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Notes

Crystal Structure of [PPN$^+$][Cr(CO)$_4$NO$^-$]: Calculations and Comparisons of Cr(CO)$_4$NO$^-$ with Mn(CO)$_5^-$

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Summary: The crystal structure of the deep red crystalline salt PPN$^+$Cr(CO)$_4$NO$^-$ has been determined and can be described as a distorted trigonal bipyramid. As expected, the NO group is equatorial, and the major distortion in Cr(CO)$_4$NO$^-$ involves the axial CO groups, with an angle C_{ax}−Cr−C_{ax} of 159.08(17)°. These CO groups form this reduced angle by bending away from the NO group. This distorted structure is not primarily due to lattice effects, since high-level MO calculations show a similar geometry for the Cr(CO)$_4$NO$^-$ part by itself. These MO calculations were also carried out on Mn(CO)$_5^-$, and as expected this anion is quite fluxional. In contrast, we were unable to find any other low-energy geometry for Cr(CO)$_4$NO$^-$.

The chromium metalate Cr(CO)$_4$NO$^-$, as the PPN$^+$ (bis(triphenylphosphoranylidene)ammonium) salt, is a readily available compound.[1] In solution it has proven to be an extremely reactive reagent for converting α-bromoacyl chlorides into ketenes or 1,3-dibromo ketones into cyclopropanones.[2] For example, in CH$_2$Cl$_2$−CHFCl$_2$ mixed solvent some of these reactions are virtually instantaneous even at −120 °C, so that very thermally unstable cyclopropanones can be observed in situ by NMR spectroscopy.[3]

The isoelectronic Mn(CO)$_5^-$ is considerably less reactive than Cr(CO)$_4$NO$^-$ in accomplishing these 1,3-dihalo elimination reactions,[2a] and we were interested in probing whether there was a structural basis for this. There are a number of X-ray studies involving Mn(CO)$_5^-$ salts, but none involving Cr(CO)$_4$NO$^-$, although solution IR studies indicate a trigonal bipyramid geometry.[1]

In addition to determining the crystal structure of Cr(CO)$_4$NO$^-$, we have calculated the structure of this anion using ab initio MO methods and have compared this calculated structure with both the crystal structure of Cr(CO)$_4$NO$^-$ and calculated and experimental structures for the Mn(CO)$_5^-$ anion.

Experimental Section

The preparation of crystalline PPN$^+$Cr(CO)$_4$NO$^-$ was carried out under N$_2$ using vacuum line techniques,[1] starting with Cr(CO)$_6$ and PPN$^+$NO$_2^-$. Tetrahydrofuran solvent was distilled under nitrogen from sodium benzophenone ketyl. The salt PPN$^+$Cr(CO)$_4$NO$^-$ forms deep red crystals from THF−diethyl ether, which were stored under nitrogen at dry ice temperature. The crystalline salt can be handled in air for short periods of time (a few minutes). Crystallographic experimental details[4] are summarized in Tables 5−11 of the Supporting Information.

The MO calculations were carried out using the Gaussian 98 suite of programs,[5] implemented on DEC-alpha computers. The anion structures were first optimized using a B3LYP/6-31G* basis set and finally using an extended basis set, B3LYP/6-311+G**. Frequency calculations were carried out on all finalized structures, and ZPVE corrections have been applied to the energy values.[6] Details concerning the calculations are reported in Table 12, which is included as Supporting Information.

Results and Discussion

Crystal Structure of [PPN$^+$][Cr(CO)$_4$NO$^-$]. The structure contains discrete PPN$^+$ cations and

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[4] C$_{40}$H$_{30}$CrN$_2$O$_5$P$_2$, crystal dimensions (mm) 0.27 × 0.15 × 0.15, triclinic $P\bar{1}$, a = 10.6655(7) Å, b = 10.6964(7) Å, c = 16.7037(10) Å, α = 76.4327(12)°, β = 76.2614(11)°, γ = 83.2213(11)°, V = 1795.5 (2) Å^3, Z = 2, μ = 0.455 mm^{-1}, data collected at −80 °C on a Bruker P4/RA/SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å), R_1 = 0.0520 (on F_o for 4500 reflections with $F_o^2 \geq 2\sigma(F_o^2)$), wR_2 = 0.1308 (for all 7291 unique data).

