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Characterization of Tricarbonyl-chromium(0), -molybdenum(0) and -tungsten(0) Complexes with 2,2-*para*-cyclophane

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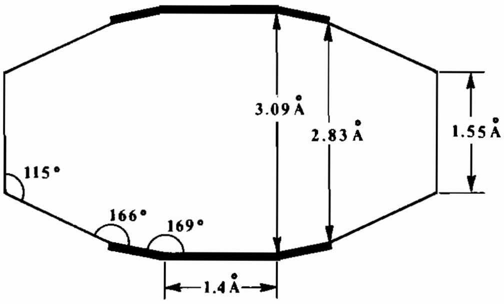
Complexes of the type $M(CO)_3(22cy)$, where M = Cr, Mo, W and 22cy = 2,2-para-cyclophane were prepared and characterised. The i.r., p.m.r., mass spectrography spectra are discussed. The Mo derivative decomposes in solution giving 22cy, $Mo(CO)_6$ and Mo, according to a first order mechanism.

Introduction

The cyclophanes appear to be an interesting new class of polynuclear π-ligands having different possibilities to act as donor molecules. One-to-one tetracyanoethylene complexes and tricarbonylchromium derivatives were prepared by Cram *et al.*[1–2] with a wide variety of *para*-cyclophanes in order to provide a new tool for the study of transannular effects. In the present paper we report on the preparation and full characterization of yellow, crystalline $M(CO)_3(22cy)$ compounds where M = Cr, Mo, W, obtained by photochemical reactions between $M(CO)_6$ and 2,2-*para*-cyclophane ($C_{16}H_{16}$ = 22cy) in ligroin (see Experimental and Table I).

Results and Discussion

As is known[3–4], in the 22cy molecule the two benzene rings are not planar, being distorted as shown in Figure 1, by the two $-C_2H_4-$ bridges.



Section of 2,2-*para*-cyclophane molecule orthogonal to ring planes, according to ref. 4.

Therefore in the i.r. spectrum of 22cy (see Table II), besides the usual expected aromatic and aliphatic absorptions, some strong bands appear; in particular those at 937 and 895 cm^{-1} were interpreted[3] as due to distortions of the aromatic system. Nevertheless, the band at 938 cm^{-1} is also present, with the same intensity and shape, in the *para*-ethyltoluene spectrum (935 cm^{-1}); moreover this band does not change significantly on going from the free ligand to our complexes.

On going from the free ligand to the complex, in the $\nu(CH)$ region no significant changes occur. Only the $\nu(CH)_{ar}$ absorption at 2950 cm^{-1} (ms) in the ligand moves to higher wavenumbers in the complexes ($\Delta\nu$ about + 22 cm^{-1}); furthermore, the absorbance of

TABLE I. Analytical Data and Electronic Spectra.

	Required %			Found %			u.v.–vis. Spectra[a]	
	C	H	m.w.	C	H	m.w.[b]	$\tilde{\nu}$ (kK)	ε
$Cr(CO)_3(22cy)$	66.3	4.7	344.3	66.1	4.7	344	28.8	10,500
$Mo(CO)_3(22cy)$	58.7	4.1	388.2	58.3	4.0	390	28.9	14,250
$W(CO)_3(22cy)$	48.3	3.3	476.2	47.6	3.3	476	29.4	21,300

All compounds are crystalline, yellow, diamagnetic, non-electrolytes, stable in solid state at room temperature, soluble in common organic solvents except hydrocarbons. In solution the chromium derivative is the most stable.
[a] In $CHCl_3$ solution. [b] By mass spectrography.

TABLE II. Infrared Assignments of the Most Intense Absorptions in cm^{-1} (KBr discs).

