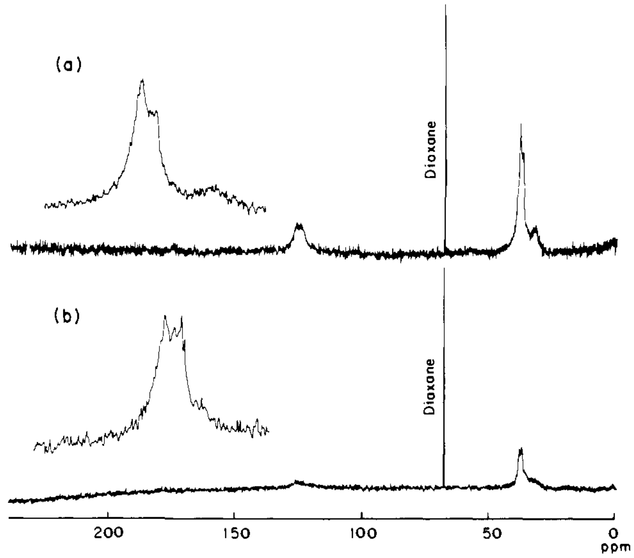

Figure 4. Carbon-13 NMR spectra of pheomelanin prepare by polyphenol oxidase polymerization of (a) **5a** and (b) [3-^{13}C]dopa and cysteine.

[β-^{13}C]-5-*S*-CD, are shown in Figure 4.[17] From these spectra it is apparent that there are two different types of carbons, (1) benzylic-type carbons indicated by the envelope of signals at ca. 35 ppm and (2) either aromatic or olefinic carbons indicated by the envelope of signals at 125 ppm. By comparison with model compounds, partial structures such as **9** and **10** could be predited to exhbit chemical shifts in the regions of 125 and 35 ppm and as such could be proposed to be possible partial monomer units in the pheomelanin polymer. While we cannot be sure that the two signals represent 100% of the tagged carbons, these results indicate that the loss of tritium documented during the biosynthesis can, in a large part, be attributed to dehydration to a structure such as **9** and not oxidation of a carbonyl, e.g., **11**, or simple exchange processes.

In comparing the NMR spectra of SP and 5-*S*-CP, it is apparent that the two pheomelanins are similar. However, it is also apparent that the spectrum of 5-*S*-CP is more defined, most likely due to a greater homogeneity of 5-*S*-CP. From these NMR studies, we conclude that (1) under suitable conditions it is possible to obtain NMR spectra of pheomelanins and to assess the type of possible units associated with a particular carbon, (2) the benzylic carbon of the alanyl side chain does not undergo extensive chemical alteration during polymerization, and (3) the loss of tritium from the β-carbon position of the alanyl side chain in the radiolabeled studies can be attributed to oxidation of the 3-position to an sp^2 carbon.

In conclusion, we have demonstrated that (1) CP polymers are more homogeneous that these from dopa and cysteine and will serve as good models for further biosynthetic studies, (2) during the biosynthesis of pheomelanin there is a significant loss of tritium from the benzylic position of 5-*S*-CD which, by carbon-13 NMR studies, corresponds to formation of an sp^2 carbon in the alanyl side chain, and (3) there appears to be a small amount of degradation of both the alanyl and cysteinyl side chains during biosynthesis, which contributes to the heterogeneity of the polymer. These results reinforce our contention that the harsh degradative methods used during the initial studies on the structure of pheomelanin led to the production of artifacts, and the structure of pheomelanin proposed by Minale et al.[6-8] does not accurately represent the structure of the intact chromophore.

Acknowledgment. This work was supported in part by the NIH (AG-02380 and AG-02381, NIOSH core support of the Center for Occupational and Environmental Health Contract No. 250-80-500) and The Johns Hopkins School of Hygiene and Public Health.

Registry No. **3**, 90140-57-1; **4**, 91384-88-2; **5**, 25565-25-7; **6**, 25565-17-7; **7**, 57954-84-4; 4-bromoveratrole, 2859-78-1; polyphenol oxidase, 9002-10-2.

