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REACTIONS OF STEREOCHEMICALLY RIGID DIISOCYANIDES WITH MANGANESE CARBONYL DERIVATIVES

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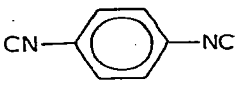
Summary

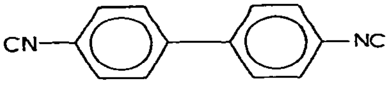
The reactions of $BrMn(CO)_5$ with the non-chelating stereochemically rigid bidentate ligands (L-L) 1,3-, and 1,4-diisocyanobenzene, 4,4′-diisocyanobiphenyl, and 4,4′-diisocyanodiphenylmethane afford well characterized complexes of the types $BrMn(CO)_4(L\text{-}L)$, $BrMn(CO)_3(L\text{-}L)_2$, and $[BrMn(CO)_4]_2(L\text{-}L)$. Similar reactions with $[RC_5H_4Mn(CO)_2NO]^+PF_6^-$ gave mixtures of oligomers of the type $[(RC_5H_4MnNO)_n(L\text{-}L)_{n+1}]^{n+}[PF_6^-]_n$.

Introduction

The coordination properties of monoisocyanides have been explored rather extensively during the past several decades [1]. By contrast, interest in the coordination properties of certain diisocyanides (e.g., 1,3-diisocyanopropane [2], 1,4-diisocyanobutane [3], 1,5-diisocyanopentane [3], etc.) began only recently with the discovery of $[Rh_2(CNCH_2CH_2CH_2NC)_4]^{2+}$ by Gray and coworkers [2]. This "windmill shaped" dinuclear rhodium complex is thought to be of particular significance for the development of "solar energy storage reactions" [4]. The above mentioned diisocyanides can be regarded as fluxional bidentate ligands in view of the low energy barrier of rotation associated with their polymethylene bridges. By comparison, diisocyanides [5] such as 1,4-diisocyanobenzene (A), 4,4′-diisocyanobiphenyl (B), 1,3-diisocyanobenzene



(A)



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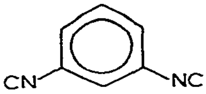

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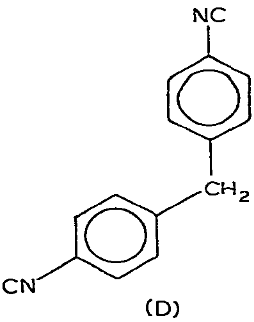

(D)

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(C), and 4,4′-diisocyanodiphenylmethane (D) can be regarded as representatives of a general class of non-chelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei. This class of bidentate ligands has been implicated in the formation of coordination polymers with most of the transition elements [6]. However, the chemistry of such ligands (A—D) is not confined to the formation of coordination polymers, and this aspect is exemplified by their reactions with $BrMn(CO)_5$ [I] and $[RC_5H_4Mn(CO)_2NO]^+PF_6^-$ [II; R = H, CH_3] which are described in the current study.

Results and discussion

The reactions of halo-manganese and rhenium pentacarbonyl with a variety of ligands have been extensively investigated by several research groups [7—11]. In the case of the reaction between I and PhNC, several substitution products of the type $BrMn(CO)_{5-n}(CNPh)_n$ [$n = 2$—5] were isolated and characterized [12]. The mono-substituted derivative ($n = 1$) was obtained by a different route, involving the cleavage of the bromo-bridged dimer $Mn_2(CO)_8Br_2$ with PhNC under mild thermal conditions.

In an attempt to ascertain the coordination properties of the aromatic diisocyanides A—D, their reactions with I under mild thermal conditions were inves-

