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^{13}C and ^{17}O NMR of Mono-Nuclear Carbonyls: A DFT Study

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ABSTRACT

DFT implemented in ADF 2012.01 was applied to11 mono-nuclear carbonyls after their optimization to ascertain the *stereo chemical* and *magnetic equivalence* of CO groups and calculation of *Effective Spin Hamiltonian(H^{Spin})* values of the metals and the carbon atoms after obtaining NMR parameters like Chemical Shifts (δ M $^{n+}$, δ^{13}C, δ^{17}O),total NMR shielding tensors (σ M^{n+}, σ^{13}C, σ^{17}O) consisting of 2 diamagnetic and 4 paramagnetic terms along with k and j parameters of constituents. This NMR study corroborated well the hitherto, already, reported IR/ Raman results to lend credence to the π - acid character of carbonyls.

Key words: Chemical Shift, Shielding Tensor, Paramagnetic Tensor,
Effective Spin Hamiltonian, Magnetic Equivalence

INTRODUCTION

DFT was, earlier, applied by Schreckenbach *et al.,*[1-15] to study ^{13}C and ^{17}O NMR spectra of some mononuclear transition metal carbonyls. But the present work would include the study of a number of NMR parameters such as Chemical Shifts of metal, the carbon and the oxygen species (δ M, δ^{13}C, δ ^{17}O), their Total NMR Shielding Tensors (σ M, σ ^{13}C, σ^{17}O) along with two diamagnetic contributions [diamagnetic core tensor{a} and diamagnetic valence tensor{b}] and four paramagnetic contributions [paramagnetic (b^) tensor{c}, paramagnetic (u^) tensor{d}, paramagnetic(s^) tensor{e} and paramagnetic gauge tensor(f). Algebraic sum of these 6 contributions was equal to their σ M, σ ^{13}C, σ ^{17}O respectively. The parameters like Fermi-contact (k) [10^{19} kg m^{-2} s^{-2} A^{-2}], spin-spin coupling (j) [p pm] were also obtained.

While the discussion on NMR of transition metal complexes[16, 17] encircled around ligand field theory[18]**,** in the late 70s, a number of review articles were collected[19] on small molecules. Debrochere (1978) published a 100 page review containing 289 references[[20] .But till then, no calculations on nuclear shielding and spin-spin coupling parameters were carried out. H F approach given by Nakatsuzi[21] presented a paper on the calculation of the above named parameters of the complexes was found lacking in high oxidation states d^{10} systems[22]. In 80s, the NMR shielding codes based on HFS or X δ method were developed. It was afterward called DFT[23-25]. In 1993, Kohn-Sham DFT[26, 27] employed IGLO[26-27] method to calculate nuclear shielding. Also, LORG approach[27] which was improved upon by GIAO DFT[28] and CSGT methods[29] was employed. Spin-spin coupling constant of complexes was first of all calculated by Malkin *et al*.,[30]. Dicken and Zieglar[31] calculated FC term[32] in1996. Later, SD term[33, 34] was included in spin- spin coupling values.

The 11 mono-nuclear carbonyls were included in this study : $[M\ (CO)_6]$(M=Cr, Mo, W), $[V(CO)_6]^{1-}$,$[M(CO)_6]^{1+}$(M=Mn , Re), $[M(CO_5)]$ (M=Fe, Ru Os),$[Co(CO)_4]^{1-}$ and $[Ni(CO)_4]$. All these carbonyls obeyed the 18 electron rule.

Need of the study

Three points necessitated this study as:

- No computational studies were reported on the *magnetic equivalence* of COs. Only their *spatial displacements/ stereo chemical equivalences* were studied.
- An important NMR parameter- Effective Spin Hamiltonian **(H^{Spin})** [17] which determines the energy of an NMR transition had, never, been calculated by DFT.
- DFT had, hardly, been applied to NMR in ascertaining the pi-acid character of metal carbonyls though IR/ Raman techniques had abundantly been exploited.

Methodology [3, 13, 32, 35, 36, 37]

ADF software was installed on Windows XP platform as "ADF jobs". A new directory was created using "File menu" of ADF jobs.

After optimization of the carbonyl compound, different commands were filled into the software to obtain NMR and IR/Raman parameters as follows:

NMR Parameters[36, 37]

The software was run by filling in certain commands like *Single Point,* LDA*, Default, None*, *Collinear,* Nosym using *DZ* or *TPZ Basis sets.* The *Unrestricted* command was left blank. Then "NMR Program" was run in three steps.

