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(17) ν(CO) (hexane): 2101 (m), 2054 (vs), 2047 (vs), 2038 (s), 2017 (m), 1988 (m), 1985 (m) cm^{-1}.
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An Example of *Pseudo* Five-Coordination in Copper(II) Complexes

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A series of potential pentadentate *bicyclic* macrocyclic ligands has been prepared by the nucleophilic addition of various dialkoxides to the copper(II) complex of tetrabenzo[*b,f,j,h*][1,5,9,13]tetraazacyclohexadecine (TAAB). The resulting complexes can be classified as pseudo square pyramidal with potential N_4S, N_4N', and N_4O donor sets with S, N′, and O occupying the axial coordination position. The complexes are all monomeric exhibiting characteristic magnetic moments for an $S = {}^1/_2$ system in the solid state. The optical spectra, as well as the X-band ESR spectra of the five donor atom macrocyclic Cu(II) complexes, are essentially identical while Q-band ESR data indicate a very slight variation in symmetry among the series. The spectroscopic differences between $Cu(TAAB)^{2+}$, a nonbridged four-coordinate $Cu(TAAB)(OCH_3)_2$ compound, a bridged four-coordinate $Cu(TAAB)[O(CH_2)_5O]$ compound, and the five-coordinate series $Cu(TAAB)[O(CH_2)_2X(CH_2)_2O]$ (X = S, NCH_3, O) compounds are discussed in terms of both a "cage effect" and the potential effect of the axial donor atom.

Introduction

Our interest in the evolution of small-molecule copper(II) systems capable of duplicating some of the aspects of protein metal chemistry has prompted our investigation of a large number of copper(II) complexes of various stereoelectronic environments.[1] Quite often our motivation has led to some very intriguing coordination chemistry, even though not always lending insight toward the metalloenzyme function. We report one such system here.

For various reasons, we recently considered the possibility of a five-coordinate copper(II) site to explain the redox stability and selective anion binding properties of the metal site in the metalloenzyme galactose oxidase.[1a,b] Copper(II) complexes with pentadentate ligands have been of considerable recent interest.[2–8] The requirements of our model system study included a pentadentate ligand which would clearly *impose* a five-coordinate environment for copper(II). Of the pentadentate ligands reportedly coordinated to copper(II), the only ones which incorporated the salient features desired were the "cagelike" compounds previously prepared by Busch and co-workers.[7,8] The other pentadentate systems coordinated to copper(II) were linear ligands where considerable doubt existed regarding the behavior of coordination of the ligand during the subsequent chemical studies we had planned.[2–6]

The bicyclic, "cagelike", pentadentate ligands of Busch and co-workers[7,8] were prepared by the nucleophilic addition of dialkoxides to $Cu(TAAB)^{2+}$ (Figure 1a), to produce a complex of copper(II) in which the metal atom was in close proximity of either an N_4S or N_4N' donor set (Figure 1b). By modifying this earlier synthetic approach we have been able to extend the series of cagelike complexes to include donor sets of N_4X, where X = S, O, $N(CH_3)$, and the special case where a CH_2 group was X. The more extended series allowed a closer evaluation of the coordination properties of the fifth, central donor atom, an understanding we needed prior to our evaluation of these systems as chemical models for copper(II) in proteins. We report now the synthetic modification we employed and the subsequent characterization of these compounds.

Experimental Section

Materials. $Cu(TAAB)(NO_3)_2$ was prepared by the method of Busch and co-workers.[9] All other chemicals and solvents were commercially obtained, were of reagent grade, and were used without further purification except for the solvents tetrahydrofuran and methylene chloride. Tetrahydrofuran was dried by distillation from Na/K alloy and benzophenone in an argon atmosphere. Methylene chloride was dried by distillation from $CaCl_2$ in an argon atmosphere.

Preparation of Dialkoxide. $HOCH_2CH_2XCH_2CH_2OH$ (X = S, O, $N(CH_3)$, CH_2) was mixed with an excess of metallic sodium in dried tetrahydrofuran under an argon atmosphere. The reaction mixture was stirred for approximately 48 h or until the reaction appeared complete as evidenced by no further H_2 evolution. The excess sodium was removed and the corresponding disodium dialkoxide filtered as a white precipitate and stored under argon.