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(17) The chemical shifts of the carbons in 5-*S*-cysteinyldopa are 171.5, 170.3, 145.6, 127.7, 127.5, 119.5, 118.9, 54.8, 53.1, 35.5, and 34.8 ppm and were assigned by comparison with chemical shifts for L-tyrosine, L-cysteine, L-dopa, and L-*3*-*S*-cysteinylcatecol.

Theoretical Study of the Metal Chemical Shift in Nuclear Magnetic Resonance Spectroscopy. Mn Complexes

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Abstract: The ^{55}Mn nuclear magnetic shielding constants of the Mn complexes, Mn(CO)$_5$L (L = H, CN, CH$_3$, Cl), are studied by the ab initio finite perturbation SCF-MO method. The ^{55}Mn chemical shifts are determined predominantly by the 3d contributions of the paramagnetic term. This is because the Mn atom has an open 3d shell. This is in sharp contrast to the previous results for the complexes of the Cu, Zn, Ag, and Cd metals which have d^{10}s$^{1-2}$p^0 configuration. The 3d contribution of the Mn complexes arises from the d-d excitations. The chemical shift is determined by the effects of the ligand on these occupied and unoccupied d orbitals. It increases with the increases in the π-donating ability and the hardness of the ligand base. For the diamagnetic term, which is a minor part of the chemical shift, the Pascal rule like formula applies as for the 1B and 2B metal complexes.

In the previous study of this series,[1] we have studied theoretically the metal NMR chemical shifts for the Cu, Zn, Ag, and Cd complexes. We have used the ab initio finite perturbation method. The results of the calculations compared well with the experimental chemical shifts. We have clarified the mechanism of the metal chemical shift in these d^{10}s$^{1-2}$p^0 metal complexes. The paramagnetic term is a major part of the chemical shift and is due to the d and p mechanisms. The former is due to the hole produced in the valence d shell of the metal by the electron-withdrawing ligands. The latter is due to the electrons in the valence p orbitals of the metal transferred from the electron-donating ligands. For

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Table I. Molecular Geometries

parameter	value[a]
$r(\text{Mn–C}_{ax})$	1.86[b]
$r(\text{Mn–C}_{eq})$	1.86[b]
$r(\text{C–O})$	1.14[b]
$\angle \text{CO}_{ax}\text{MnCO}_{eq}$	95[b]
$r(\text{Mn–H})$	1.50[c]
$r(\text{Mn–CN})$	1.98[d]
$r(\text{Mn–CH}_3)$	2.15[e]
$r(\text{Mn–Cl})$	2.37[f]
$r(\text{C–N})_{\text{cyanide}}$	1.16[d]
$r(\text{C–H})_{\text{methyl}}$	1.096[g]
$\angle(\text{HCH})_{\text{methyl}}$	109.5[g]

[a] In angstroms for the distances and in degrees for the angles. [b] We used the average values observed for $Mn(CO)_5H$, $Mn(CO)_5CH_3$, and $Mn_2(CO)_{10}$ in ref 21. [c] Reference 14a. [d] Reference 14b. [e] The sum of the covalent radii (Mn: ref 15a; C: ref 15b). [f] Reference 15c. [g] Reference 22.

the Cu complexes, the d mechanism is dominant, for the Zn and Cd complexes, the p mechanism is more important than the d mechanism, and for the Ag complexes, the p and d mechanisms are competitive. These differences in the mechanism have explained the trends in the observed and calculated metal chemical shifts. They were attributed to the differences in the atomic s, p, and d energy levels of the metals. For the diamagnetic term, which is a minor part of the chemical shift, we found a simple Pascal rule like formula.

In this paper we apply the same method to analyze the ^{55}Mn NMR chemical shifts. The manganese belongs to the 7A group in the periodic table, and it has $3d^54s^2p^0$ configuration in the ground state of the free atom. It is expected that the d contributions in the Mn complexes are larger than those of the above d^{10} metals. The purpose of this paper is to clarify the mechanisms for the Mn chemical shift, which would be different from those for the 1B and 2B metals.

The complexes studied here are the series of substituted manganese carbonyls, $Mn(CO)_5L$ (L = H, CN, CH_3, Cl). They are in the group of the diamagnetic Mn compounds, though many Mn compounds are paramagnetic. The experimental Mn chemical shifts of these complexes were reported by Calderazzo, Lucken, and Williams[2] except for the CN complex, for which no experimental value is reported for the Mn chemical shift.