- The Shielding Constants of the constituents (σ M , $\sigma\,^{13}$C, $\sigma\,^{17}$O) were obtained from the "NMR Program" by clicking on numbers of the species and *printing* them along with "*Isotropic Shielding Constants"* and "*Full Shielding Constants"*. The Chemical Shifts (δ M, δ^{13}C, δ^{17}O) were obtained from their NMR spectra.
- k and j values of constituents were obtained from the same program by *using a new Input File* and printing numbers of *Perturbing* and *Responding nuclei*.
- $\sigma\,^{13}$C, σ^{17}O, $\sigma\,^{13}$C, σ^{17}O, k and j of C and O of uncoordinated CO (g) were obtained by repeating the above mentioned two steps with reference values $\delta\,^{13}$C (-34.44) and δ^{17} O(-129.53).

IR and Raman Parameters

After *Optimization*, the software is run with *Frequencies* and *Raman full* to obtain values of frequencies of all the (3n-6) Fundamental vibration bands.

RESULTS

Table: 1 contained Acronyms and their expanded forms. Tables: 2-3 gave the optimization[38,39] and thermal parameters of the carbonyls respectively.Table: 4 contained eight NMR parameters: three shielding constants(σM, σ^{13}C, σ^{17}O),three Chemical Shifts (δ M , δ^{13}C, $\delta\,^{17}$O) and two Coordination Shifts($\Delta\ \delta\,^{13}$C , $\Delta\ \delta^{17}$O) .Six contributions consisting of two diamagnetic and four paramagnetic terms of three parameters (δ_M, δ^{13}C, δ^{17}O) were given in Tables:5-7[{a},{b}.{c},{d},{e}.{f}].Total values of two diamagnetic and four paramagnetic contributions in ó M, ó^{13}C and ó ^{17}O were given in Table: 8. Table:9 represented Spatial and Magnetic Equivalence of CO groups. Table: 10 contained **k** and **j** parameters given by software and the H ^{spin} values as calculated from **j** values

DISCUSSION

The discussion was divided into eight headings as follows:

As stated, the software gave a number of parameters which were further related a number of other parameters as follow:

Sum of 6 contributions was equal to their σ M, σ ^{13}C, σ ^{17}O[p pm] respectively.

σ **M** =Sum of 2 diamagnetic and 4 paramagnetic contributions of M |

σ **^{13}C** =Sum of 2 diamagnetic and 4 paramagnetic contributions of ^{13}C| **[1]**

σ **^{17}O** =Sum of 2 diamagnetic and 4 paramagnetic contributions of ^{17}O|

The relation between (σ) and (δ) of carbon was given as:

$$\delta^{13}C=181.1-\sigma^{13}C \qquad ...\textbf{[2]}$$

Table 1: Acronyms and their expanded forms

DFT	Density Functional Theory
ADF	Amsterdam Density Functional
ZORA	Zeroth- Order Regular Approximation
LDA	Local Density Approximation
DZ/TPZ	Double Zeta/ Triple Zeta
GGABP	Generalized Gradient Approximation
GGABP	Generalized Gradient Approximation Becke Perdew
Nysom	Normalized or True
H F	Hartree- Fock
HFS	Hartree-Fock-Dickson-Slater
IGLO	Independent or Individual Gauge of Localized Orbitals
LORG	Localized Orbitals Resonance Gauge
GIAO	Gauge Including Atomic Orbitals
CSGT	Continuous Set of Gauge Transformation
SD/ FC	Spin-dipole/ Fermi-contact

Table 2: Optimization Parameters of Mononuclear Carbonyls

Carbonyl (≈0.0D)	**Point group**	**Total bonding Energy**	**Total Energy: X c (LDA) k J mole^{-1}**	**Nucleus**	**I**
$[V(CO)_6]^{1-}$	O_h	-9885.20	-309197.58(-289776.63, -19420.95)	^{51}V	3.5
$[Cr(CO)_6]$	-do-	-9749.83	-317868.84(-298129.57,-19739.27)	^{53}Cr	1.5
$[Mo(CO)_6]$	-do-	-9761.76	-504440.84(-479759.83, -24681.02)	^{95}Mo	2.5
$[W(CO)_6]$	-do-	-9991.96	-981514.64(-947053.82, -34460.82)	^{183}W	0.5
$[Mn(CO)_6]^{1+}$	-do-	-8833.60	-326285.10(-306302.80,-19982.30)	^{55}Mn	2.5
$[Re(CO)_6]^{1+}$	-do-	-9230.86	-999049.56(-964269.91, -34779.65)	^{185}Re	2.5
$[Co(CO)_4]^{1-}$	T_d	-6757.34	-279321.74(-263582.63, -15739.11)	^{59}Co	0.5
$[Ni(CO)_4]$	-do-	-6232.74	-289903.76 (-273830.40, -16073.36)	^{61}Ni	2.5
$[Fe(CO)_5]$	D_{3h}	-8029.69	302622.68(-284764.22, -17858.46)	^{57}Fe	1.5
$[Ru(CO)_5]$	-do-	-7986.29	-496080.13(-473217.51, -22862.62)	^{101}Ru	3.5
$[Os(CO)_5]$	-do-	-8364.94	-984410.88(-951721.35, -32689.52)	^{187}Os	1.5

