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Bidentate Isocyanides
1. Synthesis of Disocyanocyclohexanes and some of their Complexes

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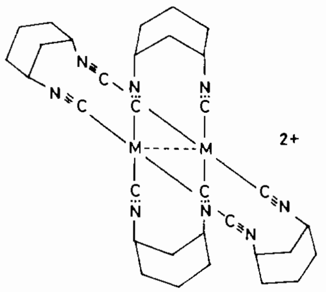
Chiral and achiral 1,2- or 1,3-diisocyanocyclohexane derivatives were prepared by three methods: dehydration of N,N′-diformylcyclohexanes by SO_2Cl or $POCl_3$, and a carbylamine reaction using a transfer reagent. Bidentate isocyanides reacted readily with Pd(cod)Cl_2, [Rh(cod)Cl]$_2$, [Ir(cod)Cl]$_2$, and di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)dipalladium to give the corresponding dinuclear complexes, respectively. These isocyanides were demonstrated to be useful ligands for the synthesis of dinuclear and polynuclear complexes.

Diisocyanides are useful ligands in the synthesis of dinuclear complexes which have direct metal–metal interactions. Recently, dinuclear isocyanide complexes of rhodium and iridium were found to have unusual spectroscopic and chemical properties, and much attention has been paid to the complexes [1–6]. However, there are only a few bidentate isocyanides. In this study we wish to report the synthesis of some new diisocyanocyclohexanes. Some of their metal complexes are also prepared.

The bidentate isocyanides were synthesized by three general methods: (1) dehydration of N,N′-diformamides by thionyl chloride, [7] (2) dehydration of N,N′-diformamides by phosphorus oxychloride, [8] and (3) a carbylamine reaction utilizing the phase transfer reagent, $(PhCH_2)Et_3NCl$ [9]. Yields and spectral data are listed in Table I.

meso-1,3-Diisocyanocyclohexane (*meso*-1,3-$C_8H_{10}N_2$) reacted with [Rh(cod)Cl]$_2$ at room temperature to give dark blue complex 1, [Rh$_2$(*meso*-1,3-$C_8H_{10}N_2$)$_4$](BPh$_4$)$_2$, followed by a methathesis with NaBPh$_4$. An analogous reaction with [Ir(cod)Cl]$_2$ gave dark blue [Ir$_2$(*meso*-1,3-$C_8H_{10}N_2$)$_4$]Cl$_2$ 2.



1 : M = Rh
2 : M = Ir

The blue color of these complexes is reminescent of a metal–metal interaction. The characteristic $1a_{2u}$–$2a_{1g}$ transition (as D_{4h}) due to a metal–metal interaction appears at 561 nm (ϵ/Rh$_2$ 8.6 × 10^3) for 1 and at 594 nm (ϵ/Ir$_2$ 5.5 × 10^3) for 2 in the electronic spectrum, respectively. We assume that 1 and 2 have a windmill type structure as proposed by Gray and coworkers [1]. Pd(cod)Cl_2 reacted with *meso*-1,2-diisocyanocyclohexane or *dl*-1,3-diisocyanocyclohexane to give very pale yellow crystals $Pd_2L_2Cl_4$ (3: L = *meso*-1,2-$C_8H_{10}N_2$; 4: L = *dl*-1,3-$C_8H_{10}N_2$) in quantitative yields. Compound 3 is soluble in CH_2Cl_2 but 4 is insoluble even in polar solvents such as CH_2Cl_2, pyridine and DMSO. 4 reacted readily with PPh_3 in CH_2Cl_2 at room temperature to give a soluble complex 5, Pd$_2$(*dl*-1,3-$C_8H_{10}N_2$)$_2$(PPh$_3$)$_2$Cl$_4$·½C_6H_6. The lowest transition in the

TABLE I. Preparation of Diisocyanocyclohexane.

Isocyanide	Method	Yield (%)	Bp(°)/torr (Mp (°C))	IR (KBr) ν_{NC} cm^{-1}
meso-1,2-Diisocyanocyclohexane	1	47	126–130/1 (44–47)	2136^a
(1R,2R)-Diisocyanocyclohexane	2	7	110–112/2	2142
(1S,2S)-Diisocyanocyclohexane	3	20	100–110/3	2142
meso-1,3-Diisocyanocyclohexane	1	34	126–127/1	2141
dl-1,3-Diisocyanocyclohexane	1	42	116–119/1	2134

^{a}Nujol.

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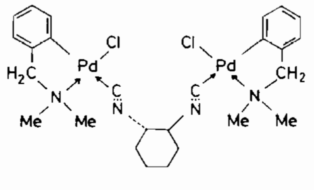
electronic spectra of 3 and 5 appeared at 314 nm (ϵ/Pd$_2$ 1700) and 340 nm (ϵ/Pd$_2$ 10700), respectively, showing the absence of a metal–metal interaction. The accurate stereochemistry of these complexes remains unknown. The reaction with (1R, 2R)-diisocyanocyclohexane proceeds with a cleavage of chloride bridges to give (1R,2R)-diisocyanocyclohexanedichloro-bis(N,N-dimethylbenzylamine-2C,N)-dipalladium(II) 6. The infrared spectrum shows a band due to a terminal isocyanide group at 2206 cm^{-1}.



