have an analogous configuration. As for the infrared spectrum of a bidentate nitrate group, the assignments given in Table II were made with reference to that of the bidentate carbonate group.[20–22]

It is evident from the infrared spectra that all of the 4:1 complexes have uncoordinated nitrate anions[23] in the solid state. Accordingly these complexes seem to be formulated as $[(TMSS)_4M]^{2+}(NO_3^-)_2$ (M = Co, Zn, Cd). Certainly this formulation is strongly supported for the cobalt complex by the reflectance spectrum (Table III and Figure 1) which exhibits the structured band around 14,000 cm^{-1} typical of a tetrahedral cobalt(II) ion.

Complexes in Solution.—Since the infrared and electronic spectra of $(TMSS)_2Co(NO_3)_2$ in dichloromethane are essentially similar to those of the solid, the configuration is possibly the same in the two states. This conclusion is also confirmed by its low molar conductance in this solution (Table IV).

The infrared spectra of all 4:1 complexes in dichloromethane show bands due to nonionic coordinated nitrate groups and, in addition, bands attributable to the uncoordinated TMSS, as listed in Table II. It appears from these results that all of the 4:1 complexes dissociate completely into 2:1 complexes and free TMSS.

$$(TMSS)_4M(NO_3)_2 \rightleftharpoons (TMSS)_2M(NO_3)_2 + 2TMSS \quad (M = Co, Zn, Cd) \quad (1)$$

This is consistent with the fact that the electronic spectrum of the 4:1 cobalt complex in dichloromethane is superimposable with that of the 2:1 complex (Figure 1). For the zinc and cadmium complexes, the low molar conductances in dichloromethane suggest that the 2:1 complexes formed according to eq 1 are nonelectrolytes, but it is not clear whether nitrate groups act as monodentate or bidentate groups.

In a more polar solvent such as nitromethane, an unexpected low value, which seems to be too small for the ionic formulation mentioned above, is obtained for the molar conductance of the 4:1 cobalt complex $(TMSS)_4Co(NO_3)_2$. The electronic spectrum of this complex in nitromethane (Table III and Figure 2) gives rise to a band at 15,100 cm^{-1} (B band) and a shoulder band at 14,300 cm^{-1} (C band), both of which may be attributable to $(TMSS)_4Co(NO_3)_2$, in addition to an absorption maximum at 16,600 cm^{-1} (A band) due to $(TMSS)_2Co(NO_3)_2$. Therefore it is apparent that $(TMSS)_4Co(NO_3)_2$ is involved in equilibrium 1 in this solution. This is confirmed by addition of an excess of TMSS to this system, which results in weakening of the A band and strengthening of the B and C bands. In accordance with this conclusion, addition of TMSS also leads to a large increase in the molar conductance (Table IV). The electronic spectrum of $(TMSS)_2Co(NO_3)_2$ in nitromethane exhibits the B band as a very weak shoulder, and thus a somewhat large molar conductance may be derived from $(TMSS)_4Co(NO_3)_2$. The 4:1 zinc and cadmium complexes in nitromethane are also involved in equilibrium 1 and some contribution of the 2:1 species encountered in the absence of an excess of the ligand is negligible when an excess of TMSS is present, since the molar conductances give sufficiently large values to assume 1:2 electrolytes. In summary, all 4:1 complexes are involved in equilibrium 1 in solution. The equilibrium is shifted completely to the right-hand side in dichloromethane, whereas a contribution of the ionic 4:1 species is increased in a polar solvent such as nitromethane.

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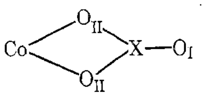
[20] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962). Although theoretical calculation (R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, **5**, 1308 (1966)) pointed out that the simple assignment is not appropriate for a bidentate nitrate group, the conventional assignment made here is not necessarily incorrect for the chemical purpose judging from the potential energy distribution.

[21] On the basis of infrared spectra alone, it is not in general possible to distinguish between monodentate and bidentate nitrate groups although possible in the case of the carbonate group.[16] This difference may be explained by comparing the structures of the two groups.



