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Palladium(II) Complexes of the Tricyanomethanide Ion*

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A series of palladium(II)–tricyanomethanide complexes of the type $[PdL_2(NCC(CN)_2)_2]$ *(L =* $P(C_6H_5)_3$, $As(C_6H_5)_3$, $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2/2$, *5-nitro-1, 10-phenanthroline, pyridine) has been synthesized by the reaction of the corresponding dichloro complex with* $Ag[C(CN)_3]$ *in acetone. The reaction of* $PdCl_2$ *with* $K[C(CN)_3]$ *in ethanol produced only the monochloro complex* $K_2[Pd(NCC(CN)_2)_3Cl]$*. All of the complexes were found to contain N-bonded tricyanomethanide groups, on the basis of solid state infrared spectral data. Visible spectral data are also reported for the complexes.*

Introduction

The tricyanomethanide ion, $C(CN)_3^-$, in addition to being classified as a pseudohalide ion[1], possesses an ambidentate bonding capability involving a rarely observed Group IV/Group V pair of donor atoms. Examples of both C- and N-bonding, as well as ionic bonding and bridge formation, have been reported,[2,3,4] with N-bonding predominating by a wide margin. Although the effects of steric hindrance on the bonding mode of the tricyanomethanide ion in palladium(II) complexes have been studied[5], no systematic study of possible electronic ligand control of the tricyanomethanide's bonding mode, comparable to those which have been carried out with palladium(II) complexes of the thiocyanate[6], selenocyanate[7] and cyanate[8] ions, has previously been reported.

Experimental

Preparation of Complexes

Potassium Tricyanomethanide, $K[C(CN)_3]$

This compound was prepared according to the method of Trofimenko, Little, and Mower[9]. Conversion to the silver salt was accomplished by a metathetical reaction with $AgNO_3$ in aqueous solution.

Potassium Chlorotris(tricyanomethanido-N) palladate(II), $K_2[Pd(NCC(CN)_2)_3Cl]$

To a slurry of 0.178 g of palladium(II) chloride in 50 ml of ethanol was added 0.560 g of potassium tricyanomethanide in 20 ml of ethanol. The solution was stirred for 2 hours, whereupon it was filtered. The filtrate was reduced to dryness. The product was extracted from the residue with warm acetone. The solution was then reduced to one third of its original volume and cooled. A yellow crystalline solid precipitated on addition of diethyl ether. Yield, 76%; melting pt., 295° C.
Anal. Calcd. for $C_{12}ClK_2N_9Pd$: C, 29.4; N, 25.8. Found: C, 29.3; N, 25.7.

Bis(tricyanomethanido-N)bis(triphenylphosphine) palladium(II), $[Pd(P(C_6H_5)_3)_2(NCC(CN)_2)_2]$

To a slurry of 0.352 g of dichlorobis(triphenylphosphine)palladium(II)[10] in 50 ml of acetone was added 0.297 g of silver tricyanomethanide. The mixture was stirred for two hrs. The solution was then warmed and filtered. The residue in the filter was washed with small portions of warm acetone, and the combined filtrates were concentrated to a volume of 10 ml. A bright yellow precipitate formed upon the addition of diethylether. This was isolated by filtration, washed with more ether and dried *in vacuo.* Yield, 47%; melting pt., 196–199° C. *Anal.* Calcd. for $C_{44}H_{30}N_6P_2Pd$: C, 65.1; H, 3.7; N, 10.3. Found: C, 64.6; H, 3.9; N, 9.5.

Bis(tricyanomethanido-N)bis(triphenylarsine) palladium(II), $[Pd(As(C_6H_5)_3)_2(NCC(CN)_2)_2]$

To a slurry of 0.204 g of dichlorobis(triphenylarsine)palladium(II)[10] in 25 ml of acetone was added 0.150 g of silver tricyanomethanide. This mixture was stirred for 2 hr, whereupon it was filtered. The residue on the filter was washed with small portions of acetone. The combined filtrates were then concentrated to 10 ml. An orange yellow precipitate formed upon the addition of diethyl ether. This was isolated by filtration, washed with more ether and dried *in vacuo.* Yield, 42%; melting point, 149–151° C. *Anal.* Calcd. for $C_{44}H_{30}As_2N_6Pd$: C, 57.8; H, 3.3; N, 9.3. Found: C, 57.9; H, 3.4; N, 9.2.

