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CYANOALKYL DERIVATIVES OF MANGANESE(I) AND IRON(I) CARBONYLS

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Summary

The reaction of $[Mn(CO)_5]^-$ and $[(h^5\text{-}C_5H_5)Fe(CO)_2]^-$ anions with the halocyanoalkanes *o*-, *m*- and *p*-$ClCH_2C_6H_4CN$ yields stable products of the type $Mn(CO)_5CH_2C_6H_4CN$ and $(h^5\text{-}C_5H_5)Fe(CO)_2CH_2C_6H_4CN$. The thermolysis and the reactions of the manganese derivatives with several nucleophiles are described. π-Coordination of the CN group to manganese was not observed in any of the products.

Introduction

The cyanoalkyl group attached to transition metals in low oxidation states shows some features which make this group markedly different from the parent alkyl derivatives. In particular, σ- or π-coordination of the CN group to another metal atom (or to the same metal atom by chelation) should occur; insertion reactions should give organic moieties with two functional groups, and the enhanced stability of the metal—carbon bond should facilitate the formation of hydridocyanoalkyl complexes [1]. We have described the preparation, spectroscopic properties, and the reactions of several cyanoalkyl complexes of the type $PtX(RCN)L_2$ and $[Pt(RCN)L_2]_2(BF_4)_2$ ($R = (CH_2)_n$, *o*-$CH_2C_6H_4$; $L = PPh_3$, PPh_2Me, $AsPh_3$; $X = Cl$, Br) [2]. When bonded to platinum, the CN group undergoes nucleophilic attack by water, alcohols and amines [2].

This paper deals with the preparation and reactions of a new series of *o*-, *m*-

and p-cyanoalkyl complexes of the type $Mn(CO)_5CH_2C_6H_4CN$ and $(h^5\text{-}C_5H_5)\text{-}Fe(CO)_2CH_2C_6H_4CN$, and with the possible π-coordination of the CN group to the manganese, a point of controversy [3—5].

Results and discussion

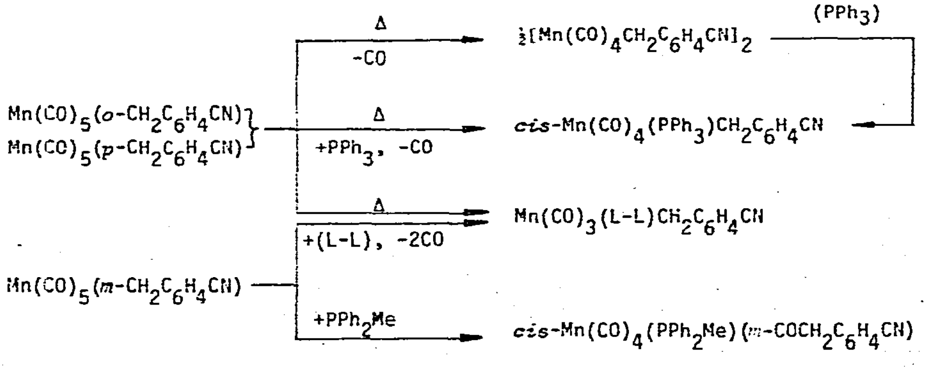
Reacting $[(h^5\text{-}C_5H_5)Fe(CO)_2]^-$ or $[Mn(CO)_5]^-$ with o-, m- and p-$ClCH_2C_6H_4CN$ give the complexes $(h^5\text{-}C_5H_5)Fe(CO)_2(o\text{-}CH_2C_6H_4CN)$ (I) and $Mn(CO)_5CH_2C_6H_4CN$ (II: o-, III: m-, IV: p-) in good yields. Melting of these compounds under argon leads to extensive decomposition in the case of I and III, whereas II and IV lose carbon monoxide with formation of higher melting products. These complexes were identified as the dimers $[Mn(CO)_4CH_2C_6H_4CN]_2$ (V: o-, VI: p-) by molecular weight measurements in dichloromethane and by their IR spectra.

The NMR and IR data for all the complexes prepared are listed in Table 1.

