO)(PPh$_3$)$_2$ was prepared by the known method.[4] 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.

Physical Measurements. Infrared and electronic absorption spectra were measured on Shimadzu IR-440 and Shimadzu UV-240. Proton NMR spectra were obtained on Bruker WP 80-MHz FT-NMR spectrometer. Conductance measurements were carried out with Wiss-Tech. Conductivity meter LBR in dichloromethane at 25°C under nitrogen. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Habor, MI.

Preparation. Standard vacuum line and Schlenk-type glassware were used in handling metal complexes.

[(CO)(PPh$_3$)$_2$Ir-*cis*-NCCH = CHCH$_2$CH$_2$CN-Ir(PPh$_3$)$_2$ (CO)] (ClO$_4$)$_2$ (1a). Addition of *cis*-NCCH=CHCH$_2$CH$_2$CN (0.054 g, 0.5 mmol) into the benzene solution (70 m*l*) of Ir(ClO$_4$)(CO)(PPh$_3$)$_2$ (0.84 g, 1.0 mmol) under nitrogen at 25°C immediately resulted in precipitation of yellow microcrystals which were collected by filtration, washed with benzene (70 m*l*), and dried under vacuum; yield 0.81 g (90% based on 1a). Anal. Calcd for Ir$_2$C$_{80}$H$_{66}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.54; H, 3.71; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 53.09; H, 3.68; N, 1.51; Cl, 4.00; P, 6.84. Λ_M = 65 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO(PPh$_3$)$_2$Ir-*trans*-NCCH = CHCH$_2$CH$_2$CN-Ir (PPh$_3$)$_2$ (CO)] (ClO$_4$)$_2$ (1b). This compound was prepared in the same manner described for 1a. Anal. Calcd for Ir$_2$C$_{80}$H$_{66}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.54; H, 3.71; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 53.00; H, 3.75; N, 1.61; Cl, 3.98; P, 7.03. Λ_M = 68 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$Ir-*trans*-NCCH$_2$CH = CHCH$_2$CN-Ir (PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (1c). This compound was prepared in the same manner described for 1a. Anal. Calcd for Ir$_2$C$_{80}$H$_{66}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.54; H, 3.71; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 52.99; H, 3.78; N, 1.51; Cl, 3.89; P, 6.98. Λ_M = 67 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$Ir-NCCH$_2$CH$_2$CH$_2$CH$_2$CN-Ir(PPh$_3$)$_2$ (CO)] (ClO$_4$)$_2$ (1d). This compound was prepared in the same manner described for 1a. Anal. Calcd for Ir$_2$C$_{80}$H$_{68}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.48; H, 3.81; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 53.21; H, 4.00; N, 1.52; Cl, 3.99; P, 7.00. Λ_M = 69

Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$(H)$_2$Ir-*cis*-NCCH = CHCH$_2$CH$_2$CN-Ir(H)$_2$ (PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (2a). A 30 m*l* CH$_2$CL$_2$ solution of 1a (0.40 g, 0.22 mmol) was stirred under the atmospheric pressure of hydrogen at 25°C. The yellow solution became a white-beige suspension within 30 minutes. Addition of hexane (70 m*l*) precipitated more white-beige solid which was collected by filtration, washed with benzene (30 m*l*), and dried under vacuum; yield 0.36 g (90% based on 2a). Anal. Calcd for Ir$_2$C$_{80}$H$_{70}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.42; H, 3.92; N, 1.56; Cl, 3.94; P, 6.89. Found: C, 53.92; H, 3.75; N, 1.61; Cl, 4.01; P, 7.01. Λ_M = 64 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$(H)$_2$Ir-*trans*-NCCH = CHCH$_2$CH$_2$CN-Ir(H)$_2$(PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (2b). This compound was prepared in the same manner described for 2a. Anal. Calcd for Ir$_2$C$_{80}$H$_{70}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.48; H, 3.82; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 53.20; H, 3.91; N, 1.49; Cl, 3.91; P, 6.92. Λ_M = 64 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$Ir-*trans*-NCCH$_2$CH = CHCH$_2$CN-Ir (H)$_2$(PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (2c). This compound was prepared in the same described for 2a. Anal. Calcd for Ir$_2$C$_{80}$H$_{70}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.48; H, 3.82; N, 1.56; Cl, 3.95; P, 6.90. Found: C, 53.98; H, 3.78; N, 1.57; Cl, 3.99; P, 6.98. Λ_M = 67 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