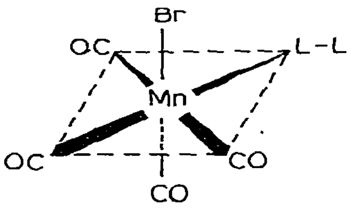
TABLE 1

DETAILS OF THE PREPARATION AND CHARACTERIZATION OF THE NEW MANGANESE COMPLEXES III, IV AND V

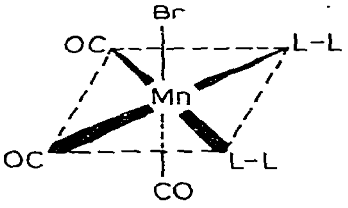
Molar amounts of reactants		Reaction time (h)	Product [a] type	Color	Yield (%)	Elemental composition (%) [b]		
$BrMn(CO)_5$	Starting ligand (L-L)					C	H	N
1	1 (A)	7	III	Yellow-orange	51	38.57 (38.43	1.15 1.08	8.03 7.47)
1	1 (B)	7	III	Orange	47	47.84 (47.92	1.90 1.79	6.42 6.21)
1	1 (C)	7	III	Orange	35	39.00 (38.43	1.32 1.08	7.85 7.47)
1	1 (D)	10	III	Yellow	75	48.95 (49.06	2.30 2.17	6.45 6.02)
1	2 (A)	7	IV	Light-yellow	30	47.95 (48.03	1.80 1.70	11.49 11.79)
1	2 (B)	10	IV	Yellow	95	59.02 (59.35	3.17 2.51	9.28 8.93)
1	2 (C)	10	IV	Light-yellow	68	48.61 (48.03	2.25 1.70	12.8 11.79)
1	2 (D)	12	IV	Light-yellow	45	60.30 (60.47	3.22 3.08	7.95 8.55)
2	1 (B)	36	V	Brown	18	38.02 (37.85	1.33 1.16	4.19 4.01)
2	1 (D)	36	V	Yellow	13	40.01 (38.70	1.55 1.42	3.80 3.93)

[a] Products from these reactions decompose gradually above 140°C. No sharp decomposition points were observed. [b] Calculated values are given in parentheses.

tigated. These reactions, which were carried out in boiling dichloromethane (b.p. 36°C), give three types of complexes depending on the molar ratio of the reactants and the duration of the reactions (Table 1). The exclusive formation of the monosubstituted mononuclear complexes III; L-L = A—D and disubstituted mononuclear complexes IV; L-L = A—D was achieved by employing the theoretically required molar ratio of reactants in these reactions. The products from these reactions are obtained in resonable to excellent yields (30—95%) after reaction times of 7—12 hours. Two monobridged dinuclear complexes of the type V; L-L = B, D were prepared in poor yields (10—18%) under similar conditions by utilizing the appropriate molar ratio of reactants and a long reaction time of 36 hours. Attempts to affect the exclusive formation of the analogous dinuclear complexes V; L-L = A, C by the above cited procedure were unsuccessful; these reactions led to mixtures of products which were difficult to separate. The nature of the new manganese complexes was established from elemental composition data (Table 1) and IR spectra. The IR spectra consist of a multitude of bands in the region 1900—2200 cm^{-1} which correspond to both carbonyl and isocyanide stretching frequencies. The highest frequency band in each spectrum, found at 2170 ± 10 cm^{-1}, corresponds most probably to a coordinated isocyanide; whereas, bands below 2070 cm^{-1} can be confidently assigned to terminal carbonyls. Rigorous assignment of bands above 2070 cm^{-1} is rather difficult, since this region may correspond to either free and/or coordinated diisocyanides and/or carbonyls.



(III ; L—L = A—D)



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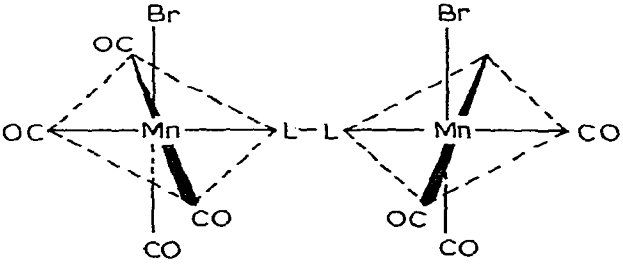
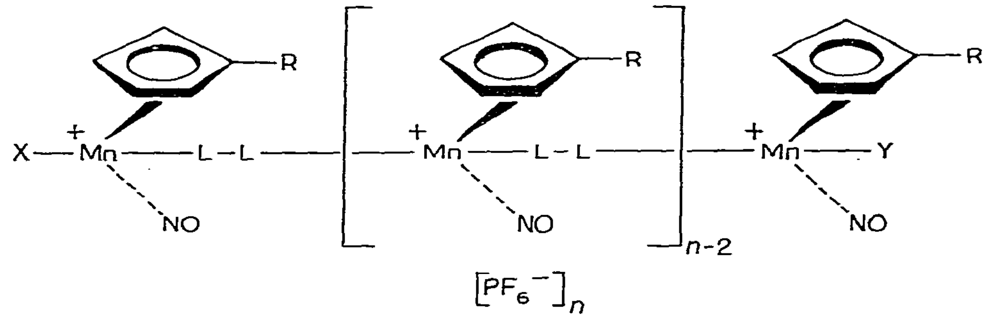