Method

The details of the calculations were described in the previous paper.[1] The magnetic shielding constant can be divided into the diamagnetic term and the paramagnetic term. Though the diamagnetic term, which is the first-order perturbation term, can be obtained easily, the paramagnetic term, which is the second-order perturbation term, requires a calculation of the perturbed wave function. For this purpose, various perturbation theoretical studies which were in the different approximation levels have been reported.[3-9] We used the finite perturbation method[10] to calculate the paramagnetic term.

The SCF calculations were carried out with a modified version of the HONDOG program.[11] The gauge origin of the magnetic field was chosen at the position of the metal nucleus. The basis set we used is the MIDI-1 set for manganese[12] and the MINI-1 set for the ligands.[13] As the manganese 4p orbitals, we added two single primitive Gaussians, whose exponents are 0.13 and 0.03511.

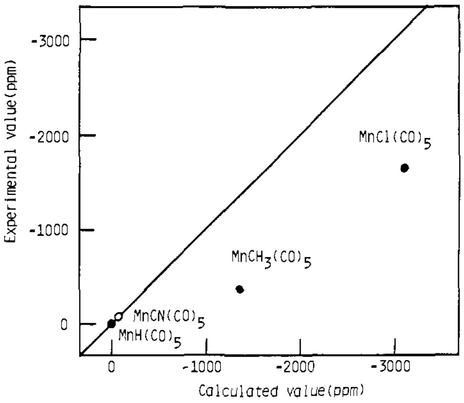

Figure 1. Comparison between experimental and calculated values for ^{55}Mn magnetic shielding constants in manganese complexes. For the $Mn(CO)_5CN$ complex, no experimental data have been reported, so the open circle shows only the calculated value.

The geometries of the Mn complexes adopted here are summarized in Table I. The geometry of the $Mn(CO)_5$ part of the complexes was fixed for all the complexes studied here. For the distances between the Mn and the ligand L, we adopted the experimental values[14] except for the $Mn(CO)_5CH_3$. For this complex, we adopted the sum of the covalent radii.[15]

^{55}Mn Chemical Shift and Its Electronic Origin

Figure 1 shows the correlation between the present theoretical results and the experimental data for the chemical shift in the ^{55}Mn nuclear magnetic resonance of the manganese carbonyl derivatives. All of the experimental data were measured in the tetrahydrofuran solutions.[2] Both of the calculated and observed chemical shifts are shown relative to the $Mn(CO)_5H$ complex. The chemical shift of the $Mn(CO)_5CN$ complex has not yet been reported, so the open circle in Figure 1 shows only the theoretical value. In Figure 1, the present theoretical values are in fair correlation with the experimental data, though the theoretical values tend to overestimate the experimental values.

Table II shows the diamagnetic and the paramagnetic terms of the Mn shielding constants and their analyses into the core and valence MO contributions. They are shown for the four complexes studied here. For the diamagnetic term, the core MO contribution is a major part (about 85%). Though the absolute values of σ^{dia} are large, their contributions to the chemical shifts are small. This is due to a transferability of the core MO's of Mn and CO, as shown below. This result is the same as those for the 1B and 2B metal complexes reported previously.[1] For the paramagnetic term, the valence MO contributions are about 100 times larger than the core MO contributions. This is in the same trend as that for the 1B and 2B metals,[1] though the valence MO contributions for the Mn complexes studied here are much larger than those for the 1B and 2B metal complexes. Thus, the total magnetic shielding constants and the chemical shifts of the manganese are almost completely determined by the valence MO contributions to the paramagnetic term. Since the valence MO's are most likely to suffer the changes in the chemical environments, the chemical shifts are mainly determined by the valence MO contributions.