[(CO)(PPh$_3$)$_2$(H)$_2$Ir-NCCH$_2$CH$_2$CH$_2$CH$_2$CN-Ir(H)$_2$ (PPh$_3$)$_2$(CO)] (ClO$_4$)$_2$ (2d). This compound was prepared in the same manner described for 2a. Anal. Calcd for Ir$_2$C$_{80}$H$_{72}$N$_2$O$_{10}$Cl$_2$P$_4$: C, 53.36; H, 4.03; N, 1.56; Cl, 3.94; P, 6.88. Found: C, 53.60; H, 3.89; N, 1.61; Cl, 3.84; P, 6.92. Λ_M = 64 Ω^{-1}cm^{2}mol^{-1} ([Ir] = 5.0 × 10^{-5} M in dichloromethane at 25°C).[5]

Attempt to prepare [Ir(cis-NCCH = CHCH$_2$CH$_2$CN) (CO)(PPh$_3$)$_2$] ClO$_4$. The reaction of excess *cis*-NCCH = CHCH$_2$CH$_2$CN (0.53 g, 5 mmol) with Ir(ClO$_4$)(CO)(PPh$_3$)$_2$ (0.84 g, 1 mmol) was carried out to prepare the monomeric complex, [Ir(*cis*-NCCH=CHCH$_2$CH$_2$CN)(CO)(PPh$_3$)$_2$] ClO$_4$ in the same manner described for 1a. It was found that the binuclear complex, 1a was the only product with 88% yield.

Catalytic Reactions. In all experiments (hydrogenation of *c*DC1B and *t*DC1B under H$_2$, isomerization of *t*DC2B under N$_2$, and hydrogenation and isomerization of *t*DC2B under H$_2$), 0.05 mmol (*ca.* 0.9 g) of 1 (or 2) and 10 mmol of the corresponding NC-A-CN were used in 25 m*l* of chlorobenzene. Experiments were carried out in the same manner described before.[2]
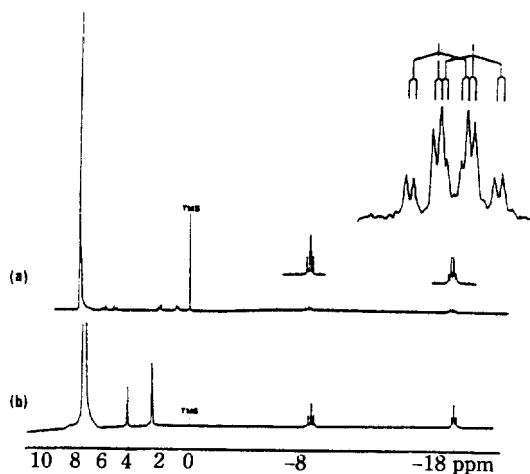
Results and Discussion

Complexes 1 and 2 have been prepared according to eq 1 and 2, and characterized by the elemental analyses, conductivity measurements, ^{1}H-NMR, infrared and electronic absorption spectral data. Complexes 1 and 2 are stable in the solid state in air at room temperature and in solution under nitrogen. The complexes 1a-1d are not soluble in nonpolar solvents (hexane, benzene) and are soluble in polar solvents (chloroform, dichloromethane) while the complexes 2a-2d are only slightly soluble in polar solvents (chloroform, dichloromethane).

Table I. Infrared (Nujol), ^{1}H-NMR (δ, CDCl$_3$) and Electronic (CH$_2$Cl$_2$) Spectral Data for [(CO)(PPh$_3$)$_2$ Ir-NC-A-CN-Ir(CO)-(PPh$_3$)$_2$](ClO$_4$)$_2$ (1) and [(CO)(PPh$_3$)$_2$(H)$_2$Ir-NC-A-CN-Ir(H)$_2$ (CO)(PPh$_3$)$_2$](ClO$_4$)$_2$ (2) (NC-A-CN = (a) cis-NCCH = CHCH$_2$-CH$_2$CN (cDC1B), (b) trans-NCCH = CHCH$_2$CH$_2$CN(tDC1B), (c) trans-NCCH$_2$CH = CHCH$_2$CN (tDC2B) and (d) NCCH$_2$CH$_2$-CH$_2$CH$_2$CN (DCB).