(V ; L—L = B, D)

The stereochemistry of the new complexes is straightforward, with the exception of IV, for which several structural isomers may be possible. The carbonyl *trans* to the bromide in I is expected to be the least susceptible towards substitution, and this could suggest the implication of equatorial carbonyls during the course of these reactions. The *cis* configuration in IV has been assigned on the basis of the work of Argelici, Basolo and Poe [13].

The results of this study exemplify the ability of non-chelating stereochemically rigid diisocyanides to function either as monodentate ligands or simple bridging ligands. Polymerization processes have not been encountered under the mild conditions and controlled ratio of reactants employed in these reactions. The formation of III; L-L = A—D contrasts with the failure to obtain the analogous phenyl isocyanide complex by a similar reaction. This difference is not entirely surprising, since the study of the reactions between I and PhNC was carried out in the presence of a relatively large excess of the isocyanide.

The reactions of the diisocyanides A—D with the cationic manganese complexes $[RC_5H_4Mn(CO)_2NO]^+PF_6^-$ (II; R = H, CH_3) were also examined during this study. Facile mono- and di-carbonyl substitution reactions [14,15] with these starting cationic complexes II were encountered with various σ-donor ligands such as phosphines, polyphosphines, and phosphites. The reaction of II; R = H and cyclohexyl isocyanide, carried out in acetone at ambient temperature for 2 minutes, was reported by Brunner and Schindler [15] to give the mono-substituted product $[C_5H_5Mn(CO)(NO)(CNC_6H_{11})]^+PF_6^-$ (VI) in 82% yield. On the basis of the foregoing, six different types of manganese complexes, which are either mononuclear (VII and VIII) and/or polynuclear (IX, X, XI and XII),



(VII ; X = CO , n = 1 , x = 1 (Mononuclear) ;

VIII ; X = L−L , n = 1 , x = 2 (Mononuclear) ;

IX ; X = Y = CO , n >L , $x = n/n-1$ (Polynuclear) ;

X ; X = CO , Y = L−L , n>1 , x = 1 (Polynuclear) ;

XI ; X = Y = L−L , n>1 , $x = n/n+1$ (Polynuclear) ;

XII ; X + Y = L−L , n>1 , x = 1 (Cyclic oligomer))

were considered plausible in the system under study. Distinction between such types of complex can be made by considering the expected differences in their IR and ^{1}H NMR spectra, as is done below.

The non-chelating stereochemically rigid diisocyanides A—D underwent facile reactions with the cationic complexes II; R = H, CH_3, in acetone at ambient temperature to afford yellow products with similar spectroscopic properties (Table 2). The IR spectra (region; 1700—2200 cm^{-1}) of these products show strong to very strong bands at 2185 ± 5, 2160 ± 5, and 1785 ± 5 cm^{-1}. In addition, a medium to very weak band is also found in the spectra at 2077 ±

7 cm^{-1}. The ^{1}H NMR spectra of these products, taken in acetone-d_6 solution, show low-field resonances centered at (τ) 2.40 ± 0.28 and 4.22 ± 0.15 due to the aromatic diisocyanide and cyclopentadienyl protons, respectively. Integration of these resonances, and the interpretation of the data obtained in terms of cyclopentadienyl to diisocyanide ligands ratio (x) indicates a range of 0.66 to 0.95 ($\bar{x}$ = 0.78; see Table 2). From this information it appears that the number of bridging ligands (L-L) in the products is invariably greater than that of the $RC_5H_4Mn(NO)$-containing units. In the absence of satisfactory elemental composition data, attempts were made to establish the nature of these products from their spectra. Elemental composition data gathered on these products were inconsistent with any of the plausible alternatives represented by VII—XII.