The $\nu(CO)$ of I—IV agree with those in the corresponding alkyl compounds and $Mn(CO)_5CH_2Ph$ [6], in accord with the Cotton—Kraihanzel rules [7]. The $\nu(CN)$ frequencies show that the cyano group is uncoordinated. It is generally accepted that bonding of the CN through the nitrogen lone pair is accompanied by an increase in $\nu(CN)$ compared with that in the free nitrile [8,9]. In contrast π-coordination shifts the $\nu(CN)$ bands to lower frequencies, as observed for $Pt(PPh_3)_2(CF_3CN)$ [10]. The $\nu(CN)$ of V and VI occur around 2260 cm^{-1} (IR and Raman), about 40 cm^{-1} higher than that in the parent compounds. This indicates σ-coordination of the CN group even though Dreiding molecular models in the case of V show a favourable geometry for π-coordination in a monomeric chelate. The same situation is found in the analogous platinum(II) complex $[Pt(o\text{-}CH_2C_6H_4CN)(L\text{—}L)]_2(BF_4)_2$ (L—L = $Ph_2PCH{=}CHPPh_2$), where the PtNCC group was shown to be linear by X-ray diffraction [11]. Thus, the o-cyanobenzyl ligand behaves like o-cyanophenyldiphenylphosphine, for which π-coordination of CN to manganese(I) was claimed [3,4], but which was shown later to bind through nitrogen [5]. So far, π-coordination of CN is known only for $Pt(PPh_3)_2(CF_3CN)$ [10] and $[Ni(CO)(C_5H_5NCN)]_2$ [12].

The substitution reactions observed for the manganese complexes II—IV are summarized in Scheme 1.

SCHEME 1



(L-L) = 2,2'-dipyridine; 1,10-phenanthroline.

TABLE 1

NMR AND IR SPECTRAL DATA

Complex		δ (H_{arom})[a] (ppm)	δ(CH_2) (ppm)	ν(C≡O)[b] (cm^{-1})	ν(C≡N)[c] (cm^{-1})
I	$(\eta^5\text{-}C_5H_5)Fe(CO)_2(o\text{-}CH_2C_6H_4CN)$[d]	7.24m (4)	2.86s (2)	2020, 1960	2222 (R 2220)[h]
II	$Mn(CO)_5(o\text{-}CH_2C_6H_4CN)$	7.25m (4)	2.52s (2)	2120, 2030, 1995	2220 (R 2223)
III	$Mn(CO)_5(m\text{-}CH_2C_6H_4CN)$	7.28m (4)	2.34s (2)	2120, 2025, 1998	2235
IV	$Mn(CO)_5(p\text{-}CH_2C_6H_4CN)$	7.36m (4)	2.39s (2)	2118, 2020, 1996	2225 (R 2225)
V	$[Mn(CO)_4(o\text{-}CH_2C_6H_4CN)]_2$	7.28m (8)	2.60s (4)	2080, 2000, 1985, 1951	2258 (R 2260)
VI	$[Mn(CO)_4(p\text{-}CH_2C_6H_4CN)]_2$	7.43m (8)	2.39s (4)	2078, 2050, 2018, 1985, 1955	2260 (R 2262)
VII	$cis\text{-}Mn(CO)_4(PPh_3)(o\text{-}CH_2C_6H_4CN)$[e]	7.48m (19)	1.94d (2)	2065, 1990, 1970, 1940	2222
VIII	$cis\text{-}Mn(CO)_4(PPh_3)(p\text{-}CH_2C_6H_4CN)$[f]	7.52m (19)	1.74d (2)	2060, 1990, 1970, 1945	2220
IX	$cis\text{-}Mn(CO)_4(PPh_2Me)(m\text{-}COCH_2C_6H_4CN)$[g]	7.53m (14)	4.04s (2)	2082, 1994, 1960, 1600 (acyl)	2238
X	$Mn(CO)_3(dipy)(o\text{-}CH_2C_6H_4CN)$	7.50m (12)	2.30s (2)	1995, 1905	2215
XI	$Mn(CO)_3(dipy)(m\text{-}CH_2C_6H_4CN)$	6.80m (12)	2.23s (2)	1995, 1908	2230
XII	$Mn(CO)_3(dipy)(p\text{-}CH_2C_6H_4CN)$	7.40m (12)	2.10s (2)	2000, 1908	2218
XIII	$Mn(CO)_3(o\text{-}phen)(o\text{-}CH_2C_6H_4CN)$	7.17m (12)	2.30s (2)	1997, 1905	2220
XIV	$Mn(CO)_3(o\text{-}phen)(m\text{-}CH_2C_6H_4CN)$	7.07m (12)	2.26s (2)	1995, 1905	2220
XV	$Mn(CO)_3(o\text{-}phen)(p\text{-}CH_2C_6H_4CN)$	7.31m (12)	2.13s (2)	2000, 1910	2215