***X c is made up of *LDA* and *GGA* components; which further contain *Exchange* and *Correlation* parts. *Bonding energy* is computed as an energy difference between the molecule and fragments. GGA is zero here

Table 3: Thermal Parameters of Mononuclear Carbonyls at 298 K

Carbonyl	Zero Point Energy (e V)	Thermal Parameters								Constant Volume Capacity (Kcal mol^{-1} K^{-1})			
		Entropy (cal mol^{-1}K^{-1})				Internal Energy (Kcal mol^{-1})							
		Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total	Trans	Rot.	Vib.	Total
$[V(CO)_6]^{1-}$	1.119	42.054	25.45	18.95	86.447	0.889	0.889	29.372	31.149	2.981	2.981	23.72	29.683
$[Cr(CO)_6]$	1.148	42.066	25.32	16.67	84.060	-do-	-do-	29.683	31.460	-do-	-do-	22.63	28.596
$[Mo(CO)_6]$	1.146	42.633	25.55	16.55	84.730	-do-	-do-	29.642	31.419	-do-	-do-	22.84	28.802
$[W(CO)_6]$	1.150	43.469	25.57	16.11	85.154	-do-	-do-	29.684	31.461	-do-	-do-	22.77	28.734
$[Mn(CO)_6]^{1+}$	1.146	42.107	28.96	27.79	98.872	-do-	-do-	31.043	32.820	-do-	-do-	20.03	25.993
$[Re(CO)_6]^{1+}$	1.181	43.494	27.69	23.25	95.874	-do-	-do-	31.527	33.305	-do-	-do-	28.25	34.212
$[Co(CO)_4]^{1-}$	0.679	41.316	25.49	15.34	82.143	-do-	-do-	18.335	20.113	-do-	-do-	15.65	21.608
$[Ni(CO)_4]$	0.667	41.298	25.47	15.41	82.177	-do-	-do-	18.335	20.113	-do-	-do-	15.78	21.740
$[Fe(CO)_5]$	0.877	41.723	27.54	19.20	88.469	-do-	-do-	23.575	25.352	-do-	-do-	20.03	25.993
$[Ru(CO)_5]$	0.888	42.351	27.69	18.12	88.163	-do-	-do-	23.697	25.475	-do-	-do-	19.86	25.822
$[Os(CO)_5]$	0.906	43.294	27.71	16.22	87.227	-do-	-do-	23.888	25.665	-do-	-do-	19.42	25.382

Table 4: σ, δ and Δ δ [ppm] values of M, C and O in Mononuclear Carbonyls

Carbonyl*	δ M[3]	σM	δ ^{13}C[2]	σ ^{13}C	Δ δ ^{3}C[4]	δO^{17} [3]	σ^{17} O	Δδ^{7}O[5]
$[V(CO)_6]^{1-}$	141.68	-141.68	206.503	-25.45	8.99	45.97	-45.97	83.56
$[Cr(CO)_6]$	1428.92	-1428.92	202.00	-20.90	13.54	74.97	-74.97	54.53
$[Mo(CO)_6]$	-1328.44	1328.44	193.12	-12.02	22.42	58.15	-58.15	71.38
$[W(CO)_6]$	-4717.10	4717.10	189.33	-8.23	26.21	51.35	-51.35	78.18
$[Mn(CO)_6]^{1+}$	4718.18	-4718.18	201.21	-20.05	14.34	123.50	-123.50	6.03
$[Re(CO)_6]^{1+}$	-3296.33	3296.33	184.01	-2.900	31.54	83.06	-83.06	46.43
$[Co(CO)4]^{1-}$	3771.98	-3771.98	200.32	-19.22	15.22	34.20	-34.20	95.33
[Ni(CO)4]	2050.46	-2050.46	179.78	1.12	35.56	42.90	-42.90	86.63
$[Fe(CO)_5]$	5117.03	-5117.03	205.91(e)	-24.80(e)	8.63 (e)	77.5 (e)	-77.5 (e)	52.08(e)
			237.40(a)	-56.30(a)	-21.86(a)	162.77(a)	-162.77(a)	-33.2(a)
$[Ru (CO)_5]$	993.92	-993.92	199.63(e)	-18.50(e)	15.92(e)	82.00 (e)	-82.00 (e)	47.53(e)
			217.27 (a)	-36.17(a)	-1.73 (a)	117.25(a)	-117.25(a)	12.28(a)
$[Os(CO)_5]$	-2061.72	2061.72	198.89(e)	-18.79(e)	15.65(e)	85.00(e)	-85.00(e)	44.53(e)
			211.72 (a)	-30.6 (a)	3.82 (a)	104.5(a)	-104.5(a)	25.04(a)