Preparation of the Bridged Copper Complexes. This procedure represents a substantial modification of that reported by Busch and co-workers.[7,8] The synthesis was similar for all of the bridged

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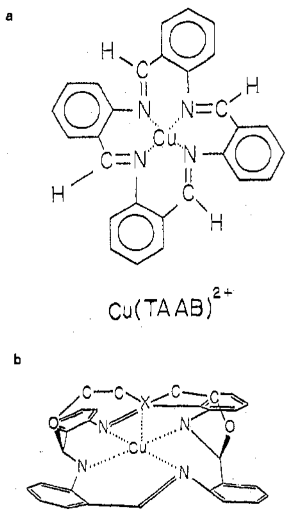


Figure 1. (a) $Cu(TAAB)^{2+}$ ion; (b) cage complex.

complexes and a general description is presented. $Cu(TAAB)(NO_3)_2$ and the appropriate disodium dialkoxide $(NaOCH_2CH_2)_2X$ (X = S, O, $N(CH_3)$, CH_2) were mixed in a 1:1 molar ratio in dried methylene chloride. Typical volumes of solvent employed were approximately 50 mL of CH_2Cl_2/g of starting $Cu(TAAB)(NO_3)_2$. An argon atmosphere was maintained throughout reagent addition and reaction. The reaction mixture was stirred at room temperature for 24 h, during which time the reaction mixture gradually changed from the initial murky green to the deep brown color characteristic of all of the bridged products. The reaction mixture was filtered to remove unreacted starting materials. (It was not necessary to carry out this step or subsequent steps under an inert atmosphere, since it is only the starting disodium dialkoxide which must be protected from hydrolysis.) Petroleum ether (boiling range 30–60 °C) was then added dropwise to the deep brown filtrate until the first signs of precipitation appeared. This bright blue impurity was removed by filtation. The dropwise addition of petroleum ether was continued until a red-brown precipitate began to form. (Five or six filtrations were necessary to reach this point.) Thin-layer chromatography of the filtrate ensured no further blue impurity was present (eluent—75:25 benzene–methanol). The filtrate was then evaporated to dryness. The remaining dark brown solid residue was dissolved in a minimum volume of CH_2Cl_2, and insoluble materials were filtered out. Petroleum ether was again added dropwise to the point of incipient precipitation. Dark brown microcrystalline products were collected upon slow evaporation of solvent. The solids were dried in vacuo at 80 °C for 16 h. Thin-layer chromatography of the dried products showed a trace amount of red impurity to be present. Separation by chromatography proved impossible because prolonged exposure of the compounds with silica and alumina columns resulted in decomposition. Yields in each case were around 20%. Anal. Calcd for $Cu(TAAB)(NO_3)_2$, $C_{28}H_{20}N_6O_6Cu$: C, 56.05; H, 3.36; N, 14.01. Found: C, 56.06; H, 3.46; N, 13.98. Calcd for $Cu(TAAB)[S(CH_2CH_2O)_2]$, $C_{32}H_{28}N_4O_2SCu$: C, 64.47; H, 4.73; S, 5.38. Found: C, 64.21; H, 4.85; S, 5.26. Calcd for $Cu(TAAB)[(CH_3)N(CH_2CH_2O)_2]$, $C_{33}H_{31}N_5O_2Cu$: C, 66.82; H, 5.27; N, 11.81. Found: C, 65.26; H, 5.63; N, 11.28. Calcd for $Cu(TAAB)[O(CH_2CH_2O)_2]$, $C_{32}H_{28}N_4O_3$: C, 66.25; H, 4.86; N, 9.66. Found: C, 65.59; H, 5.24; N, 9.15. Calcd for $Cu(TAAB)[O(CH_2)_5O]$, $C_{33}H_{30}N_4O_2$: C, 68.55; H, 5.23; N, 9.69. Found: C, 67.57; H, 5.40; N, 9.50.

Elemental analyses, obtained from Galbraith Laboratories, Knoxville, Tenn., are included here to indicate sample purity.

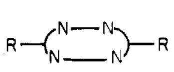
Preparation of $Cu(TAAB)(OCH_3)_2$. The method of preparing and purifying this compound was identical with that described by Busch and co-workers.[7] A satisfactory elemental analysis of this compound was obtained.