Approximate Normal Mode	22cy	$Cr(CO)_3(22cy)$	$Mo(CO)_3(22cy)$	$W(CO)_3(22cy)$
$\nu(CH)_{ar}$	3060 vw; 3030 m; 3010 w; 2950 ms; 2882 ms	3072 ms; 3030 w; 3010 mw; 2970 m; 2895 (sh)	3062 s; 3030 vw; 3010 w; 2980 m; 2890 m	3065 s; 3010 w; 2968 m; 2890 w
$\nu(CH)_{asym}$	2922 vs	2930 vs	2925 vs	2928 s
$\nu(CH)_{sym}$	2848 vs	2855 s	2850 s	2850 s
$\nu(CO)^a$ a_1	–	1968 vs	1963 vs^b	1961 vs
e	–	1895 s	1883 s^b	1881 s
$\nu(C\text{–}C)_{skel}$	1590 m 1502 ms 1412 s 1085 s	1590 m; 1538 m; 1490 s; 1452 m 1410 s 1150 s; 1072 s	1588 m; 1528 m 1492 m; 1448 m 1408 ms 1148 s; 1068 s	1515 m 1495 m; 1452 m 1410 ms 1145 s; 1068 m
$\delta(CH_2)$	1437 m	1430 m	1431 ms	1431 ms
$\delta(CH)$	1382 w; 1175 w	1390 m; 1180 m	1380 s; 1180 mw	1380 s; 1180 w
$\omega(CH_2)$	1321 w	1315 w	–	1315 w
$\tau(CH_2)$	1230 w	1232 w	1230 w	1235 w
22cy ring distorsion	937 m; 895 s;	945 m; 880 mw–845 vs	945 m–935 m; 882 ms–835 vs	947 w–937 w; 885 m–839 vs
$\delta(CCC)$?	621 s	650 m; 615 vs–570 s?	680 ms	675 m
$\omega(CH)$	807 vs	812–807 m	802 s	807 s
$\varrho(CH_2)$	720 vs	720 s	718 s	719 s
$\delta(MCO)$	–	675 vs; 637 s; 531 vs	615 vs; 590 s; 568 vs	602 s; 568 s; 500 vs
$\gamma(CCC)$	509 vs; 381 w?		495 vs?	
$\nu(M\text{–}C)$	–	485 w	446 m	455 w
$\nu(M\text{–ring})$	–	355 m; 286 w	343 ms; 282 m	347 ms; 282 w

[a] Taken in chloroform solution. [b] Freshly prepared solutions: the bands at 1963 cm^{-1} moves to 1984 cm^{-1}; the band at 1883 cm^{-1} disappearson standing.

3060 cm^{-1} (mw) absorption increases in the order W > Mo > Cr > 22cy.

In the $\nu(CO)$ region the a_1 and e absorptions typical of tricarbonyl derivatives with arene ligands[5] appear. As far as the $Mo(CO)_3(22cy)$ is concerned, this compound decomposes in $CHCl_3$ solution as discussed below.

The skeletal stretching vibrations at 1590 and 1490 cm^{-1} of the free ligand are split for the complexes into four bands, because one ring only is bonded to the metal, two of these four bands do not change while the other two move towards lower wavenumbers by about 63 and 52 cm^{-1}. Similarly, the strong 1085 cm^{-1} absorption is split into two bands, the first at higher ($\Delta\nu \simeq +63$ cm^{-1}) and the second at lower wave numbers ($\Delta\nu \simeq -16$ cm^{-1}). The absorptions near 1110 cm^{-1} in metal–arene sandwich complexes were attributed to the ring breathing mode[6].

The strong band due to the non-planarity of the ring occuring at 895 cm^{-1} is split in the complexes into two absorptions both at lower wave numbers ($\Delta\nu \simeq -13 \pm 3$ and -55 ± 6 cm^{-1}) as a consequence of the metal–ring bond.

As far as the 621 cm^{-1} band is concerned, this absorption could be attributed either to the $\delta(C\text{–}C\text{–}C)$ mode or to the particular geometry of the 22cy molecule. In any case this band is split in the spectra of the complexes into several absorptions, one of which moves towards higher wavenumbers and the other probably being mixed with the $\delta(MCO)$.