In the following paragraphs, we first discuss the diamagnetic term and then the paramagnetic term. Though the former is a

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Table II. Diamagnetic and Paramagnetic Contributions, σ^{dia}_{Mn} and σ^{para}_{Mn}, to ^{55}Mn Magnetic Shielding Constants, σ_{Mn}, and Their Analysis into Core and Valence MO Contributions (In ppm)

	σ^{dia}				σ^{para}				σ	
molecules	core	valence	total	shift	core	valence	total	shift	total	shift
$Mn(CO)_5H$	1889	318	2207	0	−141	−12927	−13068	0	−10861	0
$Mn(CO)_5CN$	1905	345	2249	42	−123	−13059	−13182	−114	−10933	−72
$Mn(CO)_5CH_3$	1898	339	2237	30	−130	−14327	−14457	−1389	−12220	−1359
$Mn(CO)_5Cl$	1929	339	2267	60	−91	−16149	−16240	−3172	−13973	−3112

Table III. An Analysis of the Diamagnetic Term σ^{dia}_{Mn} into the Metal AO and Ligand Contributions[a] (In ppm)

	Mn				Ligand			σ^{dia}_{Mn} total	
molecules[b]	s	p	d	sum	CO_{ax}	$4CO_{eq}$	L	ab initio	from eq 1
$Mn(CO)_5H$	1107	708	100	1915	57	228	7	2207	2206
$Mn(CO)_5CN$	1106	706	101	1913	57	227	52	2249	2249
$Mn(CO)_5CH_3$	1106	707	100	1913	57	227	39	2237	2236
$Mn(CO)_5Cl$	1106	707	101	1914	57	227	69	2267	2270

[a] The last two columns show the total values of σ^{dia}_{Mn} obtained by the present ab initio method and by the Pascal rule like formula, eq 1. [b] $Mn(CO)_5L$.

Table IV. Single Ligand Contributions to the Diamagnetic Term, $\sigma^{dia}(L)$, Used in the Pascal Rule Like Formula, Equation 1 (In ppm)

ligand	$\sigma^{dia}(L)$	ligand	$\sigma^{dia}(L)$
H	7	NH_3	43
CH_3	37	OH_2	40
CN	50	F	46
CO	57	Cl	71

Table V. Analysis of the Paramagnetic Term of the Metal, σ^{para}_{Mn}, into the Metal AO and Ligand Contributions (In ppm)

	Mn		Ligand		
molecules[a]	p	d	CO_{ax}	$4CO_{eq}$	L
$Mn(CO)_5H$	−129	−12983	10	30	4
$Mn(CO)_5CN$	−75	−13138	7	24	3
$Mn(CO)_5CH_3$	−106	−14385	9	27	−2
$Mn(CO)_5Cl$	1	−16276	8	24	3

[a] $Mn(CO)_5L$.

minor term, it follows an interesting formula, Pascal rule like formula, as for the 1B and 2B metal complexes.[1]

Table III shows the metal AO contribution and the ligand contribution to the diamagnetic term of the Mn shielding constant. The contributions from the Mn AO's are almost constant against the change of the axial ligand L. This is so even for the d orbitals which are the valence AO's. This fact corresponds to the fact that the complexes studied here have almost the same AO populations. (See Table VII.) The CO ligand contribution is 57 ppm per one ligand for both axial and equatorial ligands. The so-called "trans" effect of the axial ligand L does not appear for this quantity. The contributions from the axial ligand L are almost of the same values as those for the 1B and 2B metal complexes studied previously, despite of the differences of the central metals. Thus, the diamagnetic term is summarized in a Pascal rule like formula,

$$\sigma^{dia}_{Mn} = \sigma^{dia}(s_{Mn}) + \sigma^{dia}(p_{Mn}) + \sigma^{dia}(d_{Mn}) + \sum_{L} n_L \sigma^{dia}(L) = \sigma^{dia}(Mn) + \sum_{L} n_L \sigma^{dia}(L) \tag{1}$$

where the s contribution of Mn, $\sigma^{dia}(s_{Mn})$, is 1106 ppm, the p contribution, $\sigma^{dia}(p_{Mn})$, is 707 ppm, and the d contribution, $\sigma^{dia}(d_{Mn})$, is 101 ppm. These AO contributions of Mn are summarized into $\sigma^{dia}(Mn)$, which is 1914 ppm. Table IV summarizes the ligand contributions, $\sigma^{dia}(L)$, which were obtained by the previous and the present calculations. In the last two columns of Table III, we examined the validity of the Pascal rule like formula for the diamagnetic terms. The values calculated by eq 1 show an excellent agreement with the diamagnetic terms obtained by the ab initio calculations.

