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TRANSITION-METAL COMPLEXES DERIVED FROM DICYANOACETYLENE AND RELATED COMPOUNDS

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SUMMARY

The reactions of dicyanoacetylene with $(Ph_3P)_2Ir(CO)Cl$ and nickelocene give low yields of complexes containing the acetylene bonded to the metal atoms. Reactions between 2,3-dicyanobicyclo[2.2.2]octa-2,5,7-triene, or its 1,4,5,6,7,8-hexamethyl derivative, and several transition-metal compounds have given complexes in which the trienes are bonded to the metal by only two of the double bonds. The silver nitrate adduct contains three atoms of silver per molecule of triene, and it is likely that each double bond is coordinated to one metal atom. The copper(I) chloride adduct contains two molecules of CuCl, and the metal atoms are probably coordinated to the CN groups.

INTRODUCTION

In recent years, the chemistry of transition metal complexes of fluorocarbons has been extensively studied[1]; the extra stability and often unique structures conferred upon the complexes by the presence of the electron-withdrawing fluorine atoms are now well known. Complexes derived from similar compounds containing other electron-withdrawing groups are less well documented, possibly because of the high reactivity of such compounds.

The extensive organic chemistry of the cyanocarbons[2] has no parallel in transition-metal chemistry*, and early reports of the attempted reactions between tetracyanoethylene (TCNE) and metal carbonyls speak of violent reactions, or of uninviting black polymeric reaction products which defied attempts at purification[3]. With nickel carbonyl, a product containing the tetracyanoethylene anion radical, $Ni(TCNE)_2$, was isolated[4]. With various polycyanoolefins, other nickel complexes, *e.g.*, $[NiC_2(CN)_3Ph]_n$, could be obtained, and were formulated as electron-transfer complexes[5]. Tetracyanoethylene also reacts with ferrocene[6,7] and with bis(benzene)-chromium[8] to give deeply coloured products, variously supposed to be either charge-transfer complexes[7] or anion radical salts[6,8] of the corresponding cations. In the case of the ferrocene adduct, a crystal structure determination[9] and Mössbauer studies[10] favour the charge transfer formulation.

Recently, the use of compounds which are susceptible to oxidative-addition reactions has given well characterised complexes such as $(Ph_3P)_2Pt(TCNE)$[11], $(Ph_3P)_2Rh(CO)Cl(TCNE)$[12], and $(Ph_3P)_2Ir(CO)Cl(TCNE)$[12]. The iridium complex

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* A detailed review of this topic can be found in ref. 29.

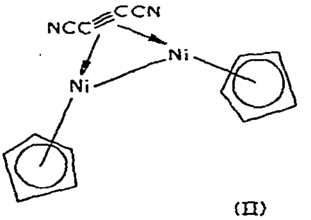
has been shown to contain a three-membered ring, involving the metal and olefinic carbon atoms[13]. Irradiation of the hexacarbonyls $M(CO)_6$ (M = Cr, Mo or W) in the presence of TCNE has given the deep blue-violet complexes $(TCNE)M(CO)_5$[14].

Part of the difficulty in investigating reactions of dicyanoacetylene has been the lack of a suitable synthesis of this compound; a method based on the dehydration of acetylenedicarboxamide[15] gives only poor yields of material unless the starting materials are rigorously purified. However, the recent publication[16] of an improved synthesis of this alkyne has made feasible a more detailed study of its reactions.

RESULTS AND DISCUSSION

We have studied some representative reactions of dicyanoacetylene (DCA) with transition metal complexes, and have found that the extreme reactivity of the alkyne unfortunately results in the formation of black tars in most reactions. Thus we were unable to characterise any products from the reactions with $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, $Mn(CO)_5Br$, and ferrocene, even when carried out at −78°.

More success was obtained in reactions with bis(triphenylphosphine)-iridium carbonyl chloride, and nickelocene, although in both cases the yields were notably lower than found in reactions of these complexes with hexafluoro-2-butyne, for example, and the product had to be extracted from amounts of black tarry material.



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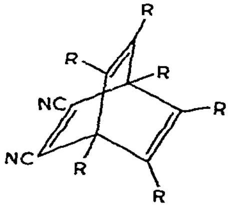

(III), R = H
(IV), R = CH_3

With $(Ph_3P)_2Ir(CO)Cl$, a rapid reaction occurred on addition of DCA, to give a pale yellow compound, which analysis indicated to be the expected addition compound, $(Ph_3P)_2Ir(CO)Cl(DCA)$ (I). The infrared spectrum showed bands at 2187 [ν(CN)], 2018 [ν(CO)] and 1706 [ν(C≡C)] cm^{-1}. After this work was completed, this complex was described by Baddley and McClure[17], whose work is in general agreement with our own. It is likely that the complex contains the three-membered ring similar to that found in related compounds, *e.g.*, $(Ph_3P)_2Ir(CO)Cl(TCNE)$[13].

