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Preliminary communication

SPECIFIC SYNTHESES AND ELECTROCHEMISTRY OF ISOMERIC $[Mn(CO)_{6-n}(CNMe)_n]^+$ (n = 3, 4) COMPLEXES

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Summary

The replacement of bromide ion in $Mn(CO)_{5-n}(CNMe)_nBr$ complexes (n = 2, 3, 4) by CO and CNMe, accomplished in the presence of the halogen acceptors $AlCl_3$ (CO reactions only) or $AgPF_6$, is found to be stereospecific, thus providing reliable routes to the pure isomeric complexes *cis*- and *trans*-$[Mn(CO)_2(CNMe)_4]^+$, and *fac*- and *mer*-$[Mn(CO)_3(CNMe)_3]^+$. Cyclic voltammetric studies on PF_6^- salts of the isomeric complexes show that $E_{1/2}$ values for the isomeric species differ substantially. The qualitative explanation for this difference, involving relative stabilizations of the (primarily) non-bonding metal 3*d* orbitals through π-interactions with CO and CNMe, is justified by molecular orbital calculations.

Recently we reported the syntheses of the series of complexes $[Mn(CO)_{6-x}(CNMe)_x]^+$ (x = 1—4) [1], according to eq. 1. We have now carried out the similar reactions described by eq. 2. The use of $AgPF_6$ instead of $AlCl_3$ as a halide acceptor in this latter reaction is necessary since $AlCl_3$ causes rapid polymerization of the isocyanide. Interestingly, the latter reaction

$$Mn(CO)_{5-x}(CNMe)_xBr + AlCl_3 + CO \xrightarrow[(-AlX_4^-)]{PF_6^-} [Mn(CO)_{6-x}(CNMe)_x]PF_6 \quad (1)$$

$(x = 1—4)$

$$Mn(CO)_{5-x}(CNMe)_xBr + AgPF_6 + CNMe \xrightarrow[(-AgBr)]{} [Mn(CO)_{5-x}(CNMe)_{x+1}]PF_6 \quad (2)$$

$(x = 2,3)$

yielded complexes which were isomers of the products described in the earlier study. Thus *fac*-$Mn(CO)_3(CNMe)_2Br$ yielded *fac*-$[Mn(CO)_3(CNMe)_3]PF_6$* and

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*This compound has been prepared by a different method [2].

$Mn(CO)_2(CNMe)_3Br$, a *mer* isomer with *cis* carbonyls, gave *cis*-$[Mn(CO)_2(CNMe)_4]PF_6$; the respective *mer* and *trans* isomers had been obtained in the carbonylation reactions [1]. Identification of the isomeric species in these reactions was readily accomplished using infrared spectroscopy, observing ν(CO) and ν(CN) vibrational frequencies. These data are provided in Table 1.

TABLE 1

INFRARED DATA

Compound	ν(CN) (cm^{-1})	ν(CO) (cm^{-1})
cis-$[Mn(CO)_2(CNMe)_4]PF_6$ [a]	2230m, 2190s, 2170vs, 2150s	2000vs, 1975vs
trans-$[Mn(CO)_2(CNMe)_4]PF_6$ [b]	2177vs	1985vs
fac-$[Mn(CO)_3(CNMe)_3]PF_6$ [a]	2240m, 2210s, 2170w	2060vs, 2000vs, 1980m(sh)
mer-$[Mn(CO)_3(CNMe)_3]PF_6$ [b]	2245m, 2220(sh), 2202s	2090m, 2020vs

[a] This work; CH_2Cl_2 solution, Beckman IR-10. [b] Ref. 1; CH_2Cl_2 solution, Perkin—Elmer 421.

It is apparent that these reactions have occurred so that the incoming ligand assumed the specific coordination position occupied by the halide ion. The retention of stereochemistry seems to argue against a simple dissociative mechanism; a five-coordinate intermediate would most likely be capable of intramolecular ligand exchange. The low polarity of the solvent, tetrahydrofuran, probably precludes full dissociation of the halide anion, in any event, and a closely associated ion pair might be postulated to precede ligand attack and halide displacement.

It must be noted that the synthesis of cationic metal carbonyls from metal carbonyl halides, halide acceptor, and ligand is a general procedure which has been applied in a great many instances [3]. Remarkably, no attention has yet been directed to determining the stereochemistry of these reactions, few mechanisms are offered, and no mechanism has been substantiated. We suggest, however, that the observations made here are quite general; and indeed a survey of the examples of such reactions involving manganese [3] appears to be in accord with this conclusion although these results are not unequivocal.