We now study the paramagnetic term which is dominant for the Mn chemical shift. Table V shows the metal AO contributions and the ligand contributions to the paramagnetic term. The metal d orbital plays a central role in the chemical shift. The metal p contribution and the ligand contributions are negligibly small. This fact is in sharp contrast to the case of the 1B and 2B metals which have d^{10} subshells. For the Cu complexes which belong to the 1B group, the d contributions were larger than the p contributions, but the ratio was about 20 even for the CuCl complex which was the largest one studied.[1] For the Cd and Zn complexes, the p contribution was larger than the d contribution, and for the Ag complexes, two contributions were competitive. For the Mn complexes studied here, the d contributions are at least 100 times larger than the p contributions. This means that the d contribution is essential for the Mn NMR chemical shift. The same would be true for the complexes of the transition metals which have incompletely occupied d subshells.

The mechanism of the d contributions in the $Mn(CO)_5L$ complexes is interesting. In Table VI, we analyzed the d contributions of the Mn shielding constants in more detail. The 3d contributions consist of the $3d_\sigma$, $3d_\pi$, $3d_{\delta1}$, and $3d_{\delta2}$ contributions. The $3d_\pi$ contribution is a sum of the contributions of the $3d_{xz}$ and $3d_{yz}$ AO's, which are degenerate. The *z* axis is parallel to the Mn–L bond. The $3d_\sigma$ is $3d_{z^2}$, $3d_{\delta1}$ is $3d_{xy}$, and $3d_{\delta2}$ is $3d_{x^2-y^2}$ in this coordinate system. Figure 2 illustrates these d orbitals. The nomenclature of the 3d orbitals is due to the symmetry with respect to the bond between the Mn and the axial ligand L. Table VI shows that the chemical shift due to the ligand L is primarily determined by the $3d_\sigma$ and $3d_\pi$ contributions. The contributions of the $3d_\sigma$ and $3d_{\delta2}$ orbitals show the same tendency that the paramagnetic shift increases on going down the rows of the table. For the $3d_\pi$ orbital, the same tendency is seen except for the CN

Table VI. Mn 3d Contributions to the Paramagnetic Shifts, $\Delta\sigma^{para}_{Mn}$ (In ppm)

	3d contributions[a]									
	$3d_\sigma$		$3d_\pi$		$3d_{\delta1}$		$3d_{\delta2}$		total	
molecules	value	shift	value	shift	value	shift	value	shift	value	shift
$Mn(CO)_5H$	−2669	0	−5313	0	−2453	0	−2548	0	−12983	0
$Mn(CO)_5CN$	−3009	−340	−5272	41	−2262	191	−2595	−47	−13138	−155
$Mn(CO)_5CH_3$	−3295	−626	−5988	−675	−2460	−7	−2641	−93	−14384	−1401
$Mn(CO)_5Cl$	−4361	−1692	−6865	−1552	−2318	135	−2732	−184	−16276	−3293

[a] $3d_\sigma = 3d_{z^2}$, $3d_\pi = 3d_{xz}$, $3d_{yz}$, $3d_{\delta1} = 3d_{xy}$, $3d_{\delta2} = 3d_{x^2-y^2}$, in the coordinate system shown in Figure 2.

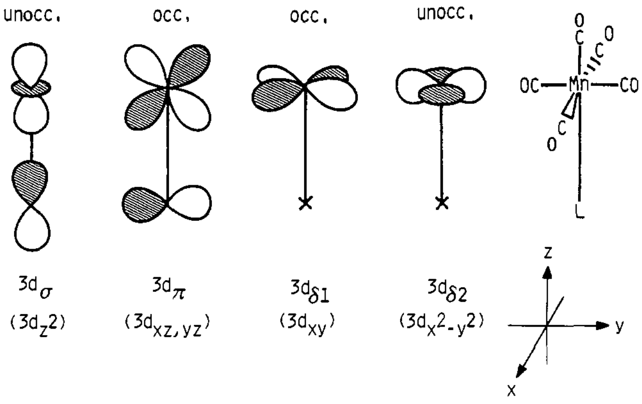

Figure 2. Illustration of the manganese 3d and ligand orbitals.