*Calculate values by relations: 2, 3, 4 and 5

δM and $\delta^{17}O$ were numerically equal to ó M and $\sigma\ {}^{17}O$ but with opposite signs

$$\sigma M = -\delta M$$

...[3]

$$\sigma^{17}O = -\delta\ {}^{17}O$$

The Coordination Shifts [$\Delta_{\delta}{}^{13}C$, $\Delta_{\delta}{}^{17}O$] and [$\sigma\ {}^{13}C$, $\sigma^{17}O$] were related as:

$$\Delta_{\delta}{}^{13}C_{=}\ \delta\ {}^{13}C\ (MCO) - (-34.44) \qquad \text{...[4]}$$

$$\Delta_{\delta}{}^{17}O_{=}\ \delta\ {}^{17}O\ (MCO) - (-129.53) \qquad \text{...[5]}$$

[B] Relative spatial displacements of constituting species were reaffirmed from shielding constants of the M, C and O [σM, $\sigma^{13}C$ (M CO)**,** $\sigma^{17}O$ (MCO)] simply by the fact that the spatially equivalent species should have same values of

Table 5: Shielding Constants [p pm] of M, Diamagnetic and Paramagnetic Contributions

Carbonyl	σ M(MCO)	Diamagnetic Contributions {a} {b}	Paramagnetic Contributions {c} {d} {e} {f}
$[V(CO)_6]^{1-}$	-141.68	1660.804,51.650	-250.309, -2096.566,493.643,-0.905
$[Cr(CO)_6]$	-1428.92	0.000 , 1821.872	0.000, -3512.409, 262.589 , -0.975
$[Mo(CO)_6]$	1328.44	3936.345,60.030	-745.997,-2900.566,979.771,-1.144
$[W(CO)_6]$	4717.10	8530.161,198.232	680.920,-3665.371,-1027.367, 0.524
$[Mn(CO)_6]^{1+}$	-4718.18	1825.324,101.135	-229.740,-6590.544,717.941,-2.301
$[Re(CO)_6]^{1+}$	3296.33	8670.042,218.625	686.109,-5466.369, -812.461,0.385
$[Co(CO)_4]^{1-}$	-3771.98	1989.201,171.689	-117.023,-6423.724, 607.811,0.071
$[Ni(CO)_4]$	-2050.46	2070.943,208.080	-132.181,-4552.960, 355.809,-0.147
$[Fe(CO)_5]$	-5117.03	1907.276,134.245	-170.891,-7686.421,699.538,-0.779
$[Ru(CO)_5]$	-993.92	4161.943,103.726	-574.583, -5456.581,771.062, 0.513
$[Os(CO)_5]$	2061.72	8814.709,246.542	569.979, -6992.715, -578.172, 1.377

Table 6: Shielding Constants [p pm] of ^{13}C, Diamagnetic and Paramagnetic Contributions

Carbonyl	σ M(MCO)	Diamagnetic Contributions {a} {b}	Paramagnetic Contributions {c} {d} {e} {f}
$[V(CO)_6]^{1-}$	-25.45	199.233,47.944	0.028 , -313.186, 39.704, 0.785
$[Cr(CO)_6]$	-20.90	0.000 , 253.438	0.000 ,-301.057, 26.316 ,0.413
$[Mo(CO)_6]$	-12.02	199.236, 50.566	0.080 ,-296.744, 34.131, 0.716
$[W(CO)_6]$	-8.23	199.232 ,50.259	-0.018 ,-295.857,37.915, 0.241
$[Mn(CO)_6]^{1+}$	-20.05	199.233,50.516	-0.014,-304.470, 34.677,-0.001
$[Re(CO)_6]^{1+}$	-2.900	199.232 ,51.670	-0.030,-288.485,34.817,-0.116
$[Co(CO)_4]^{1-}$	-19.22	199.233 ,50.726	0.037,-309.605, 40.207,0.178
[Ni(CO)4]	1.12	199.233 ,51.411	0.031 ,-285.869,36.213,0.105
$[Fe(CO)_5]$	-24.80(e)	199.233 ,50.701	0.007,-312.523, 37.832, -0.060
	-56.30(a)	199.233 ,51.687	0.031, -339.899,32.266,0.384
$[Ru(CO)_5]$	-18.50(e)	199.234 ,51.838	0.045, -299.689, 29.641, 0.414
	-36.17(a)	199.234 ,53.295	0.096 , -316.614,27.040,0.775
$[Os(CO)_5]$	-18.79(e)	199.233, 53.412	-0.001,-313.307,29.599, 0.446
	-30.6 (a)	199.233 ,51.367	0.008 ,-304.234, 34.814,0.020

