

(96:4, v/v) as the mobile phase, the chromatographic indices were as follows: $k'_{(-)}$, 2.39; $k'_{(+)}$, 7.26; α , 3.04.

The UV spectrum of **6** was recorded with a Cary Model 2290 spectrophotometer. The CD spectrum was recorded directly on the pure fractions from the TAC column, by a Jasco Model J-500 A spectropolarimeter. The recording of the spectrum (at 5 °C) and the racemization experiments were performed in a 0.1-cm water-jacketed cell attached to a circulation thermostat. The concentrations of the solutions were estimated from their UV spectra.

Racemization Experiments. The first-order rate constants (k_{rac}) for racemization of **6** were obtained by monitoring the intensity of the strong CD band at 222 nm as a function of time at 19.3, 34.5, and 50.0 °C. The free activation energies for ring inversion were calculated by the Eyring equation^{4b} with $k_{inv} = 0.5k_{rac}$.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council for a guest professorship

for I.A. and for financial support to J.S. Grants from the Knut and Alice Wallenberg Foundation to R.I. and J.S. are also gratefully acknowledged. We are also grateful to Dr. David Grace for recording the high-temperature NMR spectra and to Professor Johannes Dale for valuable discussions.

Supplementary Material Available: Figures showing the stereoscopic view of the syn form of **6** from MM2 calculations (Figure 5), projection along the C9-C9a bond in (*R,R*)-**6** (Figure 6), and projection along the C8-C7a bond in (*R,R*)-**6** (Figure 7), with ring E and the adjoining bridge removed for clarity, and tables of rate constants and free energy barriers for the (-)-**6** → (+)-**6** exchange (Table V), input data for the calculation of CD spectra (Table VI), hydrogen atom positional parameters (Table VII), thermal parameters and estimated standard deviations (Table VIII), and important bond lengths and bond angles (Table IX) (9 pages). Ordering information is given on any current masthead page.

Notes

Synthesis of Polyisocyanide Compounds via α -Metalation Reactions

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Received January 18, 1990

Introduction

α -Metalated isocyanides were first prepared over 20 years ago¹ and have since become useful reagents in organic synthesis.^{2a-c} Because the isocyanide group is readily hydrolyzed to the corresponding amine, metalated isocyanides provide a convenient means of nucleophilic introduction of α -aminoalkyl groups into organic molecules. For example, the reaction of metalated 2-isocyanopropionic ester with benzylbromide provides, following acid hydrolysis, α -methylphenylalanine.³ Alternatively, reactions of α -metalated isocyanides with various electrophilic reagents such as ketones, thioketones, Schiff bases, etc., permit an efficient route to the resulting heterocycles (oxazolines, thiazolines, imidazolines, etc.).

Our interest in isocyanides lies in the ability of the isocyanide group to form complexes with transition metals. In large part because of their ability to stabilize metal complexes in a variety of oxidation states, the organometallic chemistry of isocyanide ligands is extensive and well documented.^{4a-c} Of particular interest are binuclear complexes of rhodium and iridium in which the square planar metals are held in close proximity by bridging isocyanide groups. Since the first report of Rh_2 -(bridge)₄(BF₄)₂ in 1977 (bridge = 1,3-diisocyanopropane)

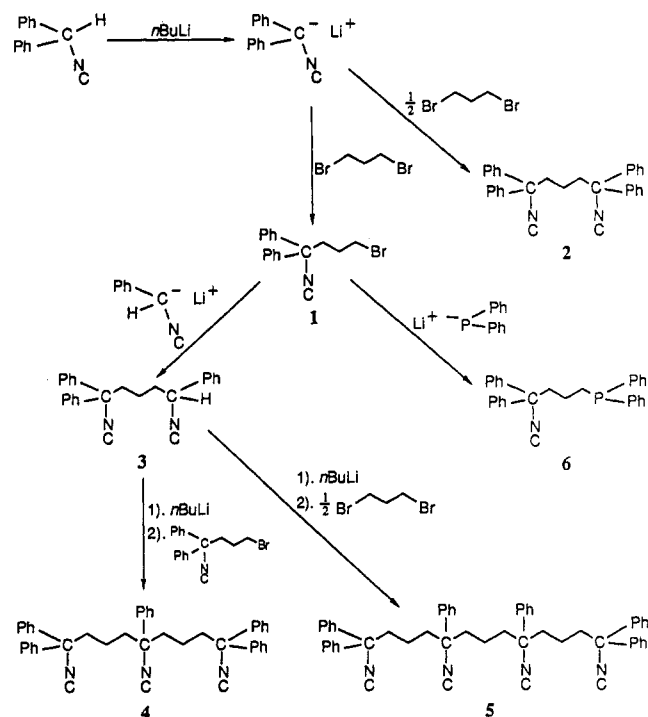


Figure 1. Synthetic reaction scheme for the preparation of compounds 1-6.