In the 700–200 cm^{-1} region the $\delta(MCO)$, $\nu(MC)$ and ν(M–ring) modes are present in very good agreement with the literature data for (π-arene)$M(CO)_3$ derivatives[7].

The PMR chemical shift values (from HMDS as external standard) for the free ligand and the complexes are listed in Table III together with the corresponding values for benzene and $Cr(CO)_3(C_6H_6)$ used for comparative purposes. In the free ligand spectrum two singlets are present at 6.86 and 3.48 ppm, which are respectively due to the aromatic and aliphatic proton resonances with an area ratio of 1:1. On passing to the complex spectra, the arene resonance is split into two singlets, while from the aliphatic one two multiplets arise.

As far as the $(CH)_{arene}$ proton resonance is concerned, one of the two singlets is shifted to lower fields by 0.36 ± 0.06 ppm with respect to the free ligand resonance whereas the other exhibits a very strong shielding effect (1.73 ± 0.11 ppm). The aliphatic resonances

TABLE III. PMR Chemical Shift Values, δ(ppm) from HMDS external, for Free Ligand and its Derivatives at 28 ± 1 °C in $CDCl_3$ Solution.

	$\delta_{(Ar)}$	$\delta_{(Alk)}$[a]
2,2-cyclophane	6.86	3.48
$Cr(CO)_3(22cy)$	7.15; 5.02	3.59; 3.18
$Mo(CO)_3(22cy)$	7.23; 5.25	3.62; 3.28
$W(CO)_3(22cy)$	7.27; 5.11	3.66; 3.26
Benzene	7.67	
$Cr(CO)_3(C_6H_6)$	5.72	

[a] For complexes δ values are referred to the center of the multiplet.

are similarly split; one of the two multiplets moves towards higher fields of 0.24 ± 0.05 ppm and the other towards lower fields by 0.14 ± 0.04 ppm (the chemical shift values being calculated at the multiplet centres) with respect to the free ligand resonance.

Comparing the chemical shift values of free benzene and of benzene-tricarbonylchromium(0) a very strong shielding effect is observed.

Therefore in 22cy derivatives the proton resonances of the ring bonded to the metal are those near 5 ppm. The strong shielding effect observed in benzene-tricarbonylchromium(0) as well as in 22cy derivatives may arise from the electron back-donation $Cr(0) \rightarrow$ arene, which seems to be of the same order of magnitude in all complexes.

In any case, comparing the absolute values of the chemical shifts, we observe that in 22cy and its chromium derivative they fall in higher fields than for benzene and $Cr(CO)_3(C_6H_6)$ respectively. This effect could be interpreted in terms of a ring–ring interaction. In fact in 22cy derivatives the proton resonances of the non-bonded ring show a moderate deshielding effect probably due to a *trans*-annular effect.

The splitting of the aliphatic resonances could be interpreted in the same way.

The most important peaks of the mass spectra are reported in Table IV with their relative intensities, taking the peak with m/e = 104 as 100%.

From these data it clearly results that the molybdenum derivative is the less stable one, the stability sequence being W > Cr > Mo. Moreover the dicarbonyl and monocarbonyl fragments are very unstable in all compounds. On the other hand, there are significant percentages of ions containing chromium or tungsten bonded only to 22cy or its fragments. This fact points out the high stability of the arene–metal bond, except in the case of molybdenum.

The peak at m/e = 104 could be assigned to the $CH_2{-}C_6H_4{-}CH_2^{+}$ ion which seems to be better stabilised by resonance than $C_6H_4{-}C_2H_4^{+}$.