In the spectra under review, the cyclopentadienyl protons resonate on average at a slightly higher field than was reported [15] for the cyclohexyl isocyanide complex VI (τ, 4.12). The direction of this shift might suggest the presence of two terminally coordinated isocyanide groups per manganese site. This interpretation is consistent with the up-field shift observed on changing from II; R = H to VI. Such a structural arrangement implies an approximate C_S symmetry at the manganese site, a situation which requires the presence of two IR active stretching [ν(NC)] modes [A' and A''], and the two high frequency bands found in the spectra of the products, Table 2, appear in the region characteristic of terminally coordinated isocyanides. Circumstantial evidence in support of this assignment is also derived from the comparison between the

TABLE 2

MOLAR RATIOS OF REACTANTS USED IN THE PREPARATIONS OF XI, AND RELEVANT SPECTROSCOPIC DATA FOR THE NEW COMPLEXES

Reactants (molar amounts)		Infrared (cm^{-1}) [a]			^{1}H NMR (τ) [b]		
Starting complex	Starting ligand (L-L)	ν(NC)	ν(NC)	ν(NO)	Aromatic protons		
					RC_5H_4	L-L	x [c]
II; R = H(1)	A (1.5)	2185vs 2165vs	2080w	1785s	4.14s	2.19m	0.72
II; R = CH_3(1)	A (1.4)	2180(vs) 2158vs	2078w	1785s	4.08m	2.12m	0.69
II; R = H(1)	B (1.4)	2190vs 2162vs	2075w	1790vs	4.13s	2.14m	0.79
II; R = H(1)	B (1.3)	2185vs 2160vs	2075m	1785s	4.15m	2.12m	0.66
II; R = H(1)	C (1.3)	2180vs 2155vs	2072vw	1783vs	4.25s	2.22m	0.96
II; R = CH_3(1)	C (1.2)	2190s 2160vs	2080vw	1785vs	4.30m	2.23m	0.94
II; R = CH_3(1)	D(1.3)	2185vs 2163vs	2084m	1782s	4.37m	2.68m	0.71

[a] IR spectra were taken in Nujol. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] ^{1}H NMR spectra were obtained in acetone-d_6, using TMS as calibrant. Abbreviations: s, singlet; m, multiplet. [c] The term x represents the cyclopentadienyl to diisocyanide ligands ratio in the complexes. These terms were calculated from the integration data by taking into account the number of protons per ligand. On the basis of these data, the mean term is x = 0.78 [$\sigma(n-1)$ = 0.12].

nitrosyl stretching frequencies [ν(NO)] in the spectra of II; R = H (1845 cm^{-1}), VI (1815 cm^{-1}) and the products under review (1785 ± 5 cm^{-1}). The direction and magnitude of the observed shift supports the assignment of two terminally coordinated isocyanide groups to each manganese site.

Further distinction between complexes types VII—XII can be made with the aid of the ligand ratio term x (Table 2). A cyclopentadienyl to diisocyanide ligand ratio of $x < 1$, when considered in the context of the IR spectral properties, seems to suggest the polynuclear system XI as the most resonable structure for the new complexes. The theoretical ligand ratio term $x = n/n + 1$ [e.g., $x(n)$ = 0.66(2), 0.75(3), 0.80(4), 0.83(5), 0.86(6), ..., 1(∞)] also provides a measure of the degree of oligomerization. The mean experimental value of $\bar{x}$ = 0.78 may suggest the preferred formation of trinuclear oligomers type XI; n = 3; for which the theoretical term is x = 0.75. Nevertheless, both specific x terms and their spread imply the formation of mixtures of either low [e.g., XI; L-L = A, B, D] or high [e.g., XI; L-L = C] oligomers. The formation of mixtures, rather than pure products, may explain the difficulties encountered in the interpretation of the elemental composition data.