Table VII. Mn Valence AO Populations

AO	L = H	L = CN	L = CH_3	L = Cl
$3d_\sigma$	0.39	0.28	0.29	0.22
$3d_\pi$	3.16	3.24	3.24	3.34
$3d_{\delta 1}$	1.41	1.45	1.40	1.43
$3d_{\delta 2}$	0.26	0.26	0.26	0.26
3d total	5.22	5.23	5.19	5.25
4s total	−0.04	−0.16	−0.13	−0.10
4p total	0.42	0.13	0.19	0.19
Mn net charge	+1.38	+1.80	+1.76	+1.63
L net charge	−0.07	−0.68	−0.49	−0.48

ligand. For the $3d_{\delta 1}$ orbital, the contribution is positive for the CN and Cl ligands.

The d contributions shown in Table VI are further analyzed in terms of the transitions involved in the second-order perturbation theory. As seen from the population analysis shown in Table VII, the $3d_\pi$ and $3d_{\delta 1}$ orbitals are occupied but the $3d_\sigma$ and $3d_{\delta 2}$ orbitals are almost empty. In Figure 3, we have shown the energy levels and the qualitative natures of the MO's of the Mn complexes. The $3d_{\delta 1}$ ($3d_{xy}$) and $3d_\pi$ ($3d_{xz}$, $3d_{yz}$) AO's appear in the HOMO or next-to-HOMO regions and the $3d_\sigma$ ($3d_z{}^2$) and $3d_{\delta 2}$ ($3d_{x^2-y^2}$) AO's appear in the unoccupied level, in accordance with the population analysis shown in Table VII. This splitting of the d orbitals is the same as that expected from the ligand field theory for the distorted octahedral environment. The MO level diagram shown in Figure 3 agrees roughly qualitatively with those obtained by Gray et al.[16] from the empirical argument. The unoccupied d orbitals are higher in our diagram than in the diagram of Gray. In a perturbation theoretic viewpoint, the 3d contribution to the Mn chemical shift arises from the transitions from the occupied d orbitals to the unoccupied d orbitals.

Between the occupied MO's localized on the $3d_\pi$ and $3d_{\delta 1}$ AO's and the unoccupied MO's localized on the $3d_\sigma$ and $3d_{\delta 2}$ AO's, there are four types of d–d transitions. They belong to the symmetry A_2 ($3d_{\delta 1} \rightarrow 3d_{\delta 2}$), B_2 ($3d_{\delta 1} \rightarrow 3d_\sigma$), E ($3d_\pi \rightarrow 3d_\sigma$), and E ($3d_\pi \rightarrow 3d_{\delta 2}$). Among these, the B_2 excitation does not contribute to the paramagnetic term, because the angular momentum operator belongs to the A_2 (lz) + E (lx,ly) symmetry. Further, for the complexes studied here, no δ bond exists between Mn and the axial ligand L. Therefore, the MO's of the δ symmetry do not interact directly with the ligand L so that their contribution to the chemical shift should be small. Thus, for the chemical shift, the excitations of the E symmetry, especially $3d_\pi \rightarrow 3d_\sigma$, are important. In Table VI we see that the $3d_\sigma$ and $3d_\pi$ contributions are much more important for the chemical shift than the $3d_{\delta 1}$ and $3d_{\delta 2}$ contributions.

The $3d_\pi$ orbital of Mn lies in the HOMO region, and its weight should increase as the ligand L becomes more π donating. Then, the paramagnetic contribution from the $3d_\pi$ orbital should increase (become more negative) in the order of CN < H < CH_3 < Cl, which is the order of an empirical π-donating ability. The $3d_\pi$ contributions given in Table VI certaintly show this order of change. We note, however, that this ordering is not seen in the $3d_\pi$ AO populations of the complexes, which are in the order of H < CN = CH_3 < Cl. This is probably due to an inadequate definition of the AO population.