The low stability of the arene–molybdenum bond is responsible for the decomposition of $Mo(CO)_3(22cy)$ in solution. In fact the infrared absorption which is present at 1963 cm^{-1} for freshly prepared solution slowly moves to 1984 cm^{-1}, while the strong band at 1883 cm^{-1} slowly disappears. The absorption at 1984 cm^{-1} indicates the formation of $Mo(CO)_6$. Moreover in the n.m.r. spectrum proton resonances at 6.86 and 3.48 ppm appear, in accordance with the formation of free 22cy. Thus the stoichiometry of decomposition is:

$$2\,Mo(CO)_3(22cy) \rightarrow Mo(CO)_6 + Mo + 22cy$$

However, the kinetic measurements, carried out by following the absorbance decrease at 1883 cm^{-1} (in chloroform solution), show that the reaction is of first order with respect to the molybdenum complex. The kinetic data and activation parameters are:

$k \times 10^4$ sec^{-1}: 3.25 (20 °C); 4.24 (25 °C); 4.83 (30 °C); 5.43 (35.4 °C); 6.28 (40 °C); $\Delta H^{\neq} = 5.4 \pm 0.2$ Kcal/mol; $\Delta S^{\neq} = -55.9 \pm 0.8$ e.u.

Therefore the supposed mechanism could be:

$$Mo(CO)_3(22cy) \xrightarrow{\text{slow}} \{Mo(CO)_3\} + 22cy$$

$$2\{Mo(CO)_3\} \xrightarrow{\text{fast}} Mo(CO)_6 + Mo$$

TABLE IV. Assignment of the Most Important M.S. Peaks and their Relative Intensities.

Metal (= M)	Chromium		Molybdenum		Tungsten	
Ions	m/e	I%	m/e	I%	m/e	I%
$[M(CO)_3(22cy)]^+$	344	7.7	390	1.0	476	24.0
$[M(CO)_2(22cy)]^+$	316	trace	362	1.0	448	4.7
$[M(CO)(22cy)]^+$	288	13.0	334	1.3	420	2.3
$[M(22cy)]^+$	260	64.9	306	3.5	392	44.2
$22cy^+$	208	13.0	208	66.7	208	41.9
$[M(C_6H_4(CH_2)_2\cdot)]^+$	156	57.1	202	trace	286	6.2
$C_6H_4(CH_2)_2^{\,+}$	104	100.0	104	100.0	104	100.0
$C_6H_6^{\,+}$	78	13.0	78	19.4	78	26.3
CO^+	28	27.9	28	39.9	28	89.1
M^+	52	148.0	98	trace	186	3.8

Experimental

Preparation of Compounds

The compounds were prepared by UV irradiation (4 hr) of a boiling solution of 22cy and an excess of $M(CO)_6$ in ligroin (100° C) under nitrogen. This method allows us to work at lower temperature than Cram *et al.*[2] This is necessary to obtain the molybdenum and tungsten derivatives which are thermally unstable in solution. The yellow crude products separate out and after soxhlet extraction with cyclohexane are recrystallised from a $CHCl_3/C_6H_{12}$ mixture. Cr(22cy) $(CO)_3$ was also obtained in high yields by reaction of $Cr(CO)_6$ in molten 22cy (325° C) in a sealed tube under nitrogen. Analytical data and physical properties are reported in Table I.

Spectrophotometric Measurements

The i.r. spectra were recorded in $CHCl_3$ solution in the $\nu(CO)$ region; as KBr discs in the range 4000–400 cm^{-1} and as Nujol mulls between CsI plates in the 450–200 cm^{-1} region with a Perkin–Elmer mod. 325 spectrophotometer. The u.v.–visible spectra were recorded in chloroform solution with a Perkin–Elmer mod. 402 instrument.

PMR Measurements

All PMR spectra were recorded with a Varian mod. A 100 spectrometer at 28 ± 1° C in $CDCl_3$ solution using HMDS as external standard.

Other Measurements

The mass spectra were recorded in the laboratory of the "Politecnico di Milano". The magnetic measurement with Gouy's method using Newport equipment at room temperature. The conductivity measurements at 25° C in nitrobenzene solution were made by a WTW bridge type LBR.

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