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Table 1. Bond Distances[a] and Bond Angles[a] in the $Cr(CO)_4NO^-$ Portion of the X-ray Structure of $PPN^+Cr(CO)_4NO^-$

bond lengths (Å)			bond angles (deg) for $[Cr(CO)_4(NO)]^-$			
atom 1	atom 2	distance	atom 1	atom 2	atom 3	angle
Cr	N1	1.711(3)	N1	Cr	C2	121.34(15)
Cr	C2	1.867(4)	N1	Cr	C3	99.39(16)
Cr	C3	1.878(4)	N1	Cr	C4	115.69(16)
Cr	C4	1.857(4)	N1	Cr	C5	101.16(16)
Cr	C5	1.866(4)	C2	Cr	C3	85.59(15)
Nl	O1	1.187(4)	C2	Cr	C4	122.96(17)
O2	C2	1.152(4)	C2	Cr	C5	87.09(16)
O3	C3	1.155(4)	C3	Cr	C4	84.88(17)
O4	C4	1.166(4)	C3	Cr	C5	159.08(17)
O5	C5	1.151(4)	C4	Cr	C5	82.73(17)
			Cr	N1	O1	178.2(3)
			Cr	C2	O2	177.9(4)
			Cr	C3	O3	178.0(4)
			Cr	C4	O4	177.5(4)
			Cr	C5	O5	177.2(3)

[a] Atoms are numbered as shown in Figure 1.

$Cr(CO)_4NO^-$ anions, separated by normal van der Waals distances, and the interatomic distances and angles for the $Cr(CO)_4NO^-$ part are given in Table 1. For the $[Cr(CO)_4(NO)^-]$ anion, the nitrogen atom was assigned as such based mainly on the observed distances about the chromium center, where the Cr−N1 distance (1.711(3) Å) is 0.146 Å less than the smallest of the Cr−C distances, which agree within a range of 0.021 Å (1.857(4)−1.878(4) Å). Less dramatic but still notable is the difference between the O1−N1 distance (1.187(4) Å) and the O−C distances (1.151(4)−1.166(4) Å). Refinement with any one of the carbonyl carbons reassigned as nitrogen, with concomitant reassignment of N1 as a carbon atom, leads to a noticeably poorer model; in the *least* severe case, assignment of C2 as a nitrogen atom (with N1 as carbon) shortens the original Cr−N1 distance by 0.012 Å, lengthens the original Cr−C2 distance by 0.015 Å (both opposite of the expected effect), decreases the equivalent isotropic displacement parameter (U_{eq}) for N1 (originally 0.0568(8) Å^2) by 0.0176 Å^2, increases the U_{eq} for C2 (originally 0.0520(9) Å^2) by 0.0245 Å^2, and results in higher observed residual indices for the converged refinement ($R_1 = 0.0554$, $wR_2 = 0.1457$).

The $Cr(CO)_4NO^-$ anion (see Figure 1) is best described as a trigonal bipyramid, with the nitrosyl group occupying an equatorial position. However, there is considerable distortion from the idealized geometry, the $C_{ax}-Cr-C_{ax}$ angle being only 159.08(17)°, with the axial CO groups directed away from the NO group in a plane approximately bisecting the two equatorial CO groups. In the equatorial plane there are two slightly larger angles, N1−Cr−C2 and C2−Cr−C4 at 121.34(15)° and 122.96(17)°, respectively, and one smaller, N1−Cr−C4 = 115.69(16)°. The equatorial and axial Cr−C bond lengths are almost equal, 1.872 (av) vs 1.862 (av).

These parameters can be compared to those of the isoelectronic $Mn(CO)_4NO$ and $Mn(CO)_5^-$ structures. The former is reported[7] to have a structure very close to an idealized trigonal bipyramid, $C_{ax}-Mn-C_{ax} = 179.6°$, and the equatorial angles are all 120 ± 1°. The anion $Mn(CO)_5^-$ has been part of a number of X-ray structures. In all cases except one, the $Mn(CO)_5^-$ structure is a slightly distorted trigonal bipyramid.[8] The exception[9] is a recent square-pyramidal geometry ($PPh_4^+Mn(CO)_5^-$) in which the metal atom sits somewhat above the square formed by the four carbonyl ligands, i.e., toward the apical CO group.