[a] In $CDCl_3$; TMS as internal standard, intensity in parentheses. [b] CCl_4 solutions. [c] Nujol mulls. [d] Cyclopentadienyl protons: δ 5.17s (5). [e] ^3J(P—H) 6 Hz. [f] ^3J(P—H) 5.8 Hz. [g] CH_3: δ 2.28 d, ^2J(P—H) 8 Hz. [h] Raman: solid sample.

Triphenylphosphine does not react with the dimers in solution, but when the solids, are melted with PPh_3 the coordinated cyano group is displaced to yield *cis*-$Mn(CO)_4(PPh_3)CH_2C_6H_4CN$ (VII—VIII). The four ν(CO) bands indicate a loss of symmetry analogous to that found in *cis*-$Mn(CO)_4LL'$ complexes [13]. These complexes are also obtained by melting II or IV with PPh_3 under argon. No carbon monoxide insertion takes place with II and IV in the presence of PPh_3 or PPh_2Me in ether or refluxing THF. The *meta* derivative III, however, reacts smoothly with an ether solution of PPh_2Me to give the insertion product *cis*-$Mn(CO)_3(PPh_2Me)$(*m*-$COCH_2C_6H_4CN$). The isomers II—IV react with melts of bidentate ligands L—L (2,2'-dipyridine; 1,10-phenanthroline) to give the substitution products $Mn(CO)_3(L—L)CH_2C_6H_4CN$ (X—XIV). All these complexes probably have *mer* configurations because two ν(CO) bands are observed in their IR spectra. Nucleophilic addition of water, alcohols and amines to the coordinated CN group of the uncharged dimers V and VI does not occur. Since such reactions do occur in the case of the analogous platinum(II) [3] and palladium(II) cationic complexes, the main factor favouring the nitrile—amide and the nitrile—imine conversion seems to be the overall positive charge on the complex.

Experimental

^1H NMR spectra were recorded with a Bruker WP-60 (60 MHz) spectrometer, IR spectra with a Perkin—Elmer 577 spectrophotometer and Raman spectra with a Spex Compact 1403 spectrometer equipped with an Ar-II laser source. Molecular weights were obtained by vapour pressure osmometry. The Institute of Organic Chemistry, Padua, carried out the microanalyses. Mass spectra were recorder with a Bell Howell CEC 21490.

Preparation of complexes

(h^5-C_5H_5)$Fe(CO)_2CH_2C_6H_4CN$ (I) and $Mn(CO)_5CH_2C_6H_4CN$ (II—IV) were made by the standard method [13], i.e. by treating Na[(h^5-C_5H_5)$Fe(CO)_2$] and Na[$Mn(CO)_5$] respectively with the appropriate $ClCH_2C_6H_4CN$ in THF. The crude product was chromatographed twice on a Florisil column using a 80/20 v/v hexane/ether eluent. Slow evaporation of the eluate gave the products as red (I) or yellow (II—IV) crystals. I: m.p. 60°C; found (calcd.) (%) C, 60.80 (61.47), H, 3.39 (3.78), N, 4.21 (4.78); II: m.p. 93—94°C (dec., CO↑), molecular weight 310 ± 3 (calcd. 311.14); m/e^+: 311, 283, 255, 227, 199 (corresponding to the successive loss of 4CO); C, 50.12 (50.18), H, 1.87 (1.94), N, 4.50 (4.50); III: m.p. 100—101°C (dec., CO↑); C, 49.60, H, 1.96, N, 4.52; IV: m.p. 109—110°C (dec.); C, 50.11, H, 1.90, N, 4.41.