I, X = C or N

According to X-ray diffraction studies,[19,22] the C–O_I distance in the bidentate carbonate group is fairly shorter than the C–O_{II} distance, but the distance of the N–O_I bond in the nitrate group is comparable with that of the N–O_{II} bond. Therefore the C–O_I bond has a considerable double-bond character and exhibits its stretching band at high frequency (1560–1643 cm^{-1}),[20] whereas the band due to the N–O_I bond with a less double-bond character appears at lower frequency (1469–1517 cm^{-1}) where the monodentate nitrate group also gives rise to a characteristic band.

[22] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 586 (1962).

[23] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, 4222 (1957).

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Facile Interconversion of Arene- and Cyanocyclohexadienylmanganese Complexes

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The reaction of cyanide ion with cationic complexes of the type $(arene)Mn(CO)_3^+$, where the arene is benzene, xylene, mesitylene, etc., has been reported[1,2] to yield the neutral complexes $(arene)Mn(CO)_2CN$. In some cases an intermediate, formulated as the ionic compound $[(arene)Mn(CO)_3]CN$, could be isolated.[1]

As part of a general survey of substitution on coordinated arenes, we have investigated the reaction of complexes $(arene)Mn(CO)_3^+$ with a range of nucleophiles. This communication deals specifically with the reaction with cyanide ion, indicating that the ionic formulation of the intermediate is incorrect.

Experimental Section

Reactions were performed under nitrogen using oxygen-free solvents. Products were stored under nitrogen and kept away from light.

Preparation of 1-Cyano-2,4,6-trimethylcyclohexadienyltricar-

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* To whom correspondence should be addressed.

[1] T. H. Coffield, R. D. Closson, and V. Sandel, Abstracts, 134th National Meeting of the American Chemical Society, 1958, p 58P.

[2] T. H. Coffield and R. D. Closson, *Chem. Abstr.*, **59**, 11558*d* (1963); U. S. Patent 3,042,693 (July 3, 1962).

TABLE I

ANALYTICAL DATA AND SPECTRA OF COMPOUNDS $((\text{arene})CN)Mn(CO)_3$

Arene	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N	C–O str freq, cm^{-1}	Nmr spectra^c
C_6H_6	49.40	2.49	5.76	49.09	2.61	5.80	2041, 1969, 1963^a	4.00 (t, 1), 4.95 (dd, 2), 6.40 (t, 1), 7.00 (dd, 2)
$C_6H_3(CH_3)_3$	54.75	4.24	4.91	54.22	4.29	5.35	2020, 1948^a	5.14 (s, 2), 6.61 (s, 1), 7,45 (s, 3), 8,27 (s, 6)
$C_6H_2(CH_3)_4$	56.20	4.71	4.68	56.28	4.78	4.71	2018, 1944^b	6.57 (d, 1), 7.14 (d, 1), 7.48 (s, 3), 7.93 (s, 3), 7.97 (s, 3), 8.24 (s, 3)

[a] In hexane solution. [b] In dichloromethane solution. [c] In $CDCl_3$ solution. Multiplicities and intensities are given in parentheses: t, triplet; dd, doublet of doublets; d, doublet; s, singlet.

bonylmanganese, $(C_6H_3(CH_3)_3CN)Mn(CO)_3$.—Mesitylenetricarbonylmanganese iodide,[3] $[(C_6H_3(CH_3)_3)Mn(CO)_3]I$ (1 mmol), was dissolved in the minimum volume of water at room temperature, and the solution was then cooled to 0°. A saturated aqueous solution of sodium cyanide (1.5 mmol) was added dropwise to this solution. An immediate white precipitate was obtained. After several hours at 0°, the precipitate was removed by filtration, washed with a large volume of ice-cold water, and dried. The product could be recrystallized from petroleum ether (bp 60–80°), giving white crystals, dec pt 108–109° (with loss of CO). The same method was used for the preparation of analogous benzene and 1,2,3,4-tetramethylbenzene complexes. Analytical data and infrared and nmr spectra of these complexes are given in Table I.