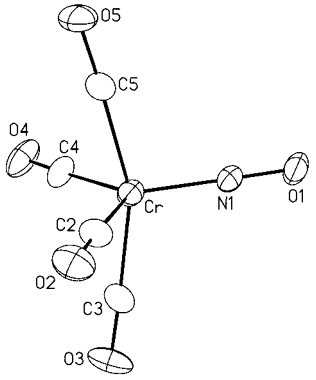

Figure 1. Perspective view of the $[Cr(CO)_4(NO)]^-$ complex ion showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

The structural variations observed in X-ray determinations of $Mn(CO)_5^-$ salts are an indication that this anion is easily distorted from a pure trigonal bipyramid geometry, presumably by crystal lattice and electrostatic factors, and this conclusion is augmented by high-level MO calculations, which yield a D_{3h} trigonal bipyramidal ground-state structure for the anion by itself. One can then ask whether the distorted $Cr(CO)_4NO^-$ structure in the PPN^+ salt, like $Mn(CO)_5^-$ crystal structures, is being affected by lattice and electrostatic considerations.

Although we have not found a second low-energy conformation for $Cr(CO)_4NO^-$, it should be noted that the ^{13}C NMR spectrum shows a single ^{13}C resonance at δ 251.25, an indication that there is a relatively low-energy transition state allowing the CO groups to become equivalent.

MO Calculations of $Mn(CO)_5^-$ and $Cr(CO)_4NO^-$ Anions. Chen et al.[10] have recently reported DFT calculations on $Mn(CO)_5^-$. In our work we have used a B3LYP/6-311+G** basis set (Gaussion 98) and, like the above authors, find a trigonal bipyramid ground state. Our bond lengths are very similar to those reported in the various X-ray structures, as shown in Table 2 (ref 8a data used for comparison). The C_{4v} structure of $Mn(CO)_5^-$ was also calculated at the same level and produced a structure with one imaginary frequency (40.0i). The geometry of this structure is in good agreement the C_{4v} X-ray structure of ref 9, as shown in Table 3. Our calculated results also compare well with the C_{4v} geometry calculated by Chen et al. The calcu-

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Table 2. Comparison of Calculated and Observed Structure Parameters for Mn(CO)$_5^-$ (Trigonal Bipyramid)

	Calc.[c]	X-ray Structure[c,d]	
Mn–C$_{ax}$	1.820	1.832 1.802	1.817
Mn–C$_{eq}$	1.798	1.791 1.818 1.804	1.804
C≡O$_{ax}$	1.153	1.143 1.162	1.152
C$_{eq}$≡O$_{eq}$	1.155	1.153 1.154 1.155	1.154
C$_{eq}$–Mn–C$_{eq}$	120	117.5 117.6 125.0	
C$_{ax}$–Mn–C$_{ax}$	180	178.2	
C$_{ax}$–Mn–C$_{eq}$	90	all 90 ± 2	

[a] As described in the text. [b] Reference 8a. [c] Distances in Å. [d] Based on one of the two independent structures in the unit cell.

Table 3. Comparison of Calculated[a] and Observed[b] Structural Parameters for Mn(CO)$_5^-$ (Square Pyramidal)

	calcd[c]	X-ray structure[c]
Mn–C$_{ax}$	1.797	1.794
Mn–C$_{eq}$	1.828	1.809
C≡O$_{ax}$	1.163	1.155
C≡O$_{eq}$	1.162	1.159
C$_{ax}$–Mn–C$_{eq}$	103.9	102.6
C$_{eq}$–Mn–C$_{eq}$	86.7	87.3

[a] As described in the text. [b] Reference 9. [c] Distances in Å.

Table 4. Comparison of Calculated[a] and Observed Structural Parameters for Cr(CO)$_4$NO$^-$

	Calc.[b]	X-ray Structure[b]	
Cr–C$_{ax}$	1.899	1.878 1.866	1.872
Cr–C$_{eq}$	1.875	1.867 1.857	1.862
Cr–N	1.705	1.711	
C≡O$_{ax}$	1.157	1.155 1.151	1.153
C≡O$_{eq}$	1.163	1.152 1.166	1.159
N≡O	1.192	1.187	
C$_{ax}$–Cr–N	97.1	99.4 101.2	100.3
C$_{ax}$–Cr–C$_{eq}$	86.4	84.9, 85.6 87.1, 82.7	85.1
C$_{eq}$–Cr–N	121.0	121.3 115.7	118.5
C$_{eq}$–Cr–C$_{eq}$	118.0	123.0	