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These studies demonstrate that diisocyanocyclohexanes prepared here coordinate readily to a variety of metal complexes and would be a useful candidate as ligands for preparation of dinuclear and polynuclear complexes.

Experimental

Infrared spectra and electronic spectra were recorded on Shimazu IR-27G spectrophotometer and Shimazu UV-180 spectrophotometer. Rotations were measured at 23 °C, the length of the tube being 10 dm. The molecular weight was measured in CH$_2$Cl$_2$ by a Mechrolab 301A vapor pressure osmometer. The calculated values of elemental analyses are omitted except those of the representative compounds in the case of a similar calculated value.

Preparation of Diformamides

meso-1,3-Diformylcyclohexane: A solution of *meso*-1,3-diaminocyclohexane (20 g, 0.26 mmol) [10] and ethyl formate (110 g, 1.5 mol) was heated at reflux for 4 h. The diformamide (34 g, 77%, M.p. 170–171 °C) was filtered and recrystallized from ethanol. *Anal.* Found: C, 56.38; H, 8.29; N, 16.53%. Calcd. for C$_8$H$_{14}$N$_2$O$_2$: C, 56.45; H, 8.29; N, 16.45%.

By using strictly analogous procedures, the following compounds were prepared. *dl*-1,3-Diformylcyclohexane (78%, M.p. 130–140 °C). *Anal.* Found: C, 56.41; H, 8.40; N, 16.50%. *meso*-1,2-Diformylcyclohexane (73%, M.p. 164–166 °C). Found: C, 56.47; H, 8.42; N, 16.48%.

Preparation of Isocyanides

Method 1

meso-1,3-Diisocyanocyclohexane: A mixture of *meso*-1,3-diformylcyclohexane (14.9 g, 0.088 mol) and DMF (270 ml) was charged in a three-necked round bottle under nitrogen atmosphere, and a solution of SOCl$_2$ (26.5 g, 0.22 mol) and DMF (70 ml) was added dropwise to the mixture at –50 °C. The temperature was allowed to rise at –35 °C. Then anhydrous Na$_2$CO$_3$ (60 g, 0.58 mol) was added to the mixture. After stirred for 7 h at room temperature, the mixture was diluted with ice-water, extracted with CH$_2$Cl$_2$, followed by washing with water and drying over anhydrous Na$_2$SO$_4$. Distillation under reduced pressure gave the colorless title compound (4.0 g)*. *Anal.* Found: C, 71.35; H, 7.59; N, 21.08%. Calcd. for C$_8$H$_{10}$N$_2$: C, 71.61; H, 7.51; N, 20.88%.

Other related compounds were also prepared according to procedures similar to those described above. *dl*-1,3-Diisocyanocyclohexane. *Anal.* Found: C, 70.95; H, 7.40; N, 21.21%. *meso*-1,2-Diisocyanocyclohexane. Found: C, 71.14; H, 7.46; H, 20.99%.

Method 2

(1R,2R)-Diisocyanocyclohexane: A solution of (1R,2R)-diformylcyclohexane (14.3 g, 0.08 mol) and pyridine (48 ml) in CH$_2$Cl$_2$ (100 ml) was charged in a three-necked round bottle. POCl$_3$ (18 g, 0.12 mol) was added to the mixture at 0 °C. The mixture was poured into ice-water, and the organic layer was separated, washed with water and dried over Na$_2$SO$_4$. The title compound was distilled under reduced pressure (0.82 g, $[\alpha]_D^{23}$ –142.6° (c, 0.904, CH$_3$CN)*. Found: C, 71.59; H, 7.50; N, 21.01%.

Method 3

(1S,2S)-Diisocyanocyclohexane: A mixture of (1S,2S)-diaminocyclohexane (22.5 g, 0.2 mol; $[\alpha]_D^{23}$ +16.3° (c, 2.39, H$_2$O)), 50% aqueous NaOH (50 ml), CHCl$_3$ (24 g, 0.2 mol), (PhCH$_2$)Et$_3$NCl (0.5 g) in CH$_2$Cl$_2$ (100 ml) was kept stirred for 4 h, and then diluted with water. The organic phase is separated, washed with water, and dried over Na$_2$SO$_4$. The title compound was distilled under reduced pressure*. $[\alpha]_D^{23}$ +109.5° (c, 0.753, CH$_2$Cl$_2$). Found: C, 70.50; H, 7.36; N, 21.45%.