	IR abs, cm^{-1}				
compd	ν(CN)^a	ν(C = C)^c	ν(CO)^d	ν(Ir-H)^c	ρ(Ir-H)^c
cDC1B	2245, 2220	1626			
tDC1B	2247,2222	1637			
tDC2B	2250				
DCB	2244				
1a	2286, 2260	1624	1999		
1b	2292,2267	1627	2008		
1c	2301		2000		
1d	2294		1995		
2a	___^{b}	1626	2017	2220, 2112	878, 852
2b	___^{b}	1628	2013	2221, 2108	879, 850
2c	2300		2006	2228, 2103	885, 831
2d	___^{b}		2016	2221, 2112	873, 851

compd	electronic abs,^{e} nm
1a	469 (1100), 407 (5420), 348 (7620)
1b	469 (1400), 407 (6340), 348 (8740)
1c	467 (1180), 405 (5790), 346 (6470)
1d	466 (1570), 404 (7270), 346 (8370)

compd	^{1}H-NMR,^{h} ppm
cDC1B	2.51 (m, CH$_2$), 5.70 (d, NCCH), 6.39 (m, CHCH$_2$)
tDC1B	2.41 (m, CH$_2$), 5.42 (d, NCCH), 6.60 (m, CHCH$_2$)
tDC2B	3.20 (m, CH$_2$), 5.79 (m, CH)
DCB	2.40 (m, CH$_2$CH$_2$CH$_2$CH$_2$), 2.78 (m, CH$_2$CN)
1a	1.09 (m, CHCH$_2$, 2H), 1.81 (m, CH$_2$CN, 2H), 4.78 (d, NCCH, 1H), 5.30 (m, CHCH$_2$, 1H), 7.25 (m, C$_6$H$_5$, 60H)
1b	1.51 (m, CHCH$_2$, 2H), 1.89 (m, CH$_2$CN, 2H), 4.91 (d, NCCH, 1H), 5.70 (m, CHCH$_2$, 1H), 7.25 (m, C$_6$H$_5$, 60H)
1c	2.60 (d, CH$_2$, 4H), 4.09 (t, CH, 2H), 7.25 (m, C$_6$H$_5$, 60H)
1d	0.42 (m, CH$_2$CH$_2$CH$_2$CH$_2$, 4H), 1.81 (m, CH$_2$CN, 4H), 7.25 (m, C$_6$H$_5$, 60H)
2a^j	-18.3 (dt, IrH$_B'$, 1H), -18.1 (dt, IrH$_B$, 1H), -8.30 (dt, IrH$_A$, 2H), 0.91 (m, CHCH$_2$, 2H), 1.88 (m, CH$_2$CN, 2H), 5.01 (m, CH = CH, 2H), 7.25 (m, C$_6$H$_5$, 60H)
2b^j	-18.2 (dt, IrH$_B'$, 1H), -18.0 (dt, IrH$_B$, 1H), -8.29 (dt, IrH$_A$, 2H), 0.90 (m, CHCH$_2$, 2H), 2.08 (m, CH$_2$CN, 2H), 5.11 (d, NCCH, 1H), 5.89 (m, CHCH$_2$, 1H), 7.25 (m, C$_6$H$_5$, 60H)
2c^k	-18.3 (dt, IrH$_B$, 2H), -8.39 (dt, IrH$_A$, 2H), 2.70 (d, CH$_2$, 4H), 4.39 (t, CH, 2H), 7.25 (m, C$_6$H$_5$, 60H)
2d^l	-18.4 (dt, IrH$_B$, 2H), -8.40 (dt, IrH$_A$, 2H), 0.61 (m, CH$_2$CH$_2$CH$_2$CH$_2$, 4H), 1.78 (m, CH$_2$CN, 4H), 7.25 (m, C$_6$H$_5$, 60H)

^{a}Weak. ^{b}Probably obscured by ν(Ir-H) absorption bands. ^{c}Weak-medium. ^{d}Very strong. ^{e}Medium-strong. ^{f}Medium. ^{g}Under nitrogen at 25°C. Extinction coefficients are given in parentheses. ^{h}Under nitrogen at 25°C at 80 MHz. Chemical shifts are relative to Me$_4$Si and coupling constants are in Hertz. ^{j}J(P, H$_A$) = 16.1, J(P, H$_B$) = 13.7, J(P, H$_{B'}$) = 13.7, J(H$_A$, H$_B$) = 3.5, J(H$_A$, H$_{B'}$) = 3.7. ^{i}J(P, H$_A$) = 16.4, J(P, H$_B$) = 13.7, J(P, H$_{B'}$) = 13.7, J(H$_A$, H$_B$) = 3.5, J(H$_A$, H$_{B'}$) = 3.5. ^{k}J(P, H$_A$) = 16.8, J(P, H$_B$) = 12.8, J(H$_A$, H$_B$) = 3.6. ^{l}J(P, H$_A$) = 16.3, J(P, H$_B$) = 13.6, J(H$_A$, H$_B$) = 3.7.