Spectroscopic Measurements. X-band and Q-band (35-GHz) ESR spectra were obtained as before.[1,10] Spectra were taken as glasses at 120 K by employing a Varian variable-temperature control apparatus with liquid nitrogen as the coolant. Optical spectra were determined at room temperature with a Cary 14 spectrometer both in the solid state as Nujol mulls and in solution in two solvents of different coordinating strengths. Infrared spectra were determined with a Perkin-Elmer 467 spectrometer as KBr disks.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at 27 °C by using the Guoy method. Pascal's constants were used to correct the measurements for diamagnetic contributions of the ligands and core electrons of the metal.[11]

Results and Discussion

We have prepared three classes of derivatives of the square-planar $Cu(TAAB)^{2+}$ complex. These can be pictured as (I) a substituted TAAB ligand, (II) a bridged TAAB ligand,



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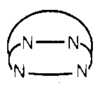

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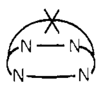

III

and (III) a bridged TAAB ligand with a donor atom in a potential coordinating position. The reaction scheme employed is represented by eq 1 and 2. This method appears more

$$HOCH_2CH_2XCH_2CH_2OH + \text{excess Na} \xrightarrow[\text{THF}]{\text{dry}} (NaOCH_2CH_2)_2X \quad (1)$$

$$Cu(TAAB)(NO_3)_2 + (NaOCH_2CH_2)_2X \xrightarrow[CH_2Cl_2]{\text{dry}} \text{bridged compound} \quad (2)$$

$$X = S,\ O,\ N(CH_3),\ CH_2$$

certain of resulting in a bridged species than the previously reported method.[7,8] This is especially true in view of the earlier workers failure to form a bridged compound upon reaction of $Ni(TAAB)^{2+}$ with 1,5-pentanediol. They obtained, instead, the addition of two nucleophiles to produce the product $Ni(TAAB)[O(CH_2)_5OH]_2$. The major disadvantage of our method is that the reactivity of the four azomethine bonds of $Cu(TAAB)^{2+}$ toward nucleophilic addition, coupled with the difunctional character of the dialkoxides, resulted in several side reactions including possible polymerization products. The choice of CH_2Cl_2 as the reaction solvent, a solvent in which the starting materials are only sparingly soluble, was based on keeping possible polymerization to a minimum.

The infrared spectra of all of the bridged compounds and the analogous unbridged $Cu(TAAB)(OCH_3)_2$ were very similar. The azomethine stretching absorption appeared at 1568 cm^{-1} for unreacted $Cu(TAAB)(NO_3)_2$. For the bridged species and the methoxide complex, this band was repositioned at 1527 cm^{-1} and can be assigned to the stretching vibration of the two remaining azomethine bonds.[3] The remainder of the spectrum for each compound contained the bands characteristic of the corresponding bridging group and was taken as further evidence that a reaction had occurred.

Electronic absorption spectra were recorded between 7000 and 50 000 cm^{-1} in two solvents (CH_2Cl_2 and DMF) and in the solid state as Nujol mulls. The detailed spectral features of these new compounds, as well as that of $Cu(TAAB)(NO_3)_2$, in solution and as solids are listed in Table I. Somewhat surprisingly, all of the complexes prepared here have quite similar optical spectra. Each spectrum contains a strong ligand field band near 121 000 cm^{-1} with extinction coefficients ranging from 420 to 820 M^{-1} cm^{-1}. In contrast, the unsubstituted $Cu(TAAB)(NO_3)_2$ complex contains only a weak feature at 15 200 cm^{-1}. In the higher energy regions, each of the new complexes shows an intense band near 21 000 cm^{-1} with extinction coefficients ranging between 12 000 and 20 000 M^{-1} cm^{-1}. In this same region the spectrum of $Cu(TAAB)(NO_3)_2$ shows only a strong band near 23 000 cm^{-1}. Thus, in total, what is observed is a shift to lower energies and an intensification of the corresponding absorption bands for the new complexes compared to those of the parent compound. The shift to lower energies is representative of a change in the