Preparation of Complexes

*[Rh$_2$(*meso*-1,3-C$_8$H$_{10}$N$_2$)$_4$](BPh$_4$)$_2$ 1*

A solution of *meso*-1,3-diisocyanocyclohexane (0.76 g, 5.7 mmol) in CH$_2$Cl$_2$ (20 ml) was added to a solution of [Rh(cod)Cl]$_2$ (0.58 g, 1.2 mmol) in CH$_2$Cl$_2$ (30 ml). The chloride salt was converted to a tetraphenylborate salt by a methathesis with NaBPh$_4$ in MeOH**. M.p. > 300 °C (dec.). *Anal.*

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*In order to minimize resinification of the diisocyanide, distillation should be done as rapid as possible.

**The insoluble compound in MeOH may be a polymer, [Ir(C$_8$H$_{10}$N$_2$)$_2$Cl]$_n$.

Found: C, 69.04; H, 5.84; N, 8.09%. Calcd. for $C_{80}H_{80}N_8B_2Rh_2$: C, 69.58; H, 5.84; N, 8.11%. IR (KBr): 2166 cm^{-1} (N≡C).

$[Ir_2(\text{meso-}1,3\text{-}C_8H_{10}N_2)_4]Cl_2$ 2

A CH_2Cl_2 solution (15 ml) of *meso*-1,3-diisocyanocyclohexane (0.17 g, 1.3 mmol) was added to a solution of $[Ir(cod)Cl]_2$ (0.13 g, 0.23 mmol) in CH_2Cl_2 (40 ml). A dark blue precipitate (0.21 g, 89%) was filtered. The precipitate was washed with MeOH. 2a (0.13 g) [12]. M.p. > 300 °C. IR (KBr): 2168 cm^{-1} (N≡C). *Anal.* Found: C, 36.84; H, 4.47; N, 10.93%. Calcd. for $C_{32}H_{44}N_8O_2Cl_2Ir_2$: C, 36.39; H, 4.58; N, 10.61%. A mixture of CH_2Cl_2 and hexane (1:1) was added to a methanol solution to give blue precipitate 2b (0.08 g). M.p. > 300 °C. IR (KBr): 2167 cm^{-1} (N≡C). Found: C, 37.00; H, 4.33; N, 10.88%.

$Pd_2(\text{meso-}1,2\text{-}C_8H_{10}N_2)_2Cl_4$ 3

To a solution of $Pd(cod)_2Cl_2$ (0.12 g, 0.42 mmol) in CH_2Cl_2 (15 ml) was added a solution of *meso*-1,2-diisocyanocyclohexane (0.065 g, 0.43 mmol) in CH_2Cl_2 (5 ml) at room temperature. After 1 h, removal of the solvent gave the crude compound 3 (0.125 g, 96%). A crystallization of the residue from CH_2Cl_2–hexane gave very pale yellow compound 3 (0.065 g). M.p. 276–278 °C (dec.). IR (KBr): 2242 cm^{-1} (N≡C). M. wt.: 635 (623). *Anal.* Found: C, 31.25; H, 3.34; N, 8.86%. Calcd. for $C_{16}H_{20}N_4Cl_4Pd_2$: C, 30.90; H, 3.24; H, 9.01%. By an analogous procedure, $Pd_2(dl\text{-}1,3\text{-}C_8H_{10}N_2)_2Cl_4$ 4 (M.p. > 300 °C (dec.)) was obtained quantitatively. IR (KBr): 2236 cm^{-1} (N≡C). Found: C, 31.26; H, 3.49; N, 9.13%.

$(C_9H_{12}NClPd)_2((1R,2R)\text{-}1,2\text{-}C_8H_{10}N_2)$ 6

To a solution of di-μ-chlorobis(N,N-dimethylbenzylamine-2C,N)dipalladium (0.11 g, 0.2 mmol) in CH_2Cl_2 (15 ml) was added a solution of (1R, 2R)-diisocyanocyclohexane (0.028 g, 0.21 mmol) in CH_2Cl_2 (5 ml) at room temperature. After 1 h, white crystalline solid 6 (0.023 g) was obtained from CH_2Cl_2–hexane. Removal of the solvent from the mother liquor gave 6 (0.085 g). Yield: 79%. M.p. 244–246 °C (dec.). IR (KBr): 2206 cm^{-1} (N≡C). NMR ($CDCl_3$): δ 1.64 (c, C_6H_8), 2.81 (s, N–CH_3), 3.95 (s, N–CH_2), 4.28 (b, CH), 7.04 (aromatic protons) ppm. *Anal.* Found: C, 46.10; H, 5.00; N, 7.97%. Calcd. for $C_{26}H_{34}N_4Cl_2Pd_2$: C, 45.50; H, 4.99; N, 8.16%.

Reaction of 4 with PPh_3

A mixture of 4 (0.065 g, 0.10 mmol) and PPh_3 (0.11 g, 0.42 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature. After 1 h, benzene was added to the mixture. The yellow solid was filtered and washed with benzene (0.098 g, 77%, M.p. 214–220 °C (dec.)). IR (KBr): 2228 cm^{-1} (N≡C). *Anal.* Found: C, 56.77; H, 4.86; N, 4.69%. Calcd. for $C_{58}H_{56}N_4Cl_4P_2Pd_2$: C, 56.84; H, 4.61; N, 4.57%.

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