as a potential solar energy storage device,⁵ the electrochemical and photophysical properties of several d⁸-d⁸ isocyanide-bridged, binuclear complexes have been studied.⁶ In an attempt to extend this chemistry to longer

(1) Schollkopf, U.; Gerhart, R. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 805.

(2) For reviews, see: (a) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 789. (b) Schollkopf, U. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 339. (c) Schollkopf, U. *Pure Appl. Chem.* 1979, 51, 1347.

(3) Schollkopf, U.; Hoppe, D.; Jentsch, R. *Chem. Ber.* 1975, 108, 1580.

(4) See for example: (a) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* 1983, 22, 209. (b) Yamamoto, Y. *Coord. Chem. Rev.* 1980, 32, 193. (c) Treichel, P. M. *Adv. Organomet. Chem.* 1973, 11, 21.

(5) Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* 1977, 99, 5525.

(6) (a) Sigal, I. S.; Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* 1980, 102, 7252. (b) Mann, K. R.; Gray, H. B. *Adv. Chem. Ser.* 1979, 173, 225. (c) Gray, H. B.; Miskowski, V. M.; Midler, S. J.; Smith, T. P.; Maverick, A. W.; Buhr, J. D.; Gladfelter, W. L.; Sigal, I. S.; Mann, K. R. *Fundam. Res. Homogeneous Catal.* 1979, 3, 819. (d) Boyd, D. C.; Matsch, P. A.; Mixa, M. M.; Mann, K. R. *Inorg. Chem.* 1986, 25, 331. (e) Sykes, A.; Mann, K. R. *J. Am. Chem. Soc.* 1988, 110, 8252.

Table I. Physical Properties of Polyisocyanides Prepared via α -Metalation Reactions

compd	mp, °C	¹ H NMR (CDCl ₃)	$\nu(\text{CN})$, cm ⁻¹	anal.:	calc (found)	yield, ^a %
1	78-80	7.35 (m, 10 H), 3.34 (t, 2 H), 2.54 (t, 2 H), 1.98 (m, 2 H)	2135	C: H: N:	64.97 (65.00) 5.14 (5.16) 4.46 (4.57)	72
2	117	7.36 (m, 20 H), 2.47 (t, 4 H), 1.65 (p, 2 H)	2136	C: H: N:	87.29 (87.35) 6.14 (6.50) 6.57 (6.50)	67
3	b	7.32 (m, 15 H), 4.61 (t, 1 H), 2.41 (t, 2 H), 1.88 (m, 2 H), 1.63 (p, 2 H)	2136		c	63
4	50-56	7.26 (m, 25 H), 2.23 (m, 4 H), 1.89 (m, 4 H), 1.51 (m, 2 H), 1.29 (m, 2 H)	2136	C: H: N:	86.40 (86.44) 6.40 (6.60) 7.19 (6.96)	61
5	50 dec	7.25 (m, 30 H), 2.15, 1.86, 1.48, 1.27, 1.15, 0.93 (m, 18 H)	2135	C: H: N:	85.90 (85.96) 6.54 (6.41) 7.56 (7.60)	10
6	120	7.32 (m, 20 H), 2.52 (t, 2 H), 2.06 (m, 2 H), 1.60 (m, 2 H)	2140	C: H: N:	83.03 (82.97) 6.25 (6.17) 3.34 (3.14)	70

^a Corresponds to final step in reaction sequence. ^b Compound was isolated as a nondistillable oil. ^c We were unable to obtain a sample of this compound pure enough for an elemental analysis. However, it was used successfully in all subsequent reactions in slightly impure form.

chains of metals, as well as to heterobimetallic compounds, we have used α -metalated isocyanides to build potential ligands with two, three, and four isocyanide groups in a linear array (Figure 1). These compounds include 1,5-diisocyno-1,1,5,5-tetraphenylpentane; 1,5-diisocyno-1,1,5-triphenylpentane; 1,5,9-triisocyno-1,1,5,9,9-pentaphenylnonane; and 1,5,9,13-tetraisocyno-1,1,5,9,13,13-hexaphenyltridecane. Additionally, we were able to use this route to synthesize the first example of a bifunctional isocyanide-phosphine ligand ((4-isocyno-4,4-diphenylbutyl)diphenylphosphine).