In the examination of the IR spectra, attention must also be given to the origin of the band found at 2077 ± 7 cm^{-1}, Table 2. Though in the region of terminal carbonyls, the assignment of this band to carbonyl-containing complexes and/or impurities (e.g., II, VII, IX and X) can be ruled out because of the absence of the corresponding nitrosyl frequencies at $\nu(NO) \geqslant 1810$ cm^{-1}. The assignment of these bands to uncoordinated isocyanide groups appears to be consistent with their relatively low intensities, which is uncommon for carbonyl frequencies. It should, however, be recognized that these bands appear at a lower frequencies than those of the free ligands (2100—2140 cm^{-1}) [5]. In aromatic diisocyanides which are coordinated at only one end, the transfer of electronic effects may conceivably take place via an inductive and/or resonance mechanism. Flow of electron density in the direction of the coordinated isocyanide, where there is an extensive bonding interaction, could explain the lowering of the frequency of the free diisocyanide group in the complexes. The ratio of terminal versus bridging diisocyanides in XI, given by the expression $2/n - 2$, determines the relative intensity of the free isocyanide band. Noteworthy in this regard, are the very weak bands found in the spectra of the products obtained from the reactions of II; R = H, CH_3 and C, which also show a high ligand ratio term x; both parameters imply the presence of extended oligomers.

Experimental

The starting materials $BrMn(CO)_5$ [16], $[RC_5H_4Mn(CO)_2NO]^+PF_6^-$ (R = H, CH_3) [14,15], and diisocyanides [5] A—D, were prepared by known procedures. The IR spectra of the new complexes were recorded on a Perkin-Elmer 237 grating infrared spectrometer, calibrated by use of a polystyrene film. The ^1H NMR spectra of the new complexes in acetone-d_6 were recorded on a Bruker HFX-10 spectrometer.

Experiments were performed under an atmosphere of N_2 or Ar.

Bromomanganese carbonyl derivatives III, IV and V

Bromomanganese pentacarbonyl (0.27 g; 1.0 mmol) and the appropriate amount of the diisocyanide (A—D) were refluxed in dichloromethane (~50 ml). The exact molar ratio of reactants, reaction periods, yields, and elemental composition data, are furnished in Table 1. Analytically pure samples of these complexes were obtained by recrystallization from dichloromethane/hexane mixtures. The IR spectra (in cm^{-1}) of the new complexes, in the region 2200—1700 cm^{-1}, are given below.

Complexes type $BrMn(CO)_4(L\text{-}L)$ [III; L-L = A—D]

A (in CH_2Cl_2): 2170m; 2138s; 2098w; 2040vs; 2005m; 1935m. B (in CH_2Cl_2): 2175m; 2145s; 2100w; 2042vs; 2002s; 1930m. C (in CH_2Cl_2): 2170(sh); 2138s; 2100w; 2042vs; 2015vs; 1940s. D (in CH_2Cl_2): 2178m; 2150s; 2120(sh); 2045vs; 2001s; 1925s.

Complexes type $BrMn(CO)_3(L\text{-}L)_2$ [IV; L-L = A—D]

A (in CH_2Cl_2): 2170w; 2142w; 2095(sh); 2052vs; 2002m. B (in CH_2Cl_2): 2175w; 2140m; 2120s; 2040vs; 2001s; 1910m. C (in Nujol): 2165m; 2070vs; 2050vs; 2020s; 1985s; 1955m. D (in Nujol): 2170m; 2140m; 2110(s); 2080w; 2022(vs); 1962s.

Complexes type $[BrMn(CO)_4]_2(L\text{-}L)$ [V; L-L = B and D]

B (in Nujol): 2180s; 2100vs; 2025vs; 1930vs. D (in Nujol): 2165w; 2095w; 2060vs; 2022vs; 2010(sh); 1970s.

Cationic cyclopentadienylmanganese nitrosyl derivatives XI

The starting dicarbonylnitrosylcyclopentadienylmanganese complexes II; R = H, CH_3 (1.5 mmol scale) and the appropriate amount of the diisocyanide (A—D), see Table 2, were stirred in dry acetone (~60 ml) at ambient temperature for 4 hours. The solvent was removed, and unchanged ligand removed by extraction with benzene. The products of these reactions were recrystallized from either acetone or dichloromethane by addition of benzene or hexane, respectively. Selected spectroscopic data of these complexes are listed in Table 2, which also gives additional ^1H NMR data. Methyl resonances in XI; R = CH_3 were observed in the range (τ) 7.7—8.0, but their rigorous assignment in most cases was made difficult because at the nearby solvent bands. The methylene resonance in the spectrum of XI; L-L = D appears at τ 6.08.

Acknowledgements

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