Spectral Data and Structures. ^{1}H-NMR and IR data in Table I confirm the binuclear formulation of the complexes 1 and 2 (see, for example, the proton ratios in Table I). It is readily understood from the following observations in Table I that both cyano groups of a NC-A-CN are bound to iridium through the notrogen atoms: (1) infrared spectra of tDC1B and DCB complexes show only one ν(CN) which is significantly higher than that of the corresponding free ligand, (2) both ν(CN) of each cDC1B and tDC1B increase considerably upon coordination to Ir(CO)(PPh$_3$)$_2$$^+$, and (3) it is well-known that ν(CN) of a nitrile increases upon coordination through the nitrogen,[1,2,6] and decreases upon coordination through the π-system of the nitrile.[7,8] Electronic absorption spectra of 1 show three bands in the visible region (Table I) and are practically identical with those of the related four-coordinated iridium(I) complexes, [IrL(CO)(PPh$_3$)$_2$]ClO$_4$ (L = monocyanoolefin coordinated through the nitrogen atom).[1] No absorption bands are observed for 2. It is well-established that the related six-coordinated dihydridoiridium(III) complexes do not show any absorption bands in visible region.[2,9] Practically no changes in ν(C = C) of NC-A-CN are observed upon coordination (Table I), which also supports the coordination through the nitrogen atoms (but not through the π-system of the olefinic group). A broad and strong band at ca. 1100 cm^{-1} observed for all 1 and 2 is attributable to the tetrahedral (T$_d$) anion ClO$_4$$^-$,[4] which supports that 1 and 2 are 1:2 electrolytes as confirmed by the conductance measurements (see Experimental Section). In addition to their binuclearity, the presence of four hydridic ligands in each of the complexes 2a-2d can also be confirmed by their ^{1}H-NMR patterns in high fields. The hydride patterns for 2 are practically identical with those of [Ir(H)$_2$L(CO)(PPh$_3$)$_2$]-ClO$_4$ (3) (L = monocyanoolefin coordinated through the nitrogen atom), where two hydrides are cis to CO and the nitrogen atom of L, respectively.[2] Each complex of 2 has two sets of hydrides which appears at ca. -8 and -18 ppm, respectively (see Table I). It is apparent by comparing the data for 2 with those for 3[2] and the related compounds[10] that the signals at ca. -8 ppm observed for 2 (Table I) are due to the hydrides (H$_A$) trans to CO and those at ca. -18 ppm to the hydrides (H$_B$) trans to the nitrogen of NC-A-CN (see I). The two hydrides (H$_A$) trans to CO in each of 2 are magnetically equivalent to appear at the same chemical shift (see Table I). On the other hand, the two hydrides (H$_B$) trans to the nitrogen atoms show slightly different shielding for 2a (at -18.3 and -18.1 ppm) and 2b (at -18.2 and -18.0 ppm) where NC-A-CN are not symmetric (see Table I and Figure 1), whereas the two hydrides (H$_B$) show the same shielding for 2c (at -18.3 ppm) and 2d (at -18.4 ppm) with the symmetric NC-A-CN. Further detailed assignments of the two different H$_B$ (denoted as H$_B$ and H$_{B'}$ in Table 1) of 2a (or 2b) to the individual nitrogen atom (NCCH = CH- or NCCH$_2$CH$_2$-) remain