We had determined earlier [1] that the ease of oxidation of the $[Mn(CO)_{6-n}(CNMe)_n]PF_6$ complexes, measured as $E_{1/2}$ values in a cyclic voltammetry experiment, was dependent on the extent of isocyanide substitution. Thus the $E_{1/2}$ value for $[Mn(CNMe)_6]PF_6$ in CH_2Cl_2 vs. SCE was +0.38 V, and sequential replacement of CNMe by CO raised this value by about 0.5 V per isocyanide. Qualitatively these data were rationalized by consideration of the ligand donor and acceptor properties; supporting this, a remarkably good linear correlation of $E_{1/2}$ values with calculated HOMO energies was found [4].

The $E_{1/2}$ values measured for the isomeric *cis*- and *trans*-$[Mn(CO)_2(CNMe)_4]PF_6$ and *mer*- and *fac*-$[Mn(CO)_3(CNMe)_3]PF_6$ complexes were found not to be the same; the difference of $E_{1/2}$ values between isomers was about 0.2 V (Table 2). This fact is not surprising in view of a similar observation made recently for the complexes *cis*- and *trans*-$M(CO)_2(DPE)_2$ (DPE =

TABLE 2

VOLTAMMETRIC DATA AND CALCULATED HOMO ENERGY VALUES

Compound	$\frac{1}{2}[E_{p,c} + E_{p,a}]$ [a] (V)	$E_{p,c}$—$E_{p,a}$ (mV)	HOMO energy [b]
cis-$[Mn(CO)_2(CNMe)_4]PF_6$	1.44	200	—10.62 ev
trans-$[Mn(CO)_2(CNMe)_4]PF_6$	1.28	270	—10.19 ev
fac-$[Mn(CO)_3(CNMe)_3]PF_6$	1.90	200	—11.86 ev
mer-$[Mn(CO)_3(CNMe)_3]PF_6$	1.73	270	—11.45 ev

[a] Cathodic and anodic peak potentials in volts vs. SCE (aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3} *M*) with Bu_4NClO_4 (0.1 *M*) as supporting electrolytes. All processes are 1*e* oxidations [1]; none meet the defined criterion for electrochemical reversibility, i.e., $E_{p,c}-E_{p,a} < 0.059$ V. [b] Calculated by the method given in ref. 4.

1,2-bis(diphenylphosphino)ethane, M = Cr, Mo, W.). In this cited work a qualitative rationale was provided for $E_{1/2}$ differences based on preferential π-bonding to the carbonyls [5]. We can now provide quantitative substantiation for this explanation from calculations for the isomeric complexes prepared in this study. For example, for $[Mn(CO)_2(CNMe)_4]^+$ complexes the calculated HOMO energy for the *trans* isomer is —10.19 eV, compared with —10.62 eV for the *cis* species (Table 2). The basis for the higher oxidation potential in the *cis* over the *trans* isomer becomes obvious when one considers the character of the HOMO in each case. In the *trans* complex (defining CO along the z axis) the HOMO orbital is determined to be 74.5% $3d_{xy}$ and 23.6% CNMe 3e ($\pi^\star$) character. The d_{xz} and d_{yz} orbitals both participate in π-bonding to CO, and are at lower energy as a consequence. In the *cis* isomer, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ all are capable of π-bonding to the carbonyls. The HOMO (defining CO along y and z axes) is a composite of metal (35.2% d_{xy}, 34.8% d_{xz}), carbonyl (10.8% 2π), *cis*-isocyanide (11.5% 3*e*) and *trans*-isocyanide (5.5% 3*e*). The conclusion to be drawn is that π-bonding to the CO group is a major factor in the stabilization of this orbital.

Calculations on *mer*- and *fac*-$[Mn(CO)_3(CNMe)_3]^+$ showed the same effect, with the *mer* isomer being found to be the easiest to oxidize.

These calculations point out that the difference in $E_{1/2}$ values for isomeric complexes is crucially related to relative donor—acceptor capabilities of the ligands. Obviously isomeric complexes of other ligands will be expected to show either greater or lesser differences in $E_{1/2}$ values. These results can be more or less predicted with a foreknowledge of ligand characteristics, derived from infrared or other electrochemical data.

Finally, we note the recent appearance of an interesting paper [6] which delineates a qualitative relationship between E^0 values and two parameters, the first defining the nature of the ligand and the second defining the degree of substitution. Our work suggests that if this approach is to be used it might be appropriate to include a third parameter, albeit of lesser importance, defining complex geometry.

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