Preparation of Cyanomesitylenedicarbonylmanganese, $(C_6H_3(CH_3)_3)Mn(CO)_2CN$.—A stirred aqueous suspension of $(C_6H_3(CH_3)_3CN)Mn(CO)_3$ was heated to the boiling point. The product was extracted into dichloromethane, and the dichloromethane solution was washed with water and then slowly concentrated by evaporation. Yellow crystals, mp 163–165° dec, were obtained. The infrared spectrum in methylene chloride solution exhibited a C–N stretching band at 2103 cm^{-1} and C–O stretching bands at 2000 and 1954 cm^{-1}. The nmr spectrum in acetone-d_6 consisted of two rather broad bands centered at τ 7.7 and 4.6 (relative intensity 3:1), corresponding to methyl groups and aromatic protons on the mesitylene. *Anal.* Calcd for $(C_6H_3(CH_3)_3)Mn(CO)_2CN$: C, 56.06; H, 4.70; N, 5.45. Found: C, 55.65; H, 4.68; N, 5.11.

Spectra.—These were recorded on a Perkin-Elmer R10 nmr spectrometer and a Perkin-Elmer 257 ir spectrophotometer.

Results and Discussion

Treatment of an aqueous solution of the mesitylene complex $[(C_6H_3(CH_3)_3)Mn(CO)_3]I$ with aqeuous potassium cyanide at 0° yields an immediate white precipitate of empirical formula $(C_6H_3(CH_3)_3)Mn(CO)_3CN$. This is presumably the compound for which the ionic formulation $[(C_6H_3(CH_3)_3)Mn(CO)_3]CN$ is given in the literature.[1,2] Although insoluble in cold water, the compound is soluble in both polar and nonpolar organic solvents, an unusual state of affairs for a supposedly ionic compound. There is also a marked shift in the C–O stretching frequencies during the reaction. Whereas the infrared spectrum of the cation $(C_6H_3(CH_3)_3)Mn(CO)_3^+$ exhibits[3] bands at 2070 and 2016 cm^{-1}, in the compound $(C_6H_3(CH_3)_3)Mn(CO)_3CN$ these have shifted to 2020 and 1948 cm^{-1}.

The incorrectness of the ionic formulation is shown clearly by the nmr spectrum. Whereas the spectrum of $(C_6H_3(CH_3)_3)Mn(CO)_3^+$ in D_2O consists of two singlets at τ 7.58 and 3.87 of relative intensity 9:3, that of $(C_6H_3(CH_3)_3)Mn(CO)_3CN$ in CCl_4 solution is more complex, consisting of four singlets: (a) τ 5.14 (intensity 2), (b) τ 6.61 (intensity 1), (c) τ 7.47 (intensity 3), and (d) τ 8.27 (intensity 6). All the experimental data can be explained if it is assumed that the reaction involves attack by cyanide ion on the mesitylene to yield $(C_6H_3(CH_3)_3CN)Mn(CO)_3$. Whereas we have obtained similar products from the analogous benzene and 1,2,3,4-tetramethylbenzene complexes, the hexamethylbenzene complex $[(C_6(CH_3)_6)Mn(CO)_3]I$ does not react in this way. We conclude that cyanide addition takes place at an unsubstituted carbon atom in the aromatic ring and hence assign the bands in the nmr spectrum as shown in Figure 1.

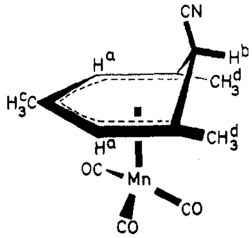

Figure 1.—Notation for protons in the proposed structure of $(C_6H_3(CH_3)_3CN)Mn(CO)_3$.

Nucleophilic addition to an *arene* ring (as opposed, for example, to the tropylium ring) has only been reported for hydride, alkyl, and aryl, and here again attack occurs preferentially at an unsubstituted carbon atom.[3-5] Assuming that the stereochemistry of cyanide addition is similar to these, the cyanide group will be in the exo position.

The mild conditions under which nucleophilic addition occurs are remarkable, as is the ease with which the carbon–carbon bond can be broken again. Thus, refluxing an aqueous suspension of $(C_6H_3(CH_3)_3CN)Mn(CO)_3$ results in conversion to $(C_6H_3(CH_3)_3)Mn(CO)_2CN$, with evolution of carbon monoxide (confirmed by gas chromatography) and transfer of cyanide ion from arene to metal. The same conversion can be effected by heating in the solid state. Further studies on the mechanism of this conversion and on related reactions are at present in progress.

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(5) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).