[a] As described in the text. [b] Distance in Å; error limits for distances are (4) and for angles (15–17).

lated energy difference between the trigonal bipyramid and C_{4v} structure of Mn(CO)$_5^-$ is only 1.66 kcal/mol, an energy difference that can obviously be surmounted by favorable lattice and electrostatic forces in Mn(CO)$_5^-$ PPh$_4^+$. Chen et al. report 3.02 kcal/mol for this energy difference. A D_{3h} and C_{4v} structural interconversion in a pentacoordinated metal involves a Berry rotation, so that in cases where these two geometries have similar energies there is expected to be almost no energy barrier associated with intermediate geometries.

The geometry calculated for Cr(CO)$_4$NO$^-$ in point group C$_s$ bears a fairly close correspondence to the X-ray structure reported here, as shown in Table 4. With reference to Figure 1, the largest differences relate to the bond angle C$_{eq}$–Cr–C$_{eq}$, where this angle is 122.96(17)° vs a calculated 118°. The more important distortion angle, C$_{ax}$–C–N, is 100.3° (av) vs 97.1° calculated. However, the parameter matches are sufficiently close that one can conclude that the X-ray structure of Cr(CO)$_4$NO$^-$ is not being distorted from an intrinsic trigonal bipyramid geometry by lattice or electrostatic forces. The likelihood of this was not inconceivable given the near trigonal bipyramid geometry of the neutral molecule Mn(CO)$_4$NO.

Behavior of Mn(CO)$_5^-$ and Cr(CO)$_4$NO$^-$ as Nucleophiles or Bases. Mn(CO)$_5^-$ has a dual personality as a solution nucleophile. It is a moderately good conventional (S$_N$2) nucleophile,[11] e.g., reaction with CH$_3$I. However, it also functions moderately well in the reactions discussed in the Introduction and in other related cases, e.g., where an α-bromo ester reacts to form Mn(CO)$_5$Br and enolate.[12]

In the gas phase Mn(CO)$_5^-$ exhibits a very low cross-section for proton capture, as compared to chloride ion. The suggested[13] rationalization of this is that the lone pair in the D_{3h} trigonal bipyramid geometry of Mn(CO)$_5^-$ is not "stereochemically active".

In contrast to this gas-phase result and given the recent X-ray observation of a C_{4v} Mn(CO)$_5^-$PPh$_4^+$ crystal structure, together with the quite small energy difference calculated for the C_{4v} vs D_{3h} geometry for Mn(CO)$_5^-$, it seems reasonable to suppose that a conventional solution nucleophilic substitution reaction of Mn(CO)$_5^-$ could involve a C_{4v} geometry in which the lone pair is "stereochemically active". This D_{3h}–C_{4v} reorganization could occur within the transition-state complex of the S$_N$2 reaction, but it is also possible that

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in solution and with counterion present there may be an actual $D_{3h} \rightleftharpoons C_{4v}$ equilibrium.

It is apparent from the Gladfelter work[1] that $Cr(CO)_4NO^-$ is a poor S_N2 nucleophile, and there is some computational evidence that may relate to this point. Starting with a C_{4v}-like geometry (in C_1 symmetry), the optimization eventually returns to the distorted trigonal bipyramid structure previously discussed. Optimization in a C_{4v} point group (NO axial) consistently failed at the SCF convergence level (unlike $Mn(CO)_5^-$). This failure to find a low-energy C_{4v} structure for $Cr(CO)_4NO^-$ may account for the marked difference in S_N2 nucleophilicity between $Mn(CO)_5^-$ and $Cr(CO)_4NO^-$.

In contrast to the above and related to our experimental work reviewed in the Introduction, the use of $Mn(CO)_5^-$ or $Cr(CO)_4NO^-$ in removing "Br^+" from dibromoketones or α-bromoacyl halides almost certainly involves SET processes,[14] specifically a single electron transfer from the metalate anion into the σ* C−Br bond. Obviously the redox properties of the metalate anion can be an additional factor in these reactions.

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Supporting Information Available: A listing of all X-ray crystal data and MO computation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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