Reaction of the alkyne with nickelocene gave a dark purple solid, which could be recrystallised from ethanol, but which was unstable in air. Analysis indicated the formula $(C_5H_5Ni)_2(C_4N_2)$, and we suggest structure (II) for this complex, by analogy with, *e.g.*, dark green $(C_5H_5Ni)_2(CF_3C_2CF_3)$. The structure is also analogous to that proposed for the complex $(C_4N_2)[Co(CO)_3]_2$[18]. The ν(CN) frequencies appear at 2205 and 2198 cm^{-1}, respectively, in these two complexes.

A striking reaction of dicyanoacetylene is the addition to aromatic hydrocarbons to give bicyclo[2.2.2]octatriene derivatives[19]. We have prepared the adducts with benzene and hexamethylbenzene [(III) and (IV), respectively] and have studied typical reactions with different transition-metal compounds. There are three likely bonding situations, in which any two of the double bonds chelate the metal atom, and the system related to that in the TCNE complexes discussed above, involving the dicyano-olefin part of the ligands.

Reaction of 2,3-dicyanobicyclo[2.2.2]octa-2,5,7-triene (III) (DCNO) with bis(benzonitrile)palladium chloride gave a bright yellow complex, shown to be $[(DCNO)PdCl_2]_n$ (V), which was insoluble in all solvents tried. The hexamethyl-substituted triene (IV) (HMDCNO) gave a similar complex $[(HMDCNO)PdCl_2]_n$ (VI). Because of their insolubility, molecular weight determinations were not possible, but it is likely that these complexes are analogous to the well-known $C_8H_{12}PdCl_2$[20]. The corresponding complex from the DCA-cyclooctatetraene adduct is also very insoluble[21].

Similar reactions with rhodium chloride gave the yellow insoluble complexes $[(DCNO)RhCl]_n$ (VII) and $[(HMDCNO)RhCl]_n$ (VIII), which from their spectral properties are presumed to be dimeric and similar to $[C_8H_{12}RhCl]_2$, with the trienes behaving as chelating dienes, and containing bridging chlorine atoms. The same complexes were obtained from the trienes and $[Rh(CO)_2Cl]_2$.

The silver nitrate adduct of DCNO (IX) was prepared in the usual way, and proved to contain three silver ions for each molecule of the triene. The adduct of HMDCNO could not be prepared under similar conditions. Each silver ion in (IX) is probably coordinated to one of the double bonds. The complex rapidly darkens in light, or on heating.

A copper(I) chloride complex of composition $[DCNO(CuCl)_2]$ (X) was also prepared, and formed an orange brown solid. In the infrared spectrum of this complex the $\nu(CN)$ is very weak. The copper complex of cyclooctadiene is reported as a white crystalline solid[22], which is dimeric, with the composition $[C_8H_{12}CuCl]_2$, in contrast to complex (X), whereas complexes containing copper bonded to CN groups have been reported as orange to red solids[23]. The colour, stoichiometry and very weak $\nu(CN)$ suggest that in (X) the copper is coordinated to the CN groups rather than to the double bonds.

Reactions between DCNO and ruthenium and iridium chlorides gave ill-defined dark coloured solids, which were insoluble and probably polymeric, and which were not investigated further. An attempt to make complexes by reacting the ligands with $(Ph_3P)_2Ir(CO)Cl$ in benzene at 50° for periods of up to one month, gave no isolable complex, although some lightening of the colour of the solution was noted.

Infrared spectra

The spectra of the ligands and complexes described above are collected in Table 1. The iridium-DCA complex (I) shows a much reduced $\nu(C\equiv C)$ stretching frequency at 1706 cm^{-1}, compared to 2119 cm^{-1} in DCA, which is in accord with the donation of π-electron density to the metal, and concomitant back-donation to the multiple bond antibonding orbitals from filled metal *d* orbitals, resulting in a reduced total bond order for the C–C bond. An alternative explanation, involving rehybridisation of the acetylenic carbon atoms from *sp* to sp^2, has also been advanced. The nickel complex (II) does not show a band attributable to the $C\equiv C$ stretch. In both complexes, $\nu(CN)$ is decreased to $\sim$2200 cm^{-1} from the 2290 cm^{-1} observed in the free acetylene.

In the spectra of DCNO and HMDCNO, ν(CN) occurs at 2220 and 2209 cm^{-1} respectively. In all except the copper complex, the ν(CN) frequency occurs in the range 2207–2220 cm^{-1}, and has a similar intensity, indicating little or no interaction of the CN group with the metal. The copper complex shows a reduction in frequency by 24 cm^{-1}, and this band appears as only a weak absorption. As mentioned above, we suggest that this complex probably contains a CN–Cu coordination.