Table I. Electronic Absorption

complex	solvent	absorption maxima, 10^3 cm^{-1} [a]				
		(A) Four-Coordinate Complexes				
Cu(TAAB)$(NO_3)_2$	Nujol	15.2 wk[c]	23.3			
Cu(TAAB)$(OCH_3)_2$	Nujol	~11.8	16.4 wf	21.5	27.4 wf	
	DMF	11.7 (740)		21.9 (15 000)	27.0 wf	
	CH_2Cl_2	11.8 (580)	17.5 wf	21.8 (14 000)	26.8 sh	38.6 (46 000)[b]
Cu(TAAB)$[O(CH_2)_5O]$	Nujol	~11.7	16.4 wf	21.6	27.2 sh	
	DMF	11.6 (700)		21.9 (16 000)	27.4 sh	
	CH_2Cl_2	11.6 (820)	16.8 wf	21.8 (20 000)	27.0 sh	37.6 (54 000)
		(B) Five-Coordinate Complexes				
Cu(TAAB)$[(CH_3)N(CH_2CH_2O)_2]$	Nujol	~11.7	16.3 wf	21.6	26.9 wf	
	DMF	11.6 (450)		21.9 (13 000)	26.6 (~6000)	
	CH_2Cl_2	11.7 (420)		21.8 (12 000)	27.0 (~7000)	39.2 (45 000)[b]
Cu(TAAB)$[O(CH_2CH_2O)_2]$	Nujol	~12.0	16.7 wf	21.5	27.2 wf	
	DMF	11.4 (650)		21.8 (16 000)	27.0 (~6000)	
	CH_2Cl_2	11.5 (650)	17.4 wf	21.9 (16 000)	27.2 (~6000)	37.2 (63 000)
Cu(TAAB)$[S(CH_2CH_2O)_2]$	Nujol	~12.3	16.9 wf	21.6 (asym)	27.2 wf	
	DMF	12.0 (710)		22.0 (17 000)	26.7 (~6000)	
	CH_2Cl_2	12.1 (580)	16.9 wf	21.9 (15 000)	26.7 (~5000)	38.6 (49 000)

[a] Number in parentheses is molar extinction coefficient in units of M^{-1} cm^{-1}. [b] Near solvent cutoff. [c] wf = weak future, sh = shoulder, wk = weak band.

Table II. Spin-Hamiltonian Parameters[a] and Solid-State Magnetic Moments

	A_{zz},[b] G	g_{zz}	g_{yy}	g_{xx}	μ_{eff}, μ_B
Cu(TAAB)$(NO_3)_2$	181 ± 1	2.185	2.012	2.012	
Cu(TAAB)$(OCH_3)_2$	159 ± 1	2.173	2.049	2.032	
Cu(TAAB)$[O(CH_2)_5O]$	154 ± 1	2.171	2.050	2.030	2.13
Cu(TAAB)-$[O(CH_2CH_2O)_2]$	147 ± 1	2.177	2.053	2.036	1.97
Cu(TAAB)-$[S(CH_2CH_2O)_2]$	147 ± 1	2.178	2.047	2.037	2.30
Cu(TAAB)-$[(CH_3)N(CH_2CH_2O)_2]$	147 ± 1	2.176	2.047	2.035	2.14

[a] Data obtained at 35.0 GHz. [b] While these A_{zz} value differences are small, the accuracy of the measurement at 35.0 GHz is quite good since no overlap of parallel and perpendicular components exists.

ligand field strength of the equatorial ligand atoms, since all examples (I, II, III) show similiar features. The differences in the molar absorptivities are related to the difference in the in-plane symmetry, as judged by the rhombic splitting of g_{xx} and g_{yy} (see below). The largest molar absorptivity corresponds to the largest difference between g_{xx} and g_{yy}. The similarity of the solid-state and solution data also indicates that the same molecular species exists in both cases. This similarity, along with the solid-state magnetic moments (Table I) and solution ESR spectra, confirms the absence of any dimerization.