shielding constants along with their constituting two diamagnetic and four paramagnetic terms respectively. All the ^{13}C and ^{17}O nuclei in each one of the four or six CO groups in T_d or O_h possessed the same values of σ, δ and also the six contributing diamagnetic and paramagnetic quantities respectively. Therefore, all the four or six CO ligands were in the same spatial displacement, i.e. stereochemically equivalent around their respective central metal ion. It would be easy to conclude that that more the value $\sigma^{13}C$, the lesser should be the value of Chemical shift (δ ^{13}C) and more would be the value of Coordination Shift (Δδ ^{13}C) for a given stereochemistry of the carbonyls as illustrated below:

Table 7: Shielding Constants [p pm] of ^{17}O, Diamagnetic and Paramagnetic Contributions

Carbonyl	σ^{17}O(MCO)	Diamagnetic Contributions {a} {b}	Paramagnetic Contributions {c} {d} {e} {f}
$[V(CO)_6]^{1-}$	-45.97	269.471 ,133.899	-0.082, -392.033, -56.213 ,-1.060
$[Cr(CO)_6]$	-74.97	0.000 , 397.850	0.000 ,-447.416, -24.582, -0.901
$[Mo(CO)_6]$	-58.15	269.471 ,130.426	0.006 , -416.371, -41.090 ,-0.597
$[W(CO)_6]$	-51.35	269.471,130.294	-0.003, -413.992, -36.338, -0.809
$[Mn(CO)_6]^{1+}$	-123.50	269.471, 127.036	0.019 , -490.879, -28.269, -0.862
$[Re(CO)_6]^{1+}$	-83.06	269.471,126.889	0.037, -454.952, -23.710 , -0.760
$[Co(CO)_4]^{1-}$	-34.20	269.472 ,134.157	0.030 , -385.614, -52.149 ,-0.091
$[Ni(CO)_4]$	-42.90	269.472 , 130.513	0.048. -402.968, -39.838, -0.125
$[Fe(CO)_5]$	-77.5 (e)	269.472 , 130.303	0.016 , -435.846, -40.978, -0.417
	-162.77(a)	269.471 ,129.490	0.016 , -533.743, -27.475, -0.532
$[Ru (CO)_5]$	-82.00 (e)	269.472 , 130.243	0.007 ,-435.040, -46.462, -0.223
	-117.25(a)	269.471, 129.274	-0.007 , -489.099, -26.478,-0.406
$[Os(CO)_5]$	-85.00(e)	269.472 , 130.204	0.018 , -442.812, -41.543 ,-0.340
	-104.50(a)	269.471, 129.192	0.001, -481.733, -20.938, -0.479

Table 8 Total Diamagnetic, Paramagnetic contributions in σ M, σ^{13}C and σ ^{17}O [p pm]

Carbonyl	σ M		σ^{13} C		σ ^{17}O	
	Diamagnetic contribution	Paramagnetic contribution	Diamagnetic contribution	Paramagnetic contribution	Diamagnetic contribution	Paramagnetic contribution
$[V(CO)_6]^{1-}$	1712.453	-1854.136	247.177	-272.669	403.370	-449.388
$[Cr(CO)_6]$	1821.872	-3250.796	253.438	-274.327	397.850	-472.899
$[Mo(CO)_6]$	3996.374	-2667.936	249.801	-261.817	399.897	-458.064
$[W(CO)_6]$	8728.393	-4011.294	249.491	-257.719	399.765	-451.142
$[Mn(CO)_6]^{1+}$	1926.459	-6104.644	249.749	-269.807	396.507	-519.991
$[Re(CO)_6]^{1+}$	8888.668	-5592.336	250.902	-253.814	396.359	-479.425
$[Co(CO)4]^{1-}$	2160.890	-5932.866	249.959	-269.182	403.628	-437.824
[Ni(CO)4]	2279.023	-4329.479	250.644	-249.520	399.985	-442.882
$[Fe(CO)_5]$	2041.521	-7158.553	250.920(e)	-307.218(e)	398.962(e)	-561.734(e)
			249.934(a)	-274.744(a)	399.775(a)	-477.218(a)
$[Ru (CO)_5]$	4265.669	-5259.589	251.072(a)	-269.590(e)	399.715(e)	-481.718(e)
			252.529(a)	-288.702(a)	398.745(a)	-515.991(a)
$[Os(CO)_5]$	9061.251	-6999.531	250.600(e)	-269.391(e)	399.676(e)	-484.677(e)
			252.645(a)	-283.263(a)	398.663(a)	-503.149(a)