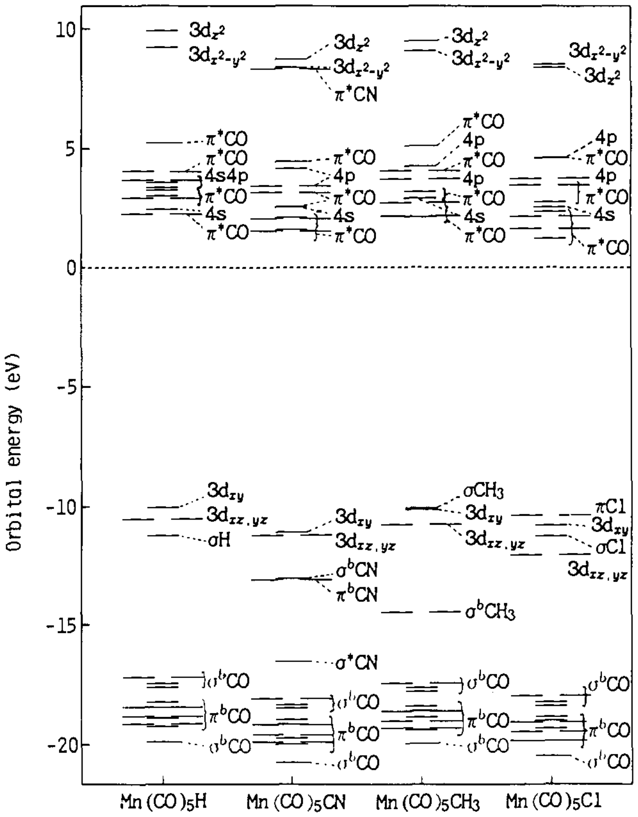

Figure 3. Orbital energy diagrams for the manganese complexes, Mn$(CO)_5L$ (L = H, CN, CH_3, Cl) ($3d_{z^2} = 3d_\sigma$, $3d_{xz,yz} = 3d_\pi$, $3d_{xy} = 3d_{\delta 1}$, $3d_{x^2-y^2} = 3d_{\delta 2}$.)

The $3d_\sigma$ orbital lies in an unoccupied MO. Its weight would increase as the interaction between the $3d_\sigma$ MO and the ligand decreases. In a limit of zero interaction, the coefficient of the $3d_\sigma$ orbital would become unity. Since $Mn(CO)_5{}^+$ is one of the typical soft Lewis acids, the interaction with the ligand L would increase as the softness of the ligand base increases. Therefore, the $3d_\sigma$ contribution to the paramagnetic chemical shift should increase (become more negative) as the softness of the ligand L decreases. Among the present complexes, the order is H^- = CN^- < $CH_3{}^-$ < Cl^-. From Table VI we see that the order of the $3d_\sigma$ contribution is H < CN < CH_3 < Cl which reflects the above reasoning.

We note that the calculated order of the chemical shift is not the order of the electronegativity, which is H (2.28) < CH_3 (2.3) < Cl (3.03) < CN (3.3).[17] The position of the CN ligand disagrees. For the $3d_\pi$ contributions, the π-donating ability is a good scale, and for the $3d_\sigma$ contributions, the hardness of the ligand base is a good scale. For the present complexes, the total chemical shift is in the order of the hardness of the ligand. However, it is generally important to consider both the π-donating ability and the hardness of the ligand base for the chemical shift of the $Mn(CO)_5L$ complexes.

Calderazzo et al.[2] explained the Mn chemical shift from the effects of the ligand on the excitation energies between the d orbitals. From the present calculations, however, there is no evident change in the difference of the occupied and unoccupied 3d orbital energies, though the orbital energy difference is a very poor approximation of the excitation energy. Indeed, even if we adopt frozen orbital approximation, the singlet excitation energy

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is $\Delta E_{i\rightarrow j} = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij}$, where ϵ, J, and K are orbital energy and Coulomb and exchange repulsion energies, respectively. Further, for transitions involving d orbitals, it is well known that the reorganization of electrons in the excited states is very large.[18] Thus, we have to compare Figure 3 with the semiempirical results of Gray et al.[16] with these points in mind.