The two extreme geometries formed from five-coordination are trigonal bipyramidal and square pyramidal. Ligand field absorptions of Cu(II) complexes with pentadentate ligands, positioned between 12 000 and 13 000 cm^{-1}, have been stated as an indication of square-pyramidal geometry, while absorptions at lower energies, 10 000–11 000 cm^{-1}, have been indicated as arising from trigonal-bipyramidal geometry (see, for example, ref 4). Using this basis, we would be tempted to assign near-square-pyramidal geometry to the complexes prepared here. However, we have prepared four-coordinate complexes of Cu(TAAB)$(OCH_3)_2$ and Cu(TAAB)$[O(CH_2)_5O]$ and have found their ligand field absorptions to be nearly identical with those of the "five-coordinate" series Cu(TAAB)$[(CH_2CH_2O)_2]$ (X = O, S, N(CH_3)). Clearly, these four-coordinate complexes can not be square pyramidal, and since their ligand field absorptions are near in energy and molar absorptivity to those of the "five-coordinate" complexes, it is doubtful that the central donor atom does more than just weakly interact with the metal in an axial position.

In an effort to more carefully ascertain if any electronic differences existed between these substituted Cu(TAAB)$^{2+}$ compounds we recorded the X- and Q-band ESR spectra of each compound. ESR has been employed extensively to differentiate between various ligand atom environments for equatorial coordination.[12] In those cases, dramatic differences between the spin-Hamiltonian parameters exist for different ligand atom types. With this in mind, we had hoped that small electronic effects which might not be obvious in the optical spectra might now be more clearly evident. The spin-Hamiltonian parameters for these compounds are given in Table II. The spin-Hamiltonian parameter which traditionally has been the most useful is A_{zz}, since small electronic effects are more likely to be evident by a small percentage change here than in A_{xx} or A_{yy}.

The values of A_{zz} in this series ranged from 181 G for Cu(TAAB)$^{2+}$ to 147 G for all of the potential five-coordinate complexes. We can reasonably assume that this change must be due to some combination of four effects: (1) in-plane π-electron-density change resulting from a substitution at the azomethine positions; (2) axial ligation due to the bridging atom group; (3) a change in the charge from 2+ to 0; (4) a change in symmetry from D_{4h} to that near C_{2v}. By comparing specific pairs of compounds through this series, we can estimate the magnitude of each of the above effects on A_{zz}.

For Cu(TAAB)$^{2+}$, A_{zz} is 181 G, while A_{zz} for Cu(TAAB)$(OCH_3)_2$ is 159 G. This lowering of 22 G is a result of in-plane π-density differences, change in charge, or symmetry effects. Cu(TAAB)$[O(CH_2)_5O]$, another four-coordinate compound in the series, has an A_{zz} value of 154 G and represents a further 5-G reduction relative to Cu(TAAB)$(OCH_3)_2$. The major differences when comparing Cu(TAAB)$(OCH_3)_2$ to Cu(TAAB)$[O(CH_2)_5O]$ is the geometric restriction created by the bridge. Since this change creates only a 5-G lowering in A_{zz}, it would seem reasonable to assign most of the 22-G lowering from Cu(TAAB)$^{2+}$ to Cu(TAAB)$(OCH_3)_2$ to an electronic or π-bonding difference rather than a symmetry difference. The A_{zz} values for the five-coordinate bridged compounds Cu(TAAB)$[X(CH_2CH_2O)_2]$ (X = S, O, N(CH_3)) were in each case 147 G. This is a lowering of 7 G relative to the value for four-coordinate Cu(TAAB)$[O(CH_2)_5O]$. The 7 G now must only result from the electronic effect of S, O, and N(CH_3). For all three atoms to create the same degree of axial perturbation was surprising, at least, and implies a similar ligand field (as predicted above from the similar optical results) in all three systems (see Table I).

The only differences through the series of potential five-coordinate complexes were the small but real changes in the ⊥ region. The Q-band spectra show the expected rhombic symmetry of the Cu(TAAB)[X(CH_2CH_2O)$_2$] and Cu(TAAB)(OCH_3)$_2$ compounds. The g_{xx} and g_{yy} values are easily calculated from the Q-band spectra. For a planar molecule with axial symmetry, such as Cu(TAAB)$^{2+}$, g_{xx} was found to be equal to g_{yy}, as expected. A small spectral difference observable only in the ESR spectra (not optical or IR) at 35 GHz indicates only a small electronic difference between the three compounds. At this point, the question of axial coordination must be addressed. It is possible to imagine a *trans-spanning* ligand containing a heteroatom but not donating electron density to the copper atom. Bailar and coworkers[13] prepared *trans-spanning* bidentate ligands coordinated to Pt(II) some time ago (even though they were only recently reported). It is our contention, from the data presented here, that no fifth, axial coordination from sulfur, nitrogen, or oxygen exists. The small electronic changes observed from the ESR data are best explained by a weak interaction of the axial donor with copper(II) but are not strong enough to be classified as a normal bond.