Parameter (ppm)	**$[V(CO)_6]^{1-}$**	**$[Cr(CO)_6]$**	**$[Mn\ (CO)_6]^{1+}$**	**$[Mo(CO)_6]$**	**$[W(CO)_6]$**	**$[Re(CO)\ _6]^{1+}$**
$\delta\ ^{13}C$	206.50	202.00	201.21	193.12	189.33	184.01
$\sigma\ ^{13}C$	-25.45	-20.90	-20.05	-12.02	-8.23	-2.9
$\Delta\delta^{13}C$	8.99	13.54	14.34	22.42	26.21	31.54

Table 9: Spatial and Magnetic Equivalence of COs in Mononuclear Carbonyls

Carbonyl	**Spatially Equivalent COs**	**Magnetically Equivalent COs**	**Types of $\sigma\ ^{13}C$ & $\sigma^{17}O$**	**No. of Spatially Different COs**
*$[V(CO)_6]^{1-}$	All	All	One	Same type of six COs
$[Cr(CO)_6]$	-do-	3 types;2 in each type	-do-	-do-
$[Mo(CO)_6]$	-do-	-do-	-do-	-do-
$[W(CO)_6]$	-do-	-do-	-do-	-do-
$[Mn(CO)_6]^{1}$	-do-	-do-	-do-	-do-
$[Re(CO)_6]^{1+}$	-do-	-do-	-do-	-do-
*$[Co(CO)_4]^{1-}$	-do-	All	One	Same type of four COs
*$[Ni(CO)_4]$	-do-	-do-	-do-	-do-
$[Fe(CO)_5]$	2 types;3(e) and 2(a)	2 types ;3(e) and 2(a)	Two	2 types ;3(e) and 2(a)
$[Ru(CO)_5]$	-do-	-do-	-do-	-do-
$[Os(CO)_5]$	-do-	-do-	-do-	-do-

*All COs are both spatially and magnetically equivalent

Table 10: k, j and H ^{spin} values of Nuclei in Mononuclear Carbonyls

Carbonyl	**Perturbing Nuclei**	**Responding Nuclei**	**k [10^{19} kg m^{-2} s^{-2} A^{-2}]**	**j (p pm)**	**H ^{spin} (10^{17}MHzmol^{-1})**
$[V(CO)_6\ ]^{1-}$	V	Each one of 6 C	364.0	290.0	3056.6725
$[Cr(CO)_6\ ]$	Cr	-do-	140.8	-24.1	-108.8657
$[Mo(CO)_6]$	Mo	-do-	673.9	133.2	1002.8295
$[W(CO)_6]$	W	-do-	502.7	63.6	95.6151
$[M\ n(CO)_6]^{1+}$	M n	-do-	464.6	346.3	2607.2061
$[Re(CO)_6]^{1+}$	Re	-do-	549.2	No spin- spin interaction due to large difference in $\gamma^{187}Re$ (0.23057) and $\gamma^{13}C$ (6.7383)	
$[Fe(CO)_5]$	Fe	Each one of 3 C(e)	447.3	43.7	65.8013
		Each one of 2 C(a)	112.8	11.0	16.5633
$[Ru\ (CO)_5]$	Ru	-do-	977.2	No spin- spin interaction as % abundance of ^{101}Ru (17.07%) and ^{13}C (1.1%) is less	
			797.6		
$[Os(CO)_5]$	Os	-do-	845.0	59.2	267.4212
			679.5	47.6	215.0211
$[Co(CO)4]^{1-}$	Co	Each one of 4 C	663.6	473.4	4989.7544
$[Ni(CO)4]$	Ni	-do-	780.1	210.6	951.333

[C] In D_{3h} stereochemistry, each one of the three ^{13}C and ^{17}O had the same values of $\sigma^{13}C$, $\delta^{13}C$, $\sigma^{17}O$ and $\delta^{17}O$ along with their six contributing terms respectively; meaning thereby that the three COs were stereo chemically equivalents. Each one of the remaining two COs also possessed same values of $\sigma^{13}C$, $\delta^{13}C$, $\delta^{17}O$ and $\delta^{17}O$ along with their contributing terms respectively. But these values were quite different from those of the other three CO s. Thus these two COs were different from the other three COs spatially*.