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Figure 1. ^{1}H-NMR spectra of $[(CO)(PPh_3)_2(H)_2Ir-NC-A-CN-Ir(H)_2-(PPh_3)_2(CO)]$ $(ClO_4)_2$ (NC-A-CN = (a) *trans*-NCCH = CHCH$_2$CH$_2$CN, (b) *trans*-NCCH$_2$CH = CHCH$_2$CN) in CDCl$_3$ at 80 MHz at 25°C under nitrogen. Chemical shifts are relative to Me$_4$Si.
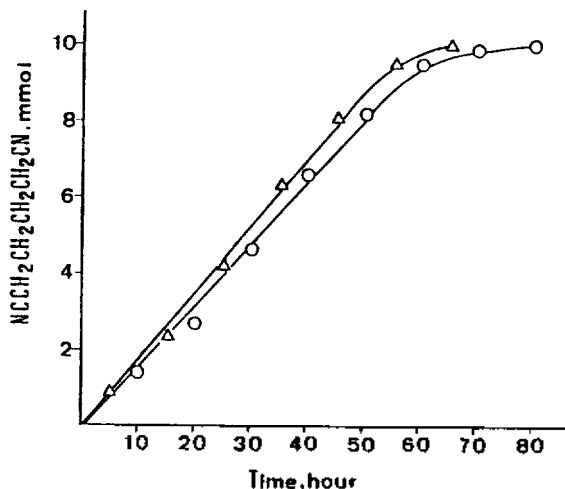
Figure 2. Hydrogenation of *cis*-NCCH = CHCH$_2$CH$_2$CN (10 mmol) with $[(CO)(PPh_3)_2(H)_2Ir$-*cis*-NCCH = CHCH$_2$CH$_2$CN-Ir(H)$_2$-$(PPh_3)_2(CO)]$ $(ClO_4)_2$ (**2a**) (0.5 mmol) (—○—○—) and *trans*-NCCH = CHCH$_2$CH$_2$CN (10 mmol) with $[(CO)(PPh_3)_2(H)_2Ir$-*trans*-NCCH = CHCH$_2$CH$_2$CN-Ir(H)$_2$(PPh$_3$)$_2$(CO)]$(ClO_4)_2$ (**2b**) (0.5 mmol) (—△—△—) in chlorobenzene (25 m*l*) at 100°C under H$_2$ (P$_{H_2}$ = 3 atm).

I
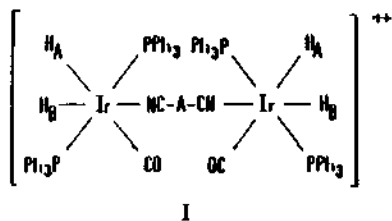
NC-A-CN: *cis*-NCCH = CHCH$_2$CH$_2$CN, *trans*-NCCH =
CHCH$_2$CH$_2$CN, *trans*-NCCH$_2$CH = CHCH$_2$CN,
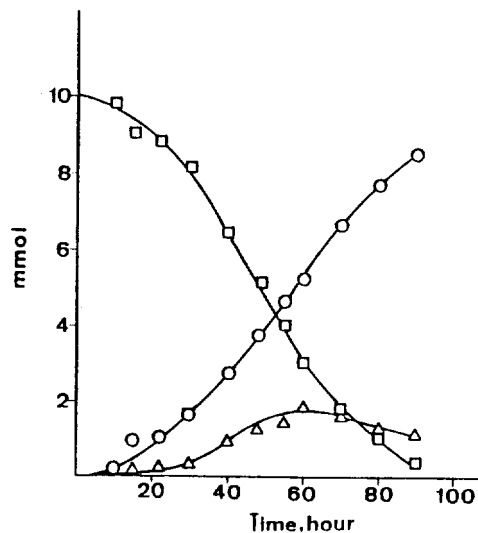NCCH$_2$CH$_2$CH$_2$CH$_2$CN

uncertain.

Catalytic Activities

It has been found that complexes **2a** and **2b** catalyze the
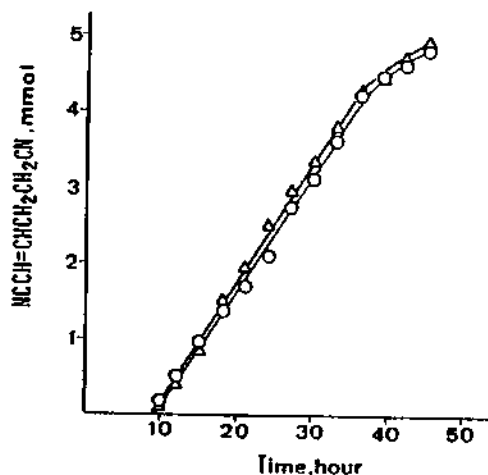
Figure 3. Isomerization of *trans*-NCCH$_2$CH = CHCH$_2$CN (10 mmol) to *cis*-NCCH = CHCH$_2$CH$_2$CN (—○—○—) and *trans*-NCCH = CHCH$_2$CH$_2$CN (—△—△—) with $[(CO)(PPh_3)_2(H)_2Ir$-*trans*-NCCH$_2$CH = CHCH$_2$CN-Ir(H)$_2$(PPh$_3$)$_2$(CO)]$(ClO_4)_2$ (**2c**) (0.05 mmol) in chlorobenzene (25 m*l*) at 100°C under nitrogen.