Experimental Section

All reactions were carried out under a nitrogen atmosphere at -78 °C in THF freshly distilled from sodium benzophenone ketyl. Diphenylmethyl⁷ and benzyl⁸ isocyanides were prepared according to literature procedures; 2.5 M *n*-BuLi in hexane and 1,3-dibromopropane were purchased from Aldrich Chemical Co. Diphenylphosphine was obtained from Strem Chemicals. ¹H NMR spectra were recorded on an IBM Bruker 200-MHz spectrometer. IR spectra (CH₂Cl₂ solution) were taken on a Perkin-Elmer 1710 FT spectrophotometer. As a typical experimental procedure:

Synthesis of 1. Ten grams (0.052 mmol) of benzhydryl isocyanide in 75 mL of THF were cooled to -78 °C in a dry ice/acetone bath. With vigorous stirring, 20.8 mL of 2.5 M *n*-BuLi in hexane were slowly added, causing the solution to turn deep red. The red solution was transferred dropwise by means of an insulated cannula to a cold (-78 °C) solution of 20 mL (0.196 mol) of 1,3-dibromopropane in 40 mL of THF.⁹ The mixture was allowed to warm to room temperature overnight, at which time the solvent was stripped off under vacuum. Once dry, the isocyanide was dissolved in a small amount of CH₂Cl₂ and chromatographed down a short column of alumina to remove solid LiBr. The product, which initially appeared as a pale yellow oil, precipitated after several hours under high vacuum (10⁻⁶ Torr). The resulting solid was washed with cold pentane and then recrystallized from hot ethanol to yield 11 g of a white crystalline solid.

Results and Discussion

The general synthetic route to these compounds is outlined in Figure 1. With the exception of 2, the first step involves reacting lithiodiphenylmethyl isocyanide with an excess of 1,3-dibromopropane to yield compound 1. Once isolated, 1 is treated with the lithium salt of benzyliso-

cyanide to give 3. Compound 3 can then be deprotonated and reacted with either 1 equiv of 1 to yield 4, or 0.5 equiv of 1,3-dibromopropane to give 5. Ligand 2 is formed directly by the reaction of lithiodiphenylmethyl isocyanide with half an equivalent of 1,3-dibromopropane. Finally, the mixed isocyanide-phosphine compound, 6, is prepared by treating diphenylphosphine with *n*-BuLi followed by slow addition of 1.

All of the compounds, with the exception of 3, are white, crystalline solids and can be purified by recrystallization from ethanol; compound 3 was obtained as a nondistillable, sticky, pale yellow oil. Table I includes physical data for the compounds 1-6. With the exception of 6, all were air stable materials but were stored in the refrigerator to prevent polymerization. Our initial attempts to prepare the Rh(I) complexes of several of these compounds have been successful and will be reported elsewhere.¹⁰

Acknowledgment. We thank Johnson-Matthey, Inc. for a generous loan of rhodium trichloride.

(10) The formation of polynuclear complexes is indicated for the compounds based on characteristic color reactions with [Rh(1,5-cyclooctadiene)(μ -Cl)]₂.¹¹ This reagent is a very useful developer for thin-layer chromatographic separations of isocyanides because it produces colors which are characteristic of the formation of oligomeric Rh(I) compounds.¹² The wavelength of absorption of the Rh(I) complex is often indicative of the number of isocyanide groups in the ligand.

(11) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* 1957, 4735.

(12) Di Pierro, M. J. Ph.D. Thesis, University of Minnesota, 1984.

An Improved Synthesis of 2-Oxathianyl Ketones

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Received February 26, 1990

The bicyclic oxathiane 1 (Scheme I)¹ has been found to be a useful chiral auxiliary both by us^{2,3} and by others.⁴

(1) Eliel, E. L.; Lynch, J. E.; Kume, F.; Frye, S. V. *Org. Synth.* 1987, 65, 215.

(7) Isenring, H. P.; Hofheing, W.; *Synthesis* 1981, 1, 385.

(8) Malatesta, L. *Gazz. Chim. Ital.* 1947, 77, 238.

(9) The slow rate of addition of lithiodiphenylmethyl isocyanide and large excess of 1,3-dibromopropane were found necessary to prevent the formation of substantial amounts of compound 2.