The values of 8 parameters : σ *M*, δ M, $\sigma^{13}C$, $\delta^{13}C$, $\Delta\delta\ ^{13}C$, $\sigma^{17}O$, $\delta^{17}O$ and $\Delta\delta\ ^{17}O$ [pp m] for the11 mononuclear carbonyls were given in Table:4. The more the value of $\sigma^{13}C$, the lower was the Chemical shift ($\delta^{13}C$) and higher was the Coordination Shift ($\Delta\delta\ ^{13}C$) for any stereochemistry. A positive $\Delta\ \delta\ ^{13}C$ is reported in O_h geometry which confirms the back-acceptor nature 0f CO. The difference between $\boldsymbol{\sigma}\ ^{17}O$ values of carbonyls and the $\boldsymbol{\sigma}\ ^{17}O$ of CO (g) was noted. This positive** shift in $\boldsymbol{\Delta\delta}\ ^{17}O$ also confirmed the transfer *s p^3d hybridization in a trigonal bipyrimidal geometry is supplemented by the *prolate* d_z^2 orbital having two opposite major lobes (m=0). A pair of opposite vertices [40] (X–M–X angle =180°) makes trigonal bipyramid a *prolate* polyhedron. Carbonyls occupying these two vertices have more electron density than the other three lying ^ to these two. **Negative in [Fe $(CO)_5$].

With two different types of spatially equivalent CO groups (**e**, **a**), the five coordinate D_{3h} carbonyls showed two types of $\boldsymbol{\sigma}\ ^{13}C$ and $\boldsymbol{\sigma}\ ^{17}O$ values. Accordingly, two values of coordination shifts called $\Delta\ \delta^{13}C_{\mathbf{a}}$ and $\boldsymbol{\Delta\delta}\ ^{13}C_{\mathbf{e}}$ were obtained. Relative order of $\boldsymbol{\Delta\delta}\ ^{13}C_{\mathbf{e}}$ in the five coordinate carbonyls is given as:

[Fe $(CO)_5$] < [Ru $(CO)_5$] H ≈ [Os $(CO)_5$]

$\Delta\ \delta\ ^{13}C_{\mathbf{a}}$ follows the order:

[Fe $(CO)_5$] < [Ru $(CO)_5$] ≈ [Os $(CO)_5$]

[D] As shielding constant (σ) of a nucleus was directly related to its electron density, any change in its σ value would serve as an indicator of change in electron density on it. So, if CO were to act as a back acceptor, $\delta\ ^{13}C$ of metal carbonyls should become more than $\sigma\ ^{13}C$ of CO (g). Some of the increased electron density on carbon was transmitted to oxygen to cause an increase in electron density on oxygen. So $\sigma\ ^{17}O$ would also increase. *The NMR results corroborate with results obtained from their IR/Raman parameters in confirming their π – acid character as follows*:

π- ligand CO would donate electron density to the metal via a dative σ bond (OC→ M) .Simultaneously, there would be a σ back donation from the filled d orbitals of metal (OC ← M) to energetically favorable and geometrically suitable vacant π* molecular orbitals of CO. The effect being synergic should cause a decrease in carbon oxygen double character and, thus, a decrease in

Parameters[p pm]	**$[V(CO)_6]^{1-}$**	**$[Mn\ (CO)_6]^{1+}$**	**$[Re(CO)_6]^{1+}$**
$\delta\ ^{13}C$	206.50	201.21	184.01
$\sigma\ ^{13}C$	-25.45	-20.05	-2.9
$\Delta\delta\ ^{13}C$	8.99	14.34	31.54
ν_{CO}	2020.0	2192.0	2197.0
Parameters	$[Cr(CO)_6]$	$[Mo(CO)_6]$	$[W(CO)_6]$
$\delta\ ^{13}C$	202.00	193.12	189.33
$\sigma\ ^{13}C$	-20.90	-12.02	-8.23
$\Delta\delta\ ^{13}C$	13.54	22.42	26.21
ν_{CO}	2118.7	2120.7	2126.2
Parameters(Equatorial)	Fe $(CO)_5$	Ru $(CO)_5$	$Os(CO)_5$
$\delta\ ^{13}C$	205.91	199.63	198.89
$\sigma\ ^{13}C$	-24.81	-18.50	-18.79
$\Delta\delta\ ^{13}C$	9.63	15.92	15.65
ν_{CO}	2022.0	2035.0	2036.0
π acceptor strength in all	Maximum	Less	Least