Figure 4. Hydrogenation and Isomerization of *trans*-NCCH$_2$CH = CHCH$_2$CN (10 mmol) with $[(CO)(PPh_3)_2(H)_2Ir$-*trans*-NCCH$_2$CH = CHCH$_2$CN-Ir(H)$_2$(PPh$_3$)$_2$(CO)]$(ClO_4)_2$ (**2c**) (0.05 mmol) in chlorobenzene (25 m*l*) at 100°C under H$_2$ (P$_{H_2}$ = 3 atm). —○—○—, NCCH$_2$CH$_2$CH$_2$CH$_2$CN; —△—△—, mixture (1:1) of *cis* and *trans*-NCCH = CHCH$_2$CH$_2$CN; —□—□—, *trans*-NCCH$_2$CH = CHCH$_2$CN.

hydrogenation of *c*DC1B and *t*DC1B, respectively to produce DCB (see Figure 2). The same results (as shown in Figure 2) have been obtained by employing **1a** and **1b** in place of **2a** and **2b**, which is readily understood since complexes **1a** and **1b** immediately react with H$_2$ to form **2a** and **2b** under the catalytic conditions. It has been also found that **2c** is catalytically active for the isomerization of *t*DC2B to *c*DC1B and *t*DC1B under nitrogen (see Figure 3). The isomerization of *t*DC2B to *c*DC1B and *t*DC1B is negligible (less than 1% for 50 hours) under the same experimental conditions in the absence of **2c**. The catalytic isomerization with **2c** in the absence of hydrogen has been in fact expected since it was already known that the isomerization of CH$_2$ = CHCH$_2$CN to *cis* and *trans*-CH$_3$CH = CHCN with $[Ir(H)_2(CH_3CH = CHCN)(CO)(PPh_3)_2]ClO_4$ occurs under N$_2$.[1] Figure 3 shows that

there is an induction period (*ca.* 8 hours) in the catalysis under N_2 while no such period of time has been observed in the catalysis under H_2 (see Figure 2). In the presence of hydrogen (H_2), complex **2c** catalyzes the isomerization of *t*DC2B to give a mixture of *c*DC1B and *t*DC1B, and hydrogenation of *t*DC2B to give DCB (Figure 4). Again, the same results (as shown in Figure 4) have been obtained by using **1c** in place of **2c** under H_2 (**1c** immediately reacts with H_2 to form **2c** under the catalytic conditions). The rate of DCB formation from *c*DC1B (or *t*DC1B) with **2a** (or **2b**) (Figure 2) seems to be significantly faster than that from *t*DC2B with **2c** (Figure 4). It is apparent in Figure 4 that DCB is formed by the hydrogenation of *c*DC1B and *t*DC1B which are produced by the isomerization of *t*DC2B although it is not clear whether DCB is also formed by the direct hydrogenation of *t*DC2B (without going through the isomerization).

Finally, it would be mentioned that the hydrogenation and isomerization of the dicyanoolefins (*t*DC2B, *c*DC1B, *t*DC1B) investigated in this study are significantly slower than those of the monocyanoolefins (*trans*-$CH_3CH = CHCN$, *cis*-$CH_3CH = CHCN$, $CH_2 = CHCH_2CN$) with $[IrL(CO)(PPh_3)_2]ClO_4$ (L = monocyanoolefin).[2]

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Synthetic beta-Lactam Antibiotics

I. Synthesis and Antibacterial Activity of 7-Amino-3-[1-(halo-substituted phenyl)-1H-tetrazole-5-yl]thiomethyl-3-cepheme-4-carboxylic acids

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The syntheses of mercaptotetrazoles and cephalothin analogs are described. Their in vitro poetency was established. The compounds exhibited high antibacterial activity against Gram-positive bacteria and moderate activity against Gram-negative bacteria.

Introduction

The cephalosporin antibiotics represent the most important class of drugs, against infectious diseases caused by bacteria. In recent years, several new cephalosporin antibiotics such as cefotaxime (1), ceftizoxime[1], and ceftazidime[2] with a broad spectrum of activity and increased activity against bacteria producing beta-lactamase have been developed[3]. Although these recently introduced cephalosporins are characterized by their excellent activity against a variety of Gram-positive and Gram-negative bacteria, they are relatively weak in anti-*Staphylococcal* activity as compared to older cephalosporins such as cephalothin (2) and cefazoline[4].