[$Mn(CO)_4CH_2C_6H_4CN$]$_2$ (V—VI) were obtained by working-up the parent monomers II and IV under argon at 110°C. When CO evolution ceased, a solution of the crude product in the minimum of dichloromethane was treated with charcoal, and the solid was recovered and crystallized from hexane. V: pale yellow; m.p. 141—143°C (dec.); molecular weight in $ClCH_2CH_2Cl$ 562 ± 5 (555.4); m/e^+: 283, 255, 227, 199 (the dimer decomposes in the mass spectrum chamber at 160°C and 10^{-6} Torr into the same tetracarbonyl species than that found in the mass spectrum of II). C, 50.81 (50.91), H, 1.98 (2.14), N, 4.62 (4.95); VI:

pale yellow; m.p. 110—113°C (dec.); C, 50.78, H, 2.12, N, 40.68. $Mn(CO)_4(PPh_3)CH_2C_6H_4CN$ (VII—VIII) and $Mn(CO)_3(L{-}L)CH_2C_6H_4CN$ (X—XV) (L—L = dipy, *o*-phen) were all prepared by melting the monomers II—IV with an excess of the appropriate ligand under argon. The crude product in ether was chromatographed twice on Florisil using a 80/20 v/v hexane/ether eluent. The PPh_3 derivatives may also be obtained by heating an ether suspension of the dimers V—VI under argon with the equimolar amount of PPh_3. VII: white; m.p. 117—119°C (dec., $CO\uparrow$); C, 65.87 (66.07), H, 4.02 (3.88), N, 2.55 (2.57); VIII: white; m.p. 150—151°C; C, 65.92, H, 3.91, N, 2.61; X: red; m.p. 155—157°C (dec.); C, 60.89 (61.33), H, 3.58 (3.43), N, 9.99 (10.22); XI; red; m.p. 144—146°C (dec.); C, 61.18, H, 3.43, N, 10.27; XII: red; m.p. 165°C (dec.); C, 61.30, H, 3.27, N, 9.85; XIII: red; m.p. 167—169°C (dec.); C, 62.93 (63.46), H, 3.20 (3.24), N, 9.52 (9.65); XIV: red; m.p. 143—145° (dec.); C, 62.65, H, 3.40, N, 9.36; XV: red; m.p. 179°C (dec.); C, 63.22, H, 3.01, N, 9.60.

$Mn(CO)_4(PPh_2Me)(m\text{-}COCH_2C_6H_4CN)$ (IX) was obtained by stirring an ether solution of III for 24 h under argon with an equimolar amount of methyldiphenylphosphine. The mixture was chromatographed on a Florisil column using ether as eluent. The yellow product was recrystallized from hexane. IX: white; m.p. 123—125°C (dec.); C, 61.49 (61.07), H, 3.98 (3.75), N, 2.69 (2.74). All yields were 80—85%.

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References

1 R. Ros, R. Bataillard and R. Roulet, J. Organometal. Chem., 118 (1976) C53.
2 R. Ros, J. Renaud and R. Roulet, Helv. Chim. Acta, 58 (1975) 133; J. Organometal. Chem., 87 (1975) 379; 104 (1976) 293.
3 D.H. Payne, Z.A. Payne, R. Rohmer and H. Frye, Inorg. Chem., 12 (1973) 2540.
4 M.F. Farona and K.F. Kraus, Inorg. Chem., 9 (1970) 1700; M.F. Farona and N.J. Bremer, J. Amer. Chem. Soc., 88 (1966) 3735.
5 B.N. Storhoff, J. Organometal. Chem., 43 (1972) 197; B.N. Storhoff and A.J. Infante, Inorg. Chem., 13 (1974) 3034.
6 D.M. Adams, "Metal ligand and related vibrations", New York, S. Martin's Press (1968); D. Drew, M.Y. and D.J. Darensbourg, J. Organometal. Chem., 85 (1975) 73.
7 F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
8 R.A. Walton, Quart. Rev., Chem. Soc., 19 (1965) 126.
9 K.F. Purcell and R.S. Drago, J. Amer. Chem. Soc., 88 (1966) 919.
10 W.J. Bland, R.D. Kemmitt and R.D. Moore, J. Chem. Soc., Dalton Trans., (1973) 1292.
11 A. Pinkerton, D. Schwarzenbach, J. Wenger and R. Roulet, to be published.
12 K. Krogmann and R. Mattes, Angew. Chem., Int. Ed. Engl., 5 (1966) 1046.
13 R.B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York (1965), p. 147.