n_{CO} in carbonyls with respect to CO(g) having ν_{CO}= 2143 cm^{1-} was expected if C O was to act as a back pi- acceptor. A comparison of σ ^{13}C, δ ^{13}C, Δ δ ^{13}C and ν_{CO} (cm^{-1}) values of the 6 and 5 coordinate(axial) carbonyls in the above table lead to the conclusion that as the Chemical Shift (δ^{13}C)decreased, ν_{CO}(cm^{1-}) would increase[41-48] to decrease the capacity to back accept electron cloud by CO.

[E] Another important element of NMR symmetry was called the "magnetic equivalence" of nuclei .Enantiotopic or homotopic nuclei though possessed the same chemical shift (δ), but might not necessarily be magnetically equivalent. Two magnetically equivalent nuclei would have the same values of σ, δ, k and j with other nuclei of the molecule in addition to having same values among themselves .Coupling between symmetry equivalent and magnetically nonequivalent nuclei would affect the appearance of NMR spectrum while coupling between both the symmetry and magnetically equivalent nuclei had no effect NMR spectra.

[F] With same δ ^{13}C, δ^{13}C, k and j values, the four COs were both spatially and magnetically equivalent in T_d.Again, the six CO groups in [V (CO) $_6$]$^{1-}$ were both spatially and magnetically equivalent with the same σ^{13}C, δ ^{13}C, k and j values. But the six COs in the remaining (O_h) mono-nuclear carbonyls were only spatially equivalent with same σ^{13}C, δ ^{13}C values as they possessed different k and j values. They were of three types. Each type having two CO groups possessed both spatial and magnetic equivalence. The three types of CO pairs had the same set of four parameters respectively *between themselves and with remaining four CO groups though the set of four COs show different values from the previous set of two COs.*

The five COs (D_{3h}) were neither spatially nor magnetically equivalent as they did not have the same set of four parameters. They consisted of two sets. The first set with two COs (a) and the second with three COs (e) showed both the spatial and magnetic equivalence *among themselves* as either type possessed same set of values of four parameters among its own members and also with members of other type of CO groups though the two sets have different values of these parameters.

(i) Spin-spin coupling (j) was field-independent and mutual ($j_{AB} = j_{BA}$).It was affected by the nature of solvent ; metal"ligand bond distances and was transmitted through bonding electrons with its magnitude falling off rapidly with the increase in number of intervening bonds. Its sign was decided as: "*it was positive if energy of A was lower when B had opposite spin as A (*αβ or βα*), and negative if energy of A was lower when B had same spin as A (*αα *or* ββ *)".*

(ii) The parameter (j) was related to another important NMR called Effective Spin Hamiltonian (H^{Spin}). It was a mathematical expression that would determine the energy of an NMR transition. It term "effective" meant that its solutions reproduced nuclear magnetic energy levels in a molecular system without reference to electrons. In a fictitious absence of surrounding electrons, the shielding constants and indirect spin-spin coupling constants would vanish leaving the NMR spectrum to be determined by Nuclear Zeeman Term and direct dipolar coupling. (H^{Spin}) values of the metal ions and the bonded carbon atoms were related to their **j** [p pm] values as given below [6] **(17)**.

$$H^{Spin} = 6.023\,\mathbf{j}_{AB}.\, I_{A.}\, I_{B.}\ \text{MHz mol}^{-1} \qquad ...[6]$$

Spin Hamiltonian [H^{Spin}] values of the metal and the bonded carbon atoms of the eleven carbonyls are calculated by applying [5] (Table: 10). [G]Individual values of 6 diamagnetic and paramagnetic quantities in σ_M, δ ^{13}C and δ ^{17}O and their sums were given in Tables: 5-8 respectively.
[H] Table: 9 showed spatial displacements of 4, 5 or 6 CO groups around the metal.

CONCLUSIONS

The originality and relevance of present work and how it moved the body of scientific knowledge forward would lie in the fact that it reaffirmed the relative spatial displacements of CO groups; classified them according to their spatial and magnetic equivalence; lent credence to σ- acid character of carbonyls by corroborating with their IR/Raman studies and hence justified the need of taking up this study.

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