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Bis(tricyanomethanido-N)(1,2-diphenylphosphinoethane)palladium(II), $[Pd(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2(NCC(CN)_2)_2]$

To a slurry of 0.208 g of dichloro(1,2-diphenylphosphinoethane)palladium(II)[10] in 25 ml of acetone was added 0.501 g of silver tricyanomethanide. The mixture was allowed to stir for 2 hr. It was then filtered and the residue washed with small portions of warm acetone. The combined filtrates were reduced to one fourth of their original volume and poured into 400 ml of diethyl ether. This produced a pale yellow precipitate. Yield, 68%; melting pt., 159–161° C. *Anal.* Calcd. for $C_{34}H_{24}N_6P_2Pd$: C, 59.6; H, 3.5; N, 12.3. Found: C, 59.5; H, 3.6; N, 12.2.

Bis(tricyanomethanido-N)(5-nitro-1,10-phenanthroline)palladium(II), $[Pd(C_{12}H_7N_3O_2)(NCC(CN)_2)_2]$

A solution of 0.276 g of silver nitrate in 10 ml of water was added to a slurry of 0.340 g of dichloro(5-nitro-1, 10-phenanthroline)palladium(II)[10] in 10 ml of water. This mixture was stirred occasionally on a steam bath for 24 hr.

The mixture was then centrifuged. The liquid layer was decanted off and filtered. The filtrate was reduced to 15 ml in volume. To the filtrate was added 0.206 g of potassium tricyanomethanide. An orange yellow precipitate formed immediately. The mixture was then filtered, and the solid thus obtained was washed with ether and dried *in vacuo.* Yield, 49%; melting pt., 176–179° C. *Anal.* Calcd. for $C_{20}H_7N_9Pd$: C, 46.0; H, 1.4; N, 24.6. Found: C, 46.1; H, 1.8; N, 24.6.

Bis(tricyanomethanido-N)bis(pyridine)palladium(II), $[Pd(C_5H_5N)_2(NCC(CN)_2)_2]$

To a slurry of 0.256 g of dichlorobis(pyridine)palladium(II)[10] in 25 ml of acetone was added 0.306 g of silver tricyanomethanide. This was allowed to stir overnight. The mixture was then filtered and the residue washed with small portions of acetone. The combined filtrates were reduced to one third of their original volume. Upon the addition of diethyl ether, a bright yellow precipitate formed. This was isolated by filtration, washed with more ether and dried *in vacuo.* Yield, 60%; melting pt., 185–187° C. *Anal.* Calcd. for $C_{18}H_{10}N_8Pd$: C, 48.6; H, 2.2; N, 25.2. Found: C, 48.5; H, 2.4; N, 25.3.

Physical Measurements

Solid state infrared spectra, in the 4000–400 cm^{-1} range, of the complexes held in Nujol suspension between potassium bromide discs were measured on a Perkin–Elmer Model 337 grating spectrophotometer. A Perkin–Elmer Model 180 spectrophotometer was used to record high resolution solid state spectra of the complexes in the C≡N stretching range. Ultraviolet–visible spectra of solutions of the complexes were recorded on a Cary 14 spectrophotometer using 1 cm quartz cells. Carbon, hydrogen, and nitrogen microanalyses were carried out by the following laboratories: Micro-Analysis, Inc., Wilmington, Delaware; Meade Microanalytical Laboratory, Amherst, Massachusetts; and Alfred Bernhardt Microanalytisches Laboratorium, Elbach-über-Engelskirchen, West Germany. Melting points were taken on a Fisher–Johns Melting Point Apparatus, and are uncorrected.