As shown in Table VII, the Mn atom has the electron configuration $3d^{5.2}4s^04p^{0.2}$. In comparison with the electronic structure of the free Mn atom $3d^54s^24p^0$, the 4s electrons delocalize over the whole complex and the 3d and 4p orbitals accept electrons from the ligands. The net charge of Mn is +1.4 ~ +1.8, in comparison with the formal charge +1.0. For the $Mn(CO)_5H$ complex, the 4p population is larger than those of the other complexes. The radial maximum of the 4p orbital is near the proton of the $Mn(CO)_5H$ complex, so most of the 4p population should be assigned to the hydrogen atom, as Guest et al. mentioned.[19]

Conclusion

In this paper, we studied the ^{55}Mn nuclear magnetic shielding constants of the Mn complexes $Mn(CO)_5L$ (L = H, CN, CH_3, Cl). The results of the ab initio finite perturbation method compare fairly well with the experimental chemical shifts. The paramagnetic term is a major part of the chemical shifts. In contrast to the d^{10} metals studied previously,[1] the 3d contribution gives a predominant contribution to the paramagnetic term, since the manganese atom has an incompletely occupied 3d shell. In the perturbation theoretic viewpoint, the 3d contribution arises from the transitions from the occupied $3d_\pi$ orbital to the unoccupied $3d_\sigma$ orbital. From the analysis of the interactions between these d orbitals and the ligands L, it is shown that the chemical shift due to the ligand increases (becomes more negative) with the increases in the π-donating ability and the hardness of the ligand.

The diamagnetic term is a minor part of the chemical shift, but the Pascal rule like formula, eq 1, applies as in the case of the 1B and 2B metal complexes studied previously. The ligand contribution $\sigma^{\mathrm{dia}}(\mathrm{L})$ in eq 1 is the same independent of the metal to which the ligand coordinates.

After completion of this paper, the referee kindly noted that the Pasal rule like formula for the diamagnetic term shown in eq 1 is a rediscovery of an old discovery by Flygare and Goodisman in 1968.[20]

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Registry No. $Mn(CO)_5H$, 16972-33-1; $Mn(CO)_5CN$, 15602-37-6; $Mn(CO)_5CH_3$, 13601-24-6; $Mn(CO)_5Cl$, 14100-30-2; Mn, 7439-96-5.

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Electronic Structures and Reactivities of Metal–Carbon Multiple Bonds; Schrock-Type Metal Carbene and Metal Carbyne Complexes

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Abstract: The electronic structures and reactivities of the metal–carbon multiple bonds are studied for the Schrock-type carbene complex, $H_2(CH_3)Nb{=}CH_2$, and the cationic and neutral carbyne complexes, $(CO)_5Cr{\equiv}CH^+$ and $Cl(CO)_4Cr{\equiv}CH$, respectively, which show different reactivities to nucleophiles. The Fischer-type carbene complexes, $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$, were studied previously. The M=C(carbene) bond in the Schrock-type complex and the Cr≡C triple bond are stronger than the M=C bond in the Fischer-type complexes. The calculated properties of these bonds agree reasonably with the available experimental data of the related compounds. The atomic charges of the carbene and carbyne carbons were calculated negative. The reactivities of the metal–carbon multiple bonds were unifiedly understood by the frontier orbital theory. For the Schrock-type complex, the HOMO has a maximum coefficient on the C_{carb} atom and the LUMO has a maximum coefficient on the Nb atom. Therefore, the electrophile attacks the C_{carb} atom and the nucleophile attacks the Nb atom. For the carbyne complexes, the differences in the reactivity between the cationic and neutral complexes were explained from the existence of the nearly degenerate LUMO and next LUMO in the frontier MO region of the neutral complex. They would never be explained by the charge-controlled mechanism.

The multiple bond between metal and carbon is of great interest as a typical bonding mode in organometallic chemistry. The formation or the breaking of these bonds is thought to be a key step in many organometallic reactions.[1-3] The compounds with a double bond between metal and carbon are called metal carbene complexes[2-5] and those with a triple bond are called metal carbyne complexes.[2,4] Further, there are two types of metal carbene complexes; one is a Fischer-type metal carbene complex in which the metal atom is in a low oxidation state,[2] the other is a Schrock-type metal carbene complex or an alkylidene complex in which the oxidation state of the metal atom is high.[3] The reactivities of these two types of complexes are different.

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