TABLE 1

INFRARED DATA FOR SOME CYANOCARBON COMPLEXES (cm^{-1})

Complex	ν(CN)	Other bands
DCA[a]	2290	2119[d]
(I)[b]	2187 ms	2018 s[e], 1706 w, 1483 w, 1435 w, 1310 vw, 1095 s, 998 w
(II)[b]	2205 s	2153 sh, 1300 vw, 1013 vw, 800 w, 738 sh, 723 m
DCNO[b]	2220 vs	1595 s, 1320 vs, 1303 s, 1085 w, 1068 m, 1051 w, 901 m, 840 m
[c]	2224 vs	1630 w, 1594 vs, 1320 vs, 1304 s, 1278 w, 1253 w, 1219 s, 1209 vs, 1193 w, 1180 m, 1163 w, 1138 w, 1088 s, 1073 m, 1055 m, 1043 w, 970 w, 944 m, 907 s, 894 w, 844 s, 780 vs, 772 vs, 729 m, 685 vs, 643 m
HMDCNO[b]	2209 vs	1594 m, 1467 s, 1447 vs, 1439 sh, 1393 vs, 1068 s, 1028 m
[c]	2209 vs	1651 w, 1613 w, 1593 s, 1393 vs, 1259 w, 1231 s, 1131 vw, 1073 vs, 1045 vw, 1021 vs, 996 w, 953 w, 791 s, 742 m, 691 w
(V)[c]	2207 m	1447 s, 1308 vs, 1260 w, 1218 s, 1175 s, 1064 w, 960 s, 920 m, 835 vs, 810 s
(VI)[c]	2217 m	1523 sh, 1517 m, 1495 s, 1419 s, 1398 vs, 1147 w, 1085 sh, 1078 m, 1062 m, 1027 vs, 1007 s, 950 w, 721 w
(VII)[c]	2218 ms	1728 m, 1615 s, 1335 w, 1300 w, 1218 m, 1120 w, 1088 vw, 1040 vw, 900 vw, 738 m
(VIII)[c]	2210 ms	1598 m, 1110 m, 1071 m, 1030 sh, 1012 s, 935 m, 723 m, 665 m
(IX)[c]	2220 s	1765 m, 1582 m, 1575 sh, 1545 m, 1085 s, 1043 s, 1030 s, 941 m, 897 m, 843 m, 810 s, 790 s, 775 s, 725 m, 720 w, 708 s, 680 s
(X)[c]	2196 vw	1573 w, 1310 s, 1298 s, 1276 w, 1238 vw, 1220 w, 1210 vw, 1198 m, 1178 w, 1167 w, 1138 w, 1087 br, 1057 m, 973 w, 928 m, 898 m, 846 m, 778 m, 768 s, 713 s, 674 s

[a] Liquid film Raman active modes [28]. [b] $CHCl_3$ solution. [c] Nujol mull. [d] $\nu(C\equiv C)$. [e] ν(CO).

The remainder of the spectra are not helpful in deciding which of the three double bonds are coordinated to the metal, and the only strong bands which are readily assignable are those attributed to methyl vibrations at 1467 and 1393 cm^{-1} in HMDCNO, 1495 and 1398 cm^{-1} in its palladium complex (VI); in the corresponding rhodium complex (VIII), the bands are hidden under the nujol absorptions.

EXPERIMENTAL

Dicyanoacetylene was prepared by pyrolysis of 4,5-dicyano-1,3-dithiol-2-one[16]; the disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate required as a precursor for this compound was prepared by a published method[24]. 2,3-Dicyanobicyclo[2.2.2]octa-2,5,7-triene (DCNO) and 2,3-dicyano-1,4,5,6,7,8-hexamethylbicyclo[2.2.2]octa-2,5,7-triene (HMDCNO) were prepared by the addition of dicyanoacetylene to benzene and hexamethylbenzene, respectively, in the presence of aluminium chloride[19].

Bis(benzonitrile)palladium chloride[25], dimeric rhodium carbonyl chloride[26], and bis(triphenylphosphine)iridium carbonyl chloride[27], were prepared by methods described in the literature.

All reactions were carried out in a nitrogen atmosphere. Infrared spectra, recorded on a Perkin–Elmer 257 double-grating instrument, are collected in Table 1; analyses of the complexes are listed in Table 2.