Results

Solid state infrared data for the palladium(II)–tricyanomethanide complexes prepared in this study are shown in Table I. The λ_{max} and E_{max} values for the lowest energy absorption bands in the visible spectra of the complexes are shown in Table II.

TABLE I. Solid State Infrared Data for Tricyanomethanide Complexes of Palladium(II) (cm^{-1}).[a, b]

Compound	Bonded CN Stretch	Nonbonded CN Stretch	ν(C==C)	C–CN Out-of-plane Bending
$K[C(CN)_3]$	–	2215sh, 2193sh, 2178s	1252m, 1240m	569m
$[Pd(P(C_6H_5)_3)_2(NCC(CN)_2)_2]$	2230s	2170s	1270m, 1220w	555s
$[Pd(As(C_6H_5)_3)_2(NCC(CN)_2)_2]$	2235m	2180s, 2170s, 2145	1275m, 1225w	555m
$[Pd(pyridine)_2(NCC(CN)_2)_2]$	2235s	2180s	1235w, 1215w 1265m, 1245w	545m
$[Pd((C_6H_5)_2P(CH_2)_2P(C_6H_5)_2)(NCC(CN)_2)_2]$	2235s	2180s, 2170s	1270w, 1235w	569s
$[Pd(5\text{-nitro-}1,10\text{-phen})(NCC(CN)_2)_2]$	2235m	2180s, 2170s, 2150m	1215w, 1210w 1270w, 1230w	555s
$K_2[Pd(NCC(CN)_2)_3Cl]$	2270m	2210s, 2190s	1250w, 1240w 1280w, 1260w	568m, 557w

[a] Nujol mulls. [b] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

TABLE II. Visible Spectra[a] of $[PdL_n(NCC(CN)_2)_2]$ Complexes in Order of Decreasing Ligand Field Strength of L.

L	n	λ_{max}, Å	E_{max}, kK
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	1	3259	30.7
$P(C_6H_5)_3$	2	3424	29.2
$As(C_6H_5)_3$	2	3694	27.1
pyridine	2	3982	25.1
5-nitro-1,10-phenanthroline	1	4070	24.6

[a] Methylene chloride solutions.

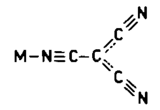
Discussion

Our original intent, with regard to the synthesis of these complexes, was to prepare potassium tetrakis(tricyanomethanido-N)palladate(II) and substitute the various other ligands for two coordinated $C(CN)_3^-$ groups. Since $K_2[Pd(NCC(CN)_2)_3Cl]$ was the only complex which could be prepared by the direct addition of potassium tricyanomethanide to $PdCl_2$, this method had to be abandoned, *i.e.*, the reaction of the $[Pd(NCC(CN)_2)_3Cl]^{2-}$ complex with the various ligands always yielded Cl^- containing products.

Using the same general procedure as that which was outlined in the Experimental, attempts were made to prepare complexes of a similar type using 1,10-phenanthroline, 2,2′-bipyridine, triphenylstibine, thiourea, 1,3-diethyl-2-thiourea, and ammonia as the other ligand in the coordination sphere. The reactions with these complexes proceeded only to partial completion. The solid state infrared spectra of Nujol mulls of the products all exhibited evidence of reaction with the silver tricyanomethanide, but the analyses indicated that chloride was still present in the coordination sphere. Attempts were made to correlate a monochloro product with the analyses, but all had an excess of chloride present in the complex. Due to the limited solubility of the products in various solvents, pure monosubstituted products could not be reclaimed from the mixtures.

Potassium tricyanomethanide is an ionic salt, and crystallographic studies have shown the resonance-stabilized $C(CN)_3^-$ ion to be essentially planar[11], having D_{3h} symmetry. It should therefore exhibit only one infrared active vibrational mode (E′) in the CN stretching region. Accordingly, an acetone solution of $K[C(CN)_3]$ exhibits[5] a single νCN stretching band at 2169 cm^{-1}. The Nujol mull infrared spectrum of this salt in the νCN stretching region (see Table I) exhibits a strong peak at 2178 cm^{-1}, two high frequency shoulders at 2215 and 2193 cm^{-1}, and one or more very weak low frequency peaks at *ca.* 2130 cm^{-1}. The appearance of the high frequency shoulders in the solid state spectrum is apparently due to lower site symmetry. The low frequency peaks are attributed to the ^{13}CN vibration(s). The free ion also exhibits a doublet at 1252, 1240 cm^{-1}, assigned to $\nu(C{=}C)$, and a C–CN out-of-plane bending band at 569 cm^{-1}.

Coordination of the tricyanomethanide group *via* its central carbon atom lowers the local symmetry of the species to C_{3v}. Hence, a C-bonded tricyanomethanide ion should exhibit two infrared active bands in the νCN region (E and A_1 modes). In addition, the destruction of the delocalization of the lone pair on the carbon atom to the CN groups should result in the disappearance of the $\nu(C{=}C)$ bands. Coordination *via* a nitrogen atom,



(I)

lowers the local symmetry of the species to C_{2v}. An N-bonded tricyanomethanide ion should therefore exhibit three νCN bands in its infrared spectrum, one band corresponding to the CN stretch of the coordinated CN group, the other two corresponding to the in-phase and out-of-phase stretches of the non-coordinated CN groups. Bands corresponding to the $\nu(C{=}C)$ vibrations would still be expected to be observed.*

As shown in Table I, all of the palladium(II)–tricyanomethanide complexes prepared in this study exhibit a sharp high frequency νCN singlet, a lower frequency νCN multiplet (sometimes broad and unresolved), and a $\nu(C{=}C)$ multiplet in their solid state infrared spectra, clearly indicative of N-bonding (structure I) in each case. Thus, unlike the thiocyanate ion[6], the tricyanomethanide ion is found to be insensitive

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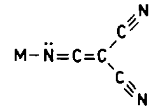
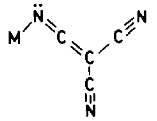
* A number of earlier investigators[2,3,12] have referred to the N-bonded tricyanomethanide ion as a "dicyanoketeniminato" group and/or have represented it thusly:



(II)

We feel that this is misleading in two respects. Firstly, the keteniminato grouping would involve a *non-linear* M–N–C linkage, *i.e.*,



(III)

Secondly, structure II(III) would be expected to exhibit a high frequency doublet and a low frequency singlet in the νCN stretching region. Precisely the opposite, *i.e.*, a high frequency singlet and a low frequency doublet, is usually observed, as would be predicted for structure I. For this reason, we favor using the structure I representation, at least until crystallographic evidence to the contrary is presented.

to the changing electronic character of the other ligands in the palladium(II) coordination sphere, behaving more like the selenocyanate[7] and cyanate[8] ions in this regard.

Indeed, C-bonding has thus far been reported for only three complexes of the tricyanomethanide ion: $[W(CO)_5(C(CN)_3)]^-$,[2,13] *trans*-$[Pt(P(C_6H_5)_3)_2(H)(C(CN)_3)]^2$, and *cis*-$[Pt(P(C_6H_5)_3)_2Cl(C(CN)_3)]^2$. The existence of C-bonding in the latter two complexes has been disputed by Lenarda and Baddley[12] who, on the basis of infrared and proton nmr data, concluded that the $C(CN)_3^-$ groups are N-bonded. The paucity of C-bonded tricyanomethanide groups is undoubtedly due to the fact that C-bonding destroys the resonance stabilization present in the free ion, whereas N-bonding does not.

The λ_{max} and E_{max} values for the lowest energy absorption bands in the visible spectra of the complexes prepared in this study (see Table II) are in excellent agreement with the relative ligand field strengths of the other ligands in the coordination sphere. Earlier studies[3,12] have shown that the ligand field strengths of $-NCC(CN)_2^-$ and $-NCS^-$ are comparable.

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