We have made to date several unsuccessful attempts to obtain the complexes in a crystalline form suitable for a single-crystal X-ray structural study.

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Registry No. Cu(TAAB)(NO_3)$_2$, 51890-18-7; Cu(TAAB)[S(CH_2CH_2O)$_2$], 69102-50-7; Cu(TAAB)[(CH_3)N(CH_2CH_2O)$_2$], 69102-51-8; Cu(TAAB)[O(CH_2CH_2O)$_2$], 69102-52-9; Cu(TAAB)[O(CH_2)$_5$O], 69102-53-0; Cu(TAAB)(OCH_3)$_2$, 31410-94-3; ($NaOCH_2CH_2$)$_2$S, 69102-37-0; ($NaOCH_2CH_2$)$_2$O, 69102-38-1; ($NaOCH_2CH_2$)$_2$N(CH_3), 69102-39-2; ($NaOCH_2CH_2$)$_2$$CH_2$, 69102-40-5.

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(Triphenylcyclopropenyl)nickel Derivatives as Catalysts for the Isomerization of Quadricyclane to Norbornadiene

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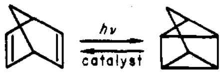
Infrared spectroscopy indicates that the (triphenylcyclopropenyl)nickel complex (C_6H_5)$_3$$C_3$Ni(CO)Cl readily loses its CO ligand in solution at room temperature but reacts with CO at room temperature and atmospheric pressure to form successively (C_6H_5)$_3$$C_3$Ni(CO)$_2$Cl and Ni(CO)$_4$. Reactions of ($C_6H_5$)$_3$$C_3$Ni(CO)Cl with various ligands in solution at room temperature rapidly give complexes with a L:Ni ratio of 2:1 of the type (C_6H_5)$_3$$C_3NiL_2$Cl (L = tetrahydrofuran, 2,2′-bipyridyl, (C_6H_5)$_2$$PCH_3$, ($C_6H_5$)$_2$PCl, $C_6H_5PCl_2$, and P(OR)$_3$ (R = phenyl, isopropyl, and methyl)). The ligand (C_6H_5)$_2$$PCH_3$ also gives an isolable 1:1 L–Ni complex of the stoichiometry (C_6H_5)$_3$$C_3$Ni[P($C_6H_5$)$_2$$CH_3$]Cl. The complex ($C_6H_5$)$_3$$C_3$Ni(CO)Cl is an active catalyst for the isomerization of quadricyclane to norbornadiene under conditions where it is converted to a carbonyl-free complex. Addition of the ligands L to (C_6H_5)$_3$$C_3$Ni(CO)Cl in L:Ni ratios from 1:1 to 3:1 gradually reduces the catalytic activity of these systems. The catalytic activities of the (C_6H_5)$_3$$C_3NiL_2$Cl derivatives (L = trivalent phosphorus ligand) increase as the coordination chemical shift decreases in their phosphorus-31 NMR spectra.

Introduction

In connection with the development of a system for the chemical storage of solar energy based on the reversible valence isomerization of norbornadiene (I) to quadricyclane (II),[1-3] we have screened diverse transition-metal complexes for catalytic activity for the exothermic conversion of quadricyclane to norbornadiene. One of the relatively few derivatives found to exhibit high catalytic activity for this reaction was the (triphenylcyclopropenyl)nickel complex originally[4] formulated as the dimer [(C_6H_5)$_3$$C_3$Ni(CO)Cl]$_2$ but subsequently[5] reformulated as the monomer (III: X = Cl) by analogy with the corresponding tri-*tert*-butylcyclopropenyl derivative shown to be a monomer by solution molecular weight determinations.

Since (triphenylcyclopropenyl)nickel derivatives represented a new type of catalyst structure and since the chemistry of such systems was only poorly known, we initiated a detailed study of the preparations and reactions of (triphenylcyclopropenyl)nickel derivatives as well as their use as catalysts for the



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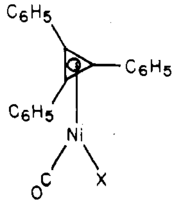

III

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