TABLE 2

ANALYTICAL DATA FOR SOME CYANOCARBON COMPLEXES

Complex		M.p.	Analyses, found (calcd.) (%)		
			C	H	N
(I)	$C_{41}H_{30}ClIrN_2OP_2$	189–190 dec.	56.75	3.7	2.9
			(57.4)	(3.5)	(3.2)
(II)	$C_{14}H_{10}N_2Ni_2$		51.6	3.2	
			(51.9)	(3.1)	
(V)	$C_{10}H_6Cl_2N_2Pd$	233–235 dec.	35.0	2.0	7.8
			(36.2)	(1.9)	(8.4)
(VI)	$C_{16}H_{18}Cl_2N_2Pd$	249–250 dec.	45.8	4.1	6.3
			(46.2)	(4.3)	(6.7)
(VII)	$C_{10}H_6ClN_2Rh$	290 dec.	39.9	2.0	8.95
			(40.4)	(2.0)	(9.5)
(VIII)	$C_{16}H_{18}ClN_2Rh$	310 dec.	51.1	4.9	7.2
			(51.0)	(4.8)	(7.4)
(IX)	$C_{10}H_6Ag_3N_5O_9$	155–157 dec.	18.4	1.1	10.8
			(18.1)	(0.9)	(10.6)
(X)	$C_{10}H_6Cl_2Cu_2N_2$	240–242 dec.	33.9	1.8	8.0
			(34.1)	(1.7)	(8.0)

Reactions of dicyanoacetylene

(*a*) *With* $(Ph_3P)_2Ir(CO)Cl$. Reaction of dicyanoacetylene (76 mg, 1 mmole) with Vaska's complex (780 mg, 1 mmole) in benzene (25 ml) gave an orange-yellow solution. After 1 h, sovent was removed, and the light yellowish-brown residue was redissolved in benzene, treated with activated charcoal, and filtered. Addition of light petroleum to the filtrate gave complex (I) as pale yellow crystals (600 mg, 70%).

(*b*) *With nickelocene.* Dicyanoacetylene (100 mg, 1.3 mmoles) in tetrahydrofuran (10 ml) was added to nickelocene (247 mg, 1.3 mmoles) in the same solvent (20 ml) at −78°, and the mixture was allowed to attain room temperature. Filtration and evaporation gave a dark purple solid, which was recrystallised from ethanol to give dark purple-black crystals of complex (II) (180 mg, 68%).

Reactions of DCNO and HMDCNO

(*a*) *With* $(PhCN)_2PdCl_2$. The palladium complex (250 mg, 0.65 mmole) in dichloromethane (5 ml) was treated with DCNO (100 mg, 0.65 mmole) in the same solvent, and the mixture was stirred at room temperature for 2 h. A bright yellow solid which separated was filtered off, and washed with dichloromethane and light petroleum to give complex (V) (152 mg, 46%).

A similar reaction with the hexamethyl compound (100 mg, 0.42 mmole) and the palladium complex (161 mg, 0.42 mmole) gave the bright yellow hexamethyl complex (VI), which was filtered and washed successively with benzene, dichloromethane and petroleum ether (180 mg, 100%).

(*b*) *With* $[Rh(CO)_2Cl]_2$. A mixture of DCNO (100 mg, 0.65 mmole) and the carbonyl chloride (120 mg, 0.3 mmole) in tetrahydrofuran (10 ml) was stirred overnight. Evaporation of excess solvent gave yellow $[(DCNO)RhCl]_2$ (VII) (110 mg, 56%), which was filtered off and washed with ether and light petroleum. This complex was insoluble in common organic solvents.

A reaction using HMDCNO (154 mg, 0.65 mmole) and the carbonyl chloride (120 mg, 0.3 mmole) in tetrahydrofuran (20 ml) gave a similar solid, which was filtered and washed with ether and light petroleum to give pure $[(HMDCNO)RhCl]_2$ (VIII) (190 mg, 79%).

(*c*) *With rhodium chloride.* A mixture of DCNO (100 mg, 0.65 mmole) and $RhCl_3 \cdot 3\,H_2O$ (171 mg, 0.65 mmole) in ethanol (25 ml) was refluxed for 1 h. A yellow solid precipitated, and after filtration and washing with water, ethanol and acetone, was found to be identical with complex (VII) obtained as in (*b*) above (115 mg, 58%).

(*d*) *With silver nitrate.* Silver nitrate (331 mg, 1.95 mmoles) dissolved in the minimum amount of water was boiled with DCNO (100 mg, 0.65 mmole) in ethanol (5 ml), and the solution was filtered. After standing overnight, light-sensitive yellow crystals deposited. Recrystallisation from ethanol gave complex (IX) (160 mg, 37%).

(*e*) *With copper(I) chloride.* Copper(I) chloride (100 mg, 1.0 mmole) dissolved in 2.5% aqueous KCl solution (20 ml) was treated with sulphur dioxide to remove traces of copper(II) salts. Excess SO_2 was boiled off,and DCNO (154 mg, 1.0 mmole) in ethanol (10 ml) was added. After about 15 min, an orange-red solid separated. This was filtered, washed with water, ethanol and acetone to give complex (X